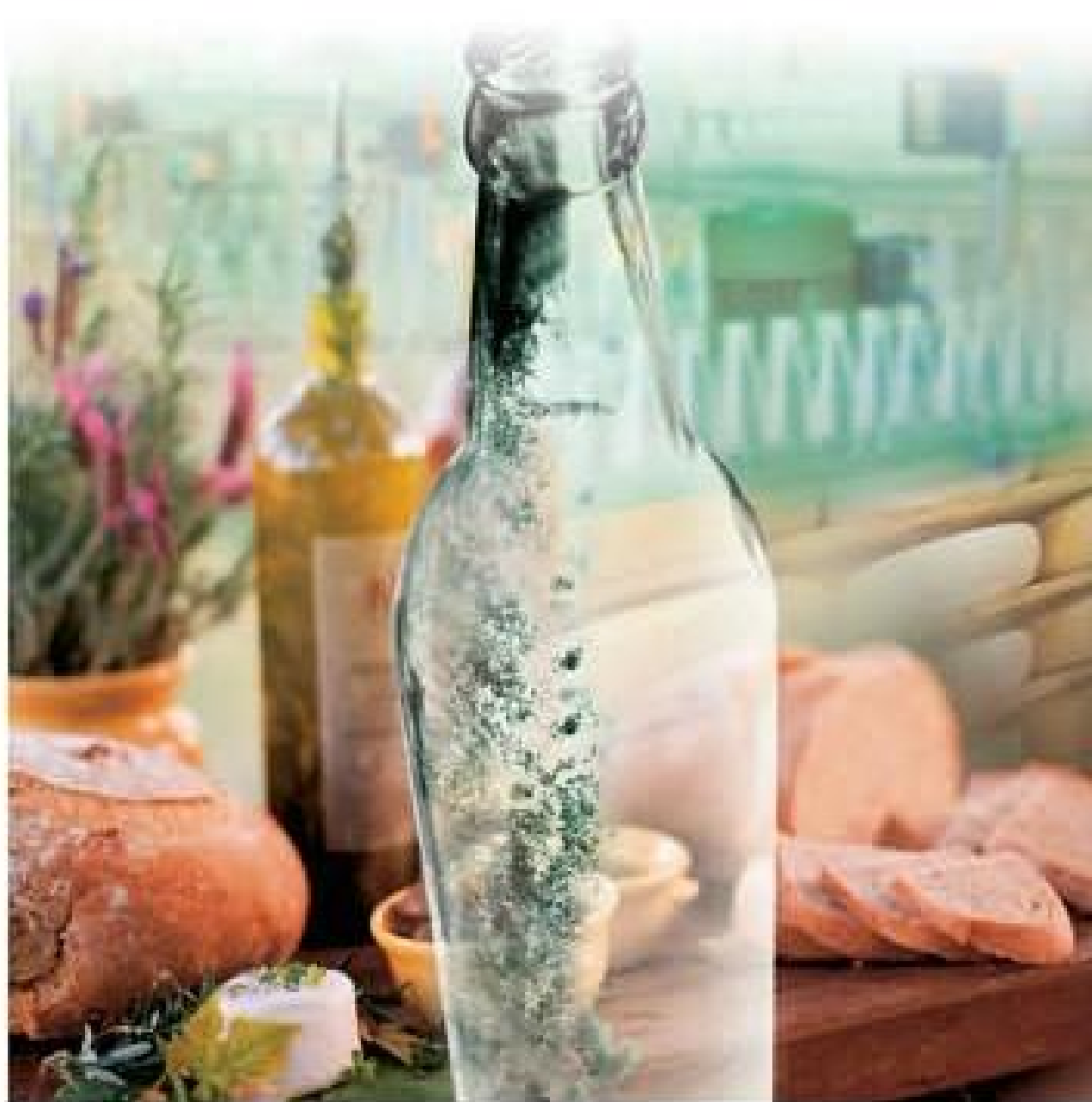


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Sanitation

Cleaning and Disinfection in the Food Industry



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Preface

Knowledge gained as a result of research carried out by private companies is regarded as the property of those companies and is normally not shared with anyone else, particularly with their competitors. Although companies may communicate with each other at many levels and may discuss many topics, only a small part of the 'know-how' is shareable. Moreover, the skills and experience of the research specialists responsible for the discoveries are not things that can be written down. They are personal attributes and are not transferable. Industry both gains and loses as a result of its secretive nature. Most employees have a reasonable idea of the products and processes but soon become out of their depth when they try to fully understand the technology and research background. Frequently, the knowledge is so linked to certain individuals that, when they retire, the knowledge disappears with them.

This book is an attempt to set up a systematic description of the theory and application of detergents and disinfectants used in food sanitation and cleaning processes, including problem solving in the field. The results of investigations and the knowledge that comes from experience are brought to bear on the problem of selecting the most effective technology of cleaning and disinfection. Thus, the book includes essential physical and chemical theory, technological principles, examples of pertinent experimental results, data derived from field studies, suggestions, and references for additional reading which, after due consideration, was considered to furnish the necessary amount of background information. Some references (mainly to the author's work) are in the form of unpublished works since they are subject to industrial confidentiality.

Water and its impurities play an important role in attaining positive or negative results in cleaning. For this reason, the first part of this book points out the main variables of water that may affect detergency. Together with water, the chemistry of food is analyzed in order to relate physical modifications and chemical interactions of soil to components of the detergent during cleaning. Sequestrants frequently prove to be the key to most of the cleaning successes in food detergency, more so than surfactants or caustics or acids. Sequestrants are recognized as the components that permit and promote those chemical events necessary to achieve cleaning. Water and soil free of polyvalent metals would be very easy to clean, but this ideal situation can also be recreated either by preventing metals from

precipitating out or even by bringing them back into solution after they have precipitated out and formed a solid and adherent deposit. This is the behavior typical of sequestrants, a behavior which softens and loosens the soil, and makes the cleaning activity of all the other components of a detergent so much easier. Consequently, a large part of this work is devoted to the theory of sequestration and the properties and behavior of each individual sequestering molecule that gives concrete benefit when applied, specifically in detergency.

The last and very important part of the book describes the various food sectors, reviews them in terms of cleaning processes, and outlines the role of detergents and the reasons for choosing the chemicals of which they consist and which enable those detergents to perform successfully. The aim is to provide a complete understanding of the principles on which detergency, applicable to foods and beverages, is based. Cleaning and disinfection are not always easy, and therefore it is essential that there should be cooperation with plant manufacturers in order to make sure that while they are designing equipment that is extremely efficient in processing foods they also bear in mind that it is just as important to be able to clean it efficiently.

We are living in an image-conscious age, and this book is copiously furnished with photographs, explanatory drawings, and graphs aimed at making clear the correlation between the concepts described and practical experience in the field.

Owing to the importance of establishing a principle rather than describing individual results, a single formulation is never considered to be the solution of any cleaning issue. A formulation continuously evolves, depending on raw materials availability, optimization, and provisions of the law. The emphasis is rather on the complexity of the interactions between soil and chemicals, that is, the chemistry of the technology, which ultimately provides the tools to optimize or select the best cleaning product. Even the concept of sanitation changes with time. From the first approach, where the most important feature of a cleaning process was thought to be its efficacy (with due attention paid to its cost), responsible companies have moved to the current approach, where sustainability (food safety with brand protection), concepts of cost control (overall costs of cleaning), and efficiency (overall costs of production) are all important.

For the most part, the use of trade names for chemicals has been avoided. If, however, in individual cases, trade names are given, it is because the specific information has been obtained using this particular material. Similar materials from other companies will show the same behavior.

Correct application comes from experience, but useful experience is frequently an unplanned side benefit of incorrect application, so one of the aims of the book is to prevent readers from repeating wrong applications. This book therefore aims to establish principles and practices that research and investigation have shown to be successful and that practical experience has vindicated. This will help users to make informed choices and to develop procedures and criteria appropriate to their specific situation. For all of these reasons, the book is intended for specialists in detergency, raw materials, and equipment manufacturing as well as schools and universities specializing in food, and consultants and specialists in food cleaning and disinfection, water, and waste water. All

these will provide an insight into this complex technology of sanitation, which forms a part of our everyday life.

General Information on the Structure of this Book

- The book comprehensively deals with several aspects of the chemistry of detergency and establishes connections between sequestrants and type of water, foods and cleaning processes, and sanitation and disinfecting chemicals. In these terms, the author develops concepts of applied detergency in order to understand and solve problems related to cleaning and disinfection of plant and environments where foods and beverages are prepared and transformed.
- The book is divided into three parts:
 - **Part One** analyzes water and its behavior as a function of the type of dissolved salts and how these salts can modify the manufacturing residues and affect the cleaning process. The theory of sequestration is investigated in depth. Theory is always linked to practical evidence.
 - **Part Two** examines the different groups of sequestrants and individual sequestrants belonging to these groups. Their capabilities of solving specific cleaning problems in combination with alkalis, acids, and surfactants are discussed, and analytical procedures to assess sequestering, dispersing, suspending, and anti-redepositing capacity are described in detail.
 - **Part Three** is the main body of the book and is of particular relevance to food manufacturers and food technology departments of schools and universities. It systematically reviews the industrial processes, the relevance to them of cleaning and disinfection, and how to find the solutions to problems. It also includes concepts of disinfection and how to select disinfectants, concepts of corrosion, and prevention of corrosion of surfaces in manufacturing plant.
 - (a) **Industrial processes:** bottlewashing, bottling and cold aseptic filling, lubrication, CIP, crossflow filtration, foam and gel cleaning, acidic detergency, tunnel pasteurization and cooling processes, biofilm, process and environment microbiology, clean rooms, ultrasonic cleaning, corrosion and preservation of metals, water and waste water treatments, boiler treatment, disinfectants, and sanitation technology.
 - (b) **Foods and beverages:** mineral waters, soft drinks, beer, wine, fruit juices, fancy beverages, dairy and cheese making, processed foods, slaughterhouses and meat preparation, fresh, preserved, and seasoned meats, eggs and cream, pasta and its derivatives, baking products, meat and vegetable sauces, ice cream, sweets, fresh-cut and preserved vegetables, and milk and intensively farmed livestock.

دینی جای
مستطوف

Acknowledgments

Science is not a piling up of data. The universal theme of science is that one explanation and one only is applicable to each event.

Louis Pasteur

I gratefully thank Franco Bruschi and acknowledge his valuable collaboration in carrying out a systematic investigation for more than 25 years. I also thank Danio Feraboli, Roberto Rossetti, Giovanni Broscritto, Monica Dammi, Giorgio Massari, Massimiliano Cittadini, and Maurizia Marzani, skilful colleagues in the Technical Department of the JohnsonDiversey Company, who daily provided their own individual input, so contributing to the development of sanitation technology.

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I particularly wish to thank the many and various publishers, organizations, and companies for their courtesy and permission to use tables, pictures, and extracts from their work.



Figure 0.1 Alchemy room—Deutsches Museum—Munich (Germany).

Acronyms

ABS	Branched alkylbenzensulphonate
abs	Absorption
AOS	α -olefinsulphonate
AOX	Adsorbed organic halogens
APIC	Association of Professionals in Infection Control
ASTM	American Society for Testing and Materials
ATMP	Aminotrimethylenephosphonic acid
BAC	Benzalconium chloride
BCDMH	Borochlorodimethyl idantoin
BiAS	Bismuth active substance
BO	Buthylenoxide
BPD	Biocide products directive
BUNA	Polybutadiene
CAF	Cold aseptic filling
CIP	Cleaning in place
CMC	Critical micellar concentration
COD	Chemical oxygen demand
COP	Cleaning out of place
DBNPA	Dibromonitrilopropionamide
DDAC	Didecyldimethyl ammonium compound
DEG	Dihydroethylglycine
DF	Diafiltration
DMAD	Fatty (C ₁₈) dimethylamine
DTPA	Diethylenetriaminopentacetic acid
DTPMP	Diethylenetriaminopentamethylenephosphonic acid
EAN	Effective atomic number
EBA	Expanded bed adsorption
EBT	Eriochrome black T indicator
ED	Electrodialysis
EDG	Ethanoldiglycine
EDTA	Ethylenediaminetetracetic acid
EDTMP	Ethylenediaminetetramethylenephosphonic acid
EFC	External filler cleaning

EO	Ethylenoxide
EOW	Electrolyzed oxidizing water
EPA	Environmental Protection Agency
EPDM	Ethylene, propylene, diene copolymer
FAEC	Fatty alcohol ethoxycarboxylate
FDA	Food and drug administration
FPM	Fluoropolymer (Viton), also FKM
FQAC	Fatty quaternary ammonium compound
GLDA	Glutamicdiacetic acid
GMP	Good manufacturing practice
HACCP	Hazard analysis and critical control points
HEDP	Hydroxyethylidenediphosphonic acid
HEDTA	Hydroxyethylenediaminotriacetic acid
HEDTMP	Hydroxyethylidenediaminotetramethylenephosph. a.
HEMP	Hexametaphosphate
HEPA	High efficiency particulate airfilter
HLB	Hydrophilic lipophilic balance
HOD	Home and office delivery
HPP	High pressure processing
ISO	International Standard Organization
IDS	Iminodisuccinic acid
LAS	Linear alkylsulphonate
LDMA	Lauryldimethylamine
LRV	Label removal value
LS	Laurylsulphonate
LSI	Langelier saturation index
M	Molarity
MBAS	Methylene blue active substance
MGDA	Methylglycinediacetic acid
MF	Microfiltration
MIC	Microbiologically influenced corrosion
mM	Millimoles
mPA	Modified polyacrylate
mV	Millivolt
MW	Molecular weight
N	Normality
NF	Nanofiltration
NPOX	Non-purgable organic halogens
μ S	MicroSiemens
NBR	Nitrile butadiene rubber
NTA	Nitrilotriacetic acid
OECD	Organization for economic cooperation and develop.
OEM	Original equipments manufacturer
PA	Polyacrylate
PAA	Peracetic acid

PAC	Polymeric ammonium compound
PAM	Polyacrylicmaleate
PASP	Polyaspartic acid
PBT	Polybutylenetherephthalate
PBTC	Phosphonobutanetricarboxylic acid
PC	Polycarbonate
PE	Polyethylene
PEF	Pulsed electric field
PEN	Polyethylenenaphthalate
PET	Polyethylenetherephthalate
PHA	Polyhydroxyalkane
PLA	Polylactic acid
PO	Propylene oxide
POM	Polyoxymethylene (acetalic polymer)
PP	Polypropylene
PPA	Phosphonopolyacrylate
PPAM	Phosphonopolyacrylicmaleate
PPC	Phosphinopolycarboxylic acid
PS	Polysulphone
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
QAC	Quaternary ammonium compound
RCF	Regenerated cellulose film
REACH	Registration, evaluation , authorization of chemicals
r.e.b	Repellent energy barrier
REF-PET	Refillable PET
RF	Radio frequency
RO	Reverse osmosis
rpm	Revolution per minute
RSI	Riznar stability index
SAS	Alkanesulphonate
SEM	Scanning electron microscopy
SIP	Sanitation in place
SMS	Soft metal safe
SPP	Sodium pyrophosphate
STP	Sodium tripolyphosphate
SW	Spiral wound membrane
TBEP	Tributoxyethylphosphate
TEA	Triethanolamine
TFC	Thin film composite membrane
TFF	Tangential flow filtration
THM	Trihalomethane (chloroform)
TMP	Transmembrane pressure
TSP	Trisodium Phosphate

TVC	Total viable count
UF	Ultrafiltration
ufc	Unit-forming colonies
UV-VIS	Ultraviolet-visible waves analyser
VIS	Visible waves analyser
WPC	Whey proteins concentration
WPI	Whey proteins isolation
WHO	World Health Organization

Part One

Chemistry and Problems of Industrial Water

دینی جای
مکتبہ

1

Chemistry of Aqueous Solutions

Water is a basic human necessity, and the total quantity of water available at any given time is crucial for agricultural, industrial, household, recreational, and environmental activities. Water covers about 71% of the earth's surface. However, roughly ninety-seven percent of the water on earth is salt water, and most of the remaining 3% (fresh water) is frozen at the North and South Poles. Only a very small volume of fresh water (~0.02%) is available in rivers, streams, aquifers, and springs as drinking and process water. The water cycle (evaporation, condensation, precipitation, percolation, and transpiration) is the self-perpetuating and self-renewing process undergone by the earth's water.

The evaporation process separates water from the pollutants gathered during its journey on the earth and restores its purity. Clouds deliver pure water everywhere and feed primary sites of reserve (glaciers, rivers, and lakes above and below the ground). To be suitable for human use, water must comply with safety standards. Man has learned and is still developing processes to free water from pollution. Water treatment dates back to the Egyptians, is documented in the Bible (Exodus), and was regularly implemented during the Industrial Revolution of the 19th century. Besides being an effective means of re-using water from sewage treatment, reverse osmosis (RO) crossflow filtration currently removes salts and bio-contaminants from salt water and makes the ocean available as a direct source of usable water. Although desalination is expensive, there is no alternative for sustaining a population in arid areas.

Water pollution is any change in the chemical, physical, and biological quality that has a harmful effect on living organisms or makes water unsuitable for a desired purpose. This definition implies three categories of pollutants:

- **Chemical:** Atmospheric impurities (dust, industrial and volcanic smoke, and gases) convert pure water into a solution and also a dispersion of foreign substances and modify its pH. Acid rain is produced when nitrogen and sulfur oxides combine with water vapor to form acids. Heavy metals (e.g., lead, cadmium, arsenic, and aluminum) and radioactive chemicals (e.g., radon,

cesium, and isotopes of iodine) can occur naturally or be introduced from industrial sources. Oil and hydrocarbons reach water from oil tankers, motor vehicles, discharges, and dumping grounds. The plant nutrients nitrogen and phosphorus originate from animal wastes, agricultural treatments, and sewage (eutrophication).

- **Physical:** Sediments from erosion, deforestation, and agriculture are sources of bulky materials and suspended solids often carrying organics, pesticides, and bacteria that destroy aquatic life and contaminate reservoirs. Heat can amount to thermal pollution, which lowers the dissolved oxygen level and exposes many aquatic organisms to the risk of death.
- **Biological:** Several millions of humans risk death each year as a result of bacterial contamination in drinking water. Polluted waters carry bacteria, fungi, viruses, algae, protozoa, and parasitic worms, and cause a variety of serious diseases.

The United States EPA (Environmental Protection Agency) sets standards for drinking water quality, and the FDA (Food and Drug Administration) those for bottled water. The European Union codifies the quality of potable water in the Drinking Water Directives 98/83/EC. The World Health Organization (WHO) publishes and reviews the volumes '*Guidelines for Drinking-Water Quality*' as the basis for regulation and standard setting to ensure the safety of drinking water.

Water sources for human and industrial use are divided into surface and sub-surface water. The surface water (rivers, lakes, wetlands, and artificial reservoirs) is restored by precipitation. Direct contact with erosion, human, and animal activities makes water unusable without specific physical (clarification) and chemical (disinfection) treatments. Sub-surface water, also known as groundwater, is fresh water located underground in pore spaces of soil and rocks and in deep, flowing aquifer areas below the water table. Sub-surface water is filtered by seepage and is well protected from environmental pollutants except for those originating from uncontrolled human activities that can pollute by seepage of fertilizers, pesticides, solvents, and other pollutants. It has a slow rate of turnover compared to surface water, so that pollution can remain for a long time. Industrial, public, and private wells extract potentially unsafe groundwater which needs treatment after extracting. There is not enough water for all user to have clean, fresh water 24 hours a day and 7 days a week. Thus, water is increasingly re-used both to have it available and to save the cost of disposing of the waste water.

Industry uses water to carry out manufacturing and cleaning processes. It is estimated that 15% of fresh water use worldwide is industrial. Fresh, potable water provides safe food, clean surfaces, cooling, and hydroelectric power among other benefits. Nevertheless, even potable water includes substances that affect the good running of processes. The next sections are concerned with chemical theory and problem solving.

1.1

Variables

An understanding of water purification requires an understanding of the reactions of the water impurities in acidic, neutral, and alkaline solutions. Heating, cooling, acidification, treatment with alkalis, softening, deionizing, evaporating, concentrating, moving, spraying, recovering, re-using, filtering, centrifuging, and disinfecting represent processes that trigger a huge quantity of chemical interactions, usually with detriment in cleaning, among metals, inorganic and organic substances present in the system. The main variables influencing aqueous solutions are briefly considered in the next sections.

1.1.1

Water

The American Dictionary [1] defines water as *'a clear colorless, near odorless and tasteless liquid, H_2O , essential for most plant and animal life and the most widely used of all solvents. Melting point $0^{\circ}C$ ($32^{\circ}F$), boiling point $100^{\circ}C$ ($212^{\circ}F$), specific gravity ($4^{\circ}C$) 1000. ...'*

The hydrogen atoms in water carry a positive charge, while the oxygen has a negative one. Dipoles attract each other, forming bonds known as 'hydrogen bonds' or 'hydrogen bridges.' They link the molecules into an aggregate responsible for all the properties of liquid water (below $100^{\circ}C$) or solid (below $0^{\circ}C$), the solid (ice) being less dense than the liquid (water).

The triple point is one of the most important values in physics. It defines the point where ice, water, and water vapor are simultaneously and continuously balanced. Figure 1.1 shows the physical parameters of the triple point and the planar structure of water.

Because of its properties, water is the lifeblood of the environment, essential to the survival of all living things. It has been said that water promises to be to the 21st century what oil was to the 20th century [2]. All foods contain water in different proportions. Foods considered dry (e.g., cereals, flour, walnuts. ...) contain 10–15% water, bread 29–40%, meat 60–80%, potato 70–80%, milk 86–88%, beer and wine 85–90%, and peeled watermelon up to 97% [3].

Pure water is colorless, tasteless, and odorless, and possesses an extraordinary property: the ability to dissolve every substance occurring in the earth's crust and in the atmosphere. Ca, Mg, Al, Fe, and Si (important elements in detergency) occur in the earth's crust at average concentrations of 3.6, 2.1, 8.2, 5.0 and 27.7% respectively [4]:

Owing to its solvent property, water carries impurities, and these may cause trouble for industries. The types of impurities in raw water are broadly classified as dissolved and suspended solids and dissolved gases [5]. The ability to solvate and to dissolve makes water the primary agent of cleaning. Together with other parameters, the evaluation of the amount of water in a process is often the key

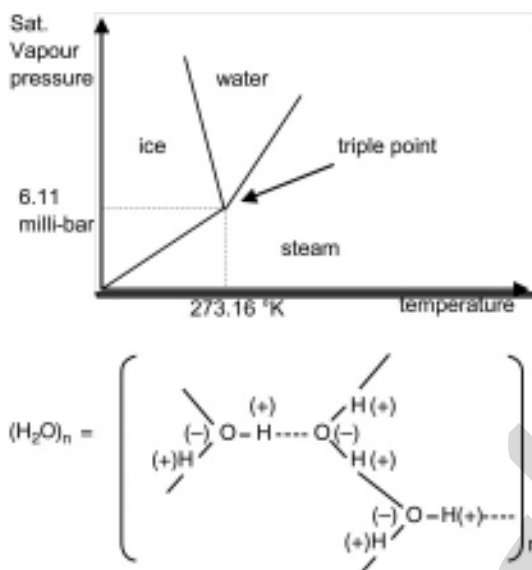


Figure 1.1 Triple point and planar structure of water.

factor in discovering the reason behind unsatisfactory results of cleaning, poor lubrication, insufficient rinsing, and other failures.

Rocks are dissolved by water seeping into the crystal lattice, by hydrolysis mainly involving silicates, by redox reactions when rocks come into contact with oxygenated waters, and by acidic attack from carbonic, sulfuric, and nitric acids. An example of the dissolution of potassium feldspar is described in Garrels and Christ [4]:



Natural organic matter such as tannin and lignin derivatives are generically present in water as colloidal suspensions [6]. Humic compounds together with clay constitute a major impurity typical of water collected near rivers and marshes. After water is collected from strata, the colloids which it contains destabilize, agglomerate, and deposit inside pipelines and equipment. Deposits can become detached and transferred to food by water hammer.

All the organisms living in water are considered to be organic matter. They sometimes interact with inorganic salts (e.g., iron, sulfate) and modify the original salinity of water. All over the world water is suspected to be the vehicle for 80% of infection in people, and the danger is sometimes not obvious [2]. The appearance of chemical and biological reactions depends on the quantity of water in food and in the environment. Cappelli and Vannucchi [7] give a graph of the main events that occur during food storage as a function of the water activity (a_w) (Figure 1.2):

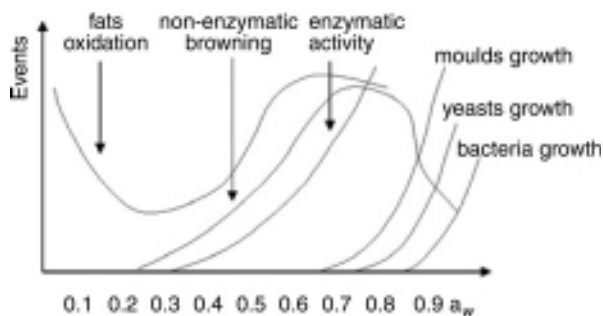


Figure 1.2 Main events in a food as a function of the water activity.

The less water present, the less is the biological activity. The activity of bacteria and fungi (living matter) is more water-dependent than are the chemical reactions.

1.1.1.1 Hardness

Water hardness directly depends on the content of alkaline-earth salts and defines the chemical quality of a water. One of the aims of the pre-cleaning investigation is to determine this. It is quite impossible to plan a cleaning procedure without knowing the water hardness.

Salts differ in their solubility, and some of them may remain soluble while others precipitate under the influence of temperature and pH change. Consequently, hardness is divided into

- permanent such as chlorides and nitrates (salts that remain soluble)
- temporary such as bicarbonates (precipitating salts)
- total sum of permanent and temporary hardness.

As the competition between precipitating and solubilizing agents involves multi-valent cations, the industrial cleaning takes the total hardness (the sum of all the salts). Hardness is reported in degrees as follows:

• calcium carbonate (CaCO_3)/liter	French degree	dF
• calcium carbonate (CaCO_3)/UK gallon	English degree	dE
• calcium carbonate (CaCO_3)/US gallon	American degree	dA
• calcium oxide (CaO)/liter	German degree	dG.

where 10 mg L^{-1} of calcium carbonate corresponds to 1 French, 0.7 English, 0.59 American and 0.56 German degrees. The French degree is preferred because of its decimal scale. The unit 'ppm' (parts per million) is often used as an alternative to mg L^{-1} .

The calcium found in a system derives both from water and contamination of the process. In order to arrive at a suitable choice of a detergent and its correct concentration, the overall content of calcium should be considered even if this

Table 1.1 Calcium contents of some foods.

Food	Ca (mg/100g)
Skimmed milk	120
Fresh cheese	>400
Seasoned cheese	up to 1200
Whole egg	50
Lettuce	45
Veal meat	14
Sole	12
Squid	144

value is not easy to calculate. Examples of calcium contents in some foods are given in Table 1.1 [7].

Iron and magnesium are metals often ignored, but they assume great importance in meat and vegetable processes. Blood (hemoglobin) contains iron, and chlorophyll magnesium. For instance, sequestrants assist detergents in accelerating the solubilization rate of dried blood and the deposits removed in vegetable blanching. Sometimes, the cleaning process must be reversed, starting with acid instead of alkaline detergent (e.g., blood cleaning).

1.1.1.2 Salinity

Salinity is the sum of all the salts dissolved in water. It increases and assumes importance every time a loss of pure water occurs in the system. Cooling towers, tunnel pasteurizers, and boilers represent typical processes where evaporation is the main event and salts increase their concentration many times. Giving a soiled surface time to dry means concentration of salts. It is an event which opposes detergency because of the formation of a lattice containing inorganic salts, organic matter, and surface ions. Moreover, polymerization, which frequently occurs in these conditions, interferes with cleaning even more seriously.

The ratio between the concentration of solids dissolved in the system and their concentration in the make-up water is known as the cycle of concentration. The number of cycles is easily calculated by comparing the concentration of a single soluble salt, e.g., chloride, in the system and make-up:

$$\text{Cycle of concentration} = \frac{[\text{chlorides}] \text{ in the system}}{[\text{chlorides}] \text{ in the make-up}}$$

Actually, every time a warm or hot rinse is performed on a warm or hot surface is wetted, an evaporation process is generated and a potential risk of salinity deposits may occur. The final section of a bottlewasher and a tunnel pasteurizer are examples.

1.1.1.3 Alkalinity

The dissociation constant of water into hydrogen and hydroxyl ions is 10^{-14} . Thus, 10^{-7} defines the point of neutrality where the two components are equally

balanced. However, even though pH 7 is theoretically considered as neutrality, pH 7 means very little in itself. In practice, the point dividing acidity and alkalinity is not 7 but 'M', the methyl orange endpoint corresponding to pH 3.6, and 'P', the phenolphthalein endpoint corresponding to pH 8.2. These endpoints tell us the ranges over which bicarbonate exists and weak acids may be present, the most prominent of these being carbonic acid-carbon dioxide solution [6]. Below ca. pH 4 the solution includes H_2CO_3 , H_2O and H^+ , the interval from 4 to 8 is the HCO_3^- range, while CO_3^{2-} is found above 8, together with OH^- . The following well-known table (Table 1.2) gives the relationship between bicarbonate, carbonate and hydroxide as a function of the P and M points.

Bicarbonate-carbonate-carbonic acid form a buffer which, acting both as acid and base, may strongly affect categories of products such as lubricants and disinfectants. Generally speaking, the reversible reaction between carbonic acid and carbon dioxide, and the influence of temperature, pressure, and the addition of acids or alkalis are the main factors responsible for the alteration of the balance in raw waters and their detergent solutions. In terms of detergency, alkalinity is divided into four zones:

- **pH from 7 to 8.3:** field of raw water and neutral detergents/disinfectants
- **pH from 8.3 to 10:** mild alkalinity where calcium salts show the greatest adherent behavior
- **pH from 10 to 12:** medium alkalinity, where sequestrants have the greatest difficulty in controlling precipitation. A higher concentration is needed (critical pH).
- **pH above 12:** caustic zone, where floc-shaped hydroxide agglomerates precipitate. Less adhesion to the surface and greater difficulty in rinsing occur.

Table 1.2 is also useful to assess caustic soda carbonation by carbon dioxide absorption. Since 50% of sodium carbonate is titrated with the phenolphthalein end point and the last 50% with the methyl orange end point, the difference between alkalinity P and M gives the concentration of NaOH and NaCO_3 . Carbonation occurs when carbon dioxide comes into contact with caustic soda. Atmospheric carbon dioxide is slowly absorbed in this way. However, some industrial processes (e.g., brewing) produce and make use of carbon dioxide.

Table 1.2 Relationship between bicarbonate, carbonate, and hydroxide as a function of P and M points.

Alkalinity	Hydroxide	Carbonate	Bicarbonate
P = 0	0	0	M
P = M	P	0	0
2P = M	0	2P	0
2P < M	0	2P	M - 2P
2P > M	2P - M	2 (P - M)	0

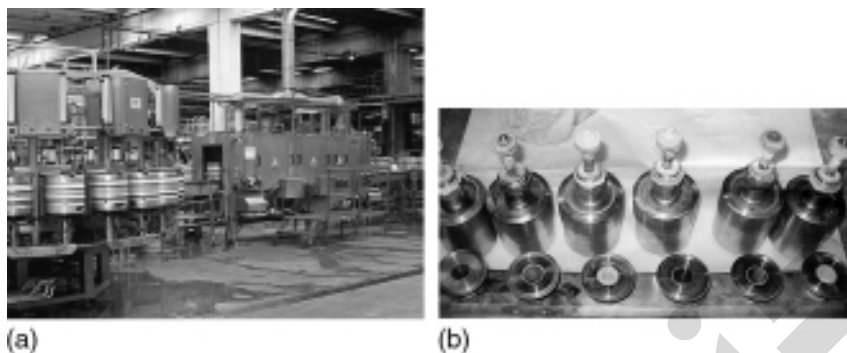
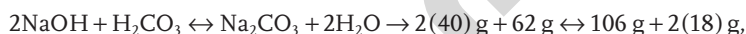
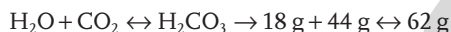


Figure 1.3 (a) Processing of beer kegs and (b) carbonate-incrusted valves.

Under standard conditions 1 mole of CO_2 occupies 22.4 liters. The molecular weight of CO_2 is 44. Thus, 44 g of CO_2 occupies 22.4 liters. Since



80 g of caustic soda react with 22.4 liters of carbon dioxide (or 1 m^3 of CO_2 will react with 3.6 kg of NaOH) with a reduction in volume. Risk of implosion and deposits on surfaces and valves are possible. Carbonation of caustic soda frequently occurs in the cleaning of beer kegs. Precipitation of sodium carbonate on valves of the washing equipment is quite usual (Figure 1.3).

Cylindrical fermenters and bright beer tanks suffer from a risk of implosion. For this reason, acid cleaning is mandatory under a CO_2 atmosphere. Acid cleaning does not require a CO_2 purge, and diminishes the risk of oxidation of beer, down time, and CO_2 waste.

Understanding how much caustic soda reacts with carbon dioxide enables one to quantify the reaction products, primarily sodium carbonate. The use of conductivity readings as a guide to caustic concentration in CO_2 environments is very misleading, as the conductivity probes measure all the conducting species, not just the caustic soda. In order to determine caustic soda and carbonate levels, a double titration is performed using two indicators, phenolphthalein and screened methyl orange.

Sodium carbonate has a negligible effect on cleaning. Cleaning needs caustic soda. A periodic check of chemicals serves the purpose of controlling the concentration of the effective agent. Part of the graph in Figure 1.4 shows a constant conductivity of the solution even though caustic soda decrease is replaced by carbonate, so that conductivity is not a good guide to composition.

1.1.1.4 pH

The pH is the hydrogen ion concentration expressed in logarithmic form ($-\log[\text{H}^+]$). It depends on the type of dissolved salts. Bicarbonates buffer raw

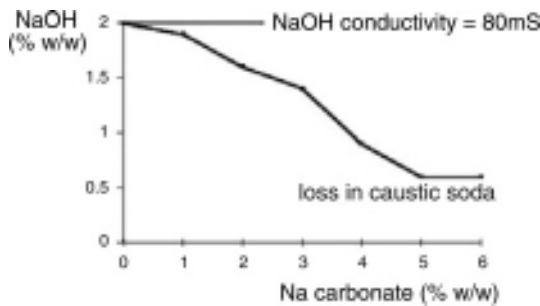


Figure 1.4 Conductivity remains constant even if the caustic soda decrease is replaced by carbonate.

waters at a pH between 7 and 8, while carbon dioxide decreases the pH to below 7. Buffering is the ability of some salts to confine pH within narrow limits. In practice, pH is buffered in order to obtain the best performance in critical processes such as soap- and amine-based lubrication, enzymatic processes, and disinfecting applications.

Sequestrants are sensitive to pH. Not only their solubility is affected (e.g., EDTA is unstable in acidic pH), but sequestrants normally increase in sequestering power when the pH rises. Hydrogen ion adversely affects the stability of the complex, which is prised by a complete deprotonation. Conversely, the hydroxyl ion takes a positive part in the formation of coordination bonds and contributes for forming and stabilizing the complexes. A critical pH has been identified, which divides sequestrants into two groups. The first group shows the best activity in a caustic medium, the second in neutral conditions.

The pH can also indicate potentially corrosive solutions. The iron oxide film on an iron surface is continually dissolved at an acidic pH (below 4). The corrosion between pH 4 and pH 10 depends on oxygen diffusion and is almost independent of pH. Iron becomes increasingly passive above pH 10 [5]. A pH of less than 4 is typical of descalers and acidic detergents, while a pH above 9 is characteristic of alkaline and chlorinated alkaline detergents.

Several categories of sequestrants behave as cathodic inhibitors at an acidic pH, and sometimes the choice of a sequestrant is made purely with this in mind (e.g., acid soak of aluminum molds).

1.1.1.5 Conductivity

The very slight ionization of pure water cannot conduct current, while salts and other ionizable matter dissolved in water cause it to have electrical conductivity. Conductivity depends on the ability of an ion to conduct electricity. The higher the content of minerals in water, the higher is the conductivity. Thus, conductivity is a measure of the concentration of dissolved minerals in water and can also be used to monitor the concentration of a detergent solution. Thus, detergents are recommended to have sufficient conductivity to allow electronic devices to control their concentration automatically [8].

Corrosion takes place faster, the more freely the current can move through the water.

A nonlinear relationship is obtained when conductivity is plotted against the concentration of chemicals. The conductivity reaches a maximum and then falls off as the concentration increases. This nonlinearity arises because of the individual contributions of anions and cations, the viscosity of the solution, and interactions between ionic species and the solvent. This occurs in the presence of high concentrations of salts. However, a linear relation is observed at low concentrations (below 10%) where only the individual contributions of anions and cations are relevant [9]. The graphs in Figure 1.5 show the relationships.

Detergents work at relatively low concentrations, from 0.5 to 5% on average, and for practical purposes electronic devices can control these concentrations reproducibly.

Conductivity strongly depends on temperature. Increase in temperature leads to increased conductivity, but linearity is maintained at low concentrations of chemicals. As small molecules lead to high conductivity, the large molecular size of sequestrants and organic materials (e.g., organic acids) leads to very low conductivity. However, the conductivity of caustic soda and potash, hydrochloric, sulfuric, sulfamic, and phosphoric acids and their salts gives cleaning solutions that can be controlled automatically.

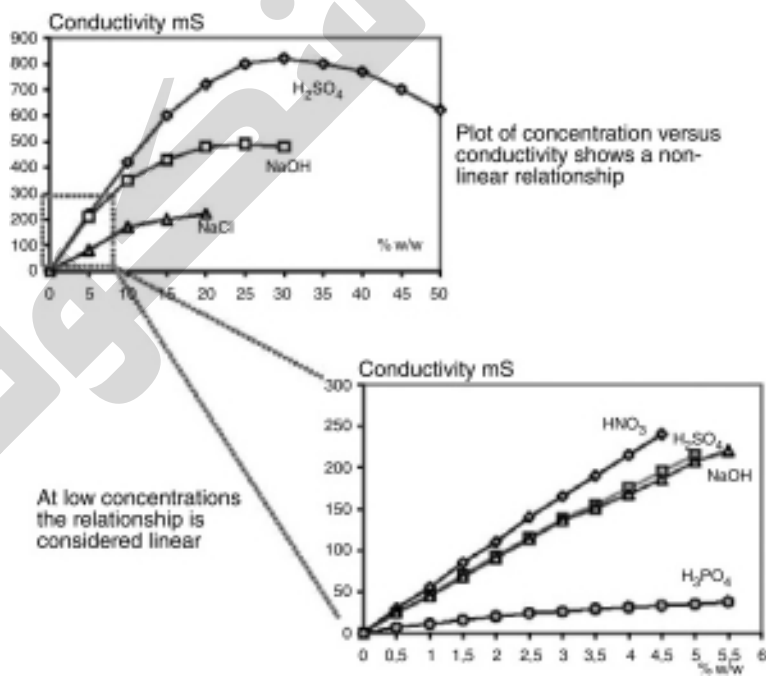


Figure 1.5 Linearity of conductivity at low concentration.

1.1.1.6 Scaling Tendency or Corrosion Tendency

Temperature, calcium concentration, alkalinity, dissolved solids, and pH represent the main factors influencing scale formation. The tendency of water to either form scale or corrode is indicated by the Langelier Saturation Index (LSI):

$$LSI = 2pH_a - pH_s$$

In order to determine how much scale or corrosion will occur, Riznar's equation is applied, giving the Riznar Stability Index (RSI):

$$RSI = 2pH_s - pH_a$$

where:

pH_a = pH of water under operating conditions

pH_s = pH of saturated solution derived from the following equation:

$$pH_s = (9.3 + A + B) - (C + D)$$

Where A, B, C, D factors are calculated as follows:

A Factor

The A factor involves the total dissolved solids. It is deduced from the water conductivity [μS] reported in ppm:

$$ppm = \mu S \times 0.55.$$

When the ppm is known, the A-factor is found from Table 1.3.

B Factor

The B factor is derived from the water temperature according to Table 1.4.

C Factor

The C factor is obtained from the calcium hardness and is expressed as ppm of calcium carbonate (Table 1.5).

D Factor

The D factor is derived from the M alkalinity expressed as ppm of calcium carbonate according to Table 1.6.

A positive LSI means a tendency of water to scale. A negative LSI means a tendency of water to corrode. The RSI predicts the extent of the scaling or corrosion (Table 1.7).

Table 1.3 A factor.

ppm	A factor
50–300	0.1
400–1000	0.2

Table 1.4 B factor.

Temperature (°C)	B factor
0–1	2.6
2–6	2.5
7–9	2.4
10–13	2.3
14–17	2.2
18–21	2.1
22–27	2.0
28–31	1.9
32–37	1.8
38–43	1.7
44–50	1.6
51–56	1.5
57–63	1.4
64–71	1.3
72–81	1.2

Table 1.5 C factor.

Calcium hardness Ca carbonate (ppm)	C factor
10–11	0.6
12–13	0.7
14–17	0.8
18–22	0.9
23–27	1
28–34	1.2
35–43	1.3
44–55	1.4
56–69	1.5
70–87	1.6
88–110	1.7
111–138	1.8
139–174	1.9
175–229	2
230–279	2.1
280–349	2.2
350–439	2.3
440–559	2.4
560–699	2.5
700–879	2.6
880–1000	2.7

Table 1.6 D factor.

'M' alkalinity Ca carbonate (ppm)	D factor
10–11	1
12–13	1.1
14–17	1.2
18–22	1.3
23–27	1.4
28–35	1.5
36–44	1.6
45–69	1.7
70–88	1.8
89–110	1.9
111–139	2
140–176	2.1
177–229	2.2
230–279	2.3
280–359	2.4
360–449	2.5
450–559	2.6
560–699	2.7
700–889	2.8
890–1000	2.9

Table 1.7 Expectation from RSI value.

RSI value	Expectation
4.0	Heavy precipitation
5.0	Light precipitation
6.0	Limit of precipitation
7.0	Starting corrosion
8.0	Heavy corrosion
9.0	Intolerable corrosion

1.1.2 Salts

The solvent power of pure water leads to the presence of various dissolved salts. The quantity and type of salts depend on the strata through which the water has been running [10]. The solubility product of the strata components and the duration of contact with the water are crucial parameters determining the amount of salts taken into solution. Examples of typical salt contents in water are given in Table 1.8.

Table 1.8 Typical salt contents in water.

Ions (mg L ⁻¹)		Sample A ^{a)}	Sample B ^{b)}	Sample C ^{c)}	Sample D ^{d)}
Sodium	Na ⁺	4.38	1.45	21.60	2.30
Potassium	K ⁺	0.17	1.75	2.70	0.91
Calcium	Ca ²⁺	0.70	17.50	51.60	280.00
Magnesium	Mg ²⁺	0.56	1.05	31.37	76.60
Strontium	Sr ²⁺	–	traces	3.10	10.50
Chloride	Cl ⁻	7.00	0.65	11.35	4.20
Sulfate	SO ₄ ²⁻	0.65	8.20	53.28	802.50
Bicarbonate	HCO ₃ ⁻	3.96	53.10	280.60	234.85
Silicate	SiO ₂	6.50	4.80	11.50	10.50
Nitrate	NO ₃ ⁻	0.20	0.60	0.66	0.60
Phosphate	PO ₄ ³⁻	Traces	–	Traces	–
Total hardness (dF)		0.40	4.78	25.60	(>50)
pH		5.65	7.65	7.70	7.03

a) From 'AMOROSA' mineral water (analysis: July 20, 1984).

b) From 'LEVISSIMA' mineral water (analysis: March 19, 1982).

c) From 'FONTEMURA' mineral water (analysis: March 10, 1978).

d) From 'S. SILVESTRO' mineral water (analysis: April 30, 1981).

Bicarbonate, silicate, sulfate, calcium, magnesium, and iron are the main ions involved in the competition between solubilization and precipitation. Among these, calcium and bicarbonate are usually the most important ions in the chemistry of water [10]. Whenever a cation meets an anion and forms an insoluble salt, precipitation and scale are to be expected unless a particular anion in the system is able to compete with the precipitant for the cation and keep it soluble, suspended, or dispersed. Aqueous solutions of detergents show two opposite types of behavior: precipitation and sequestration. Sequestration is used to prevent adherent deposits, and this result can be achieved in different ways described as solubilization, dispersion, suspension, inert flocculation, and antiredeposition. All of these play a role in attaining and preserving clean surfaces.

1.1.2.1 Precipitation

Most of the detergency functions are based on the competition between compounds tending to precipitate and chemicals tending to prevent precipitation or bring back the precipitate to solubility. Whenever a chemical reaction occurs in an aqueous medium, the final products are insoluble, soluble, or gaseous.

- When insoluble (e.g., calcium carbonate), they nucleate and precipitate on the surface.
- When soluble, they may either remain soluble (e.g., potassium soaps) or separate from the solution (e.g., calcium soaps).
- When gaseous (e.g., carbon dioxide), they leave the solution.

Each of these types of behavior modifies the internal equilibrium of the solution. Problems deriving from these changes must be managed with suitable detergents.

The solubility product of salts governs their precipitation:

$$K_{sp} = \frac{[M^{n+}][An^{m-}]}{[MAn^{(n-m)}]}$$

Some salts have low values of K_{sp} and therefore have negligible solubility. Examples are given in the Table 1.9.

The solubility product governs not only the solubility of mineral salts but also that of the organic matter. Calcium soaps, for instance, have values in the range 10^{-5} – 10^{-7} mol L⁻¹ [14]. Solubility or precipitation of more complex organic molecules (e.g., proteins and starches) can be described with similar concepts. Actually, besides physical modifications induced by temperature, the adsorption of alkaline-earth cations sensitively affects the aqueous equilibrium of such materials.

Naturally, raw waters do not exactly correspond to solutions of well-defined salts but rather of different combinations of these. For instance, carbonates are found protonated as bicarbonates, sulfates are linked with sodium and potassium but also with barium and magnesium, and hydroxyl ions are in solutions close to neutrality. Interference modifying the original equilibrium may lead to insoluble salts and cause precipitation and scale. Alkalinity and temperature changes, evaporation, concentration, and filtration are usually responsible for the collapse of the original equilibrium. Fortunately, scale is formed by mixtures of salts where carbonates are usually predominant. Since carbonate is thermodynamically

Table 1.9 Examples of solubility products.

Salts	Solubility product
[Ca ²⁺] [CO ₃ ²⁻]	1×10^{-8} [11]
[Mg ²⁺] [CO ₃ ²⁻]	2.6×10^{-5} [11]
[Ba ²⁺] [CO ₃ ²⁻]	5×10^{-9} [11]
[Ba ²⁺] [SO ₄ ²⁻]	1×10^{-10} [11]
[Ca ²⁺] [SO ₄ ²⁻]	6×10^{-5} [11]
[Mg ²⁺] [2OH ⁻]	1.2×10^{-11} [11]
[Fe ³⁺] [3OH ⁻]	1.6×10^{-38} [12]
[3Ca ²⁺] [2PO ₄ ³⁻]	5×10^{-30} [12]
[5Ca ²⁺] [3PO ₄ ³⁻] [OH ⁻]	3×10^{-58} [12] apatite
[Cu ²⁺] [2H ₃ N ⁺ CH ₂ COO ⁻]	7.9×10^{-16} [12] copper aminoacetate
[Ca ²⁺] [C ₂ O ₄ ²⁻]	2.6×10^{-11} [13] calcium oxalate

unstable in acidic pH, acids easily solubilize it. The solubilization of carbonate allows the other insoluble salts to be removed and dispersed as insoluble matter (e.g., silicate, sulfate, and phosphate).

The type of salts dissolved in water has considerable practical implications. One of the consequences is the reduction of heat exchange by scale. The increase in energy required to keep the equilibrium at the steady condition is considerable, as illustrated in Figure 1.6 [15].

Since water has a permanent hardness, it is useful to know in advance, from the total hardness, how much deposit could adhere to a surface. When the ion content in water is known, it is possible to quantify the scale on a surface from the following equation:

$$W^{\circ} = \text{water hardness (dF)} \times \frac{P}{10}$$

where:

W° = quantity of scale on the surface expressed as CaCO_3 in mg L^{-1}

P = percentage of precipitation correlated to the water salts through the experimental equation

$$P = 91.1 - 47.31 \log a.$$

where a is derived from the ratio between the sum of all the ions and bicarbonate:

$$a = \frac{2[\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^{+}] + [\text{K}^{+}] + \dots + [\text{SO}_4^{-}] + [\text{Cl}^{-}] + [\text{SiO}_3^{-}] + \dots}{[\text{HCO}_3^{-}]}$$

When $a = 1$, calcium bicarbonate is the only constituent of the water

When $a < 1$, water contains calcium bicarbonate and carbon dioxide

When $a > 1$, water contains other salts besides calcium bicarbonate.

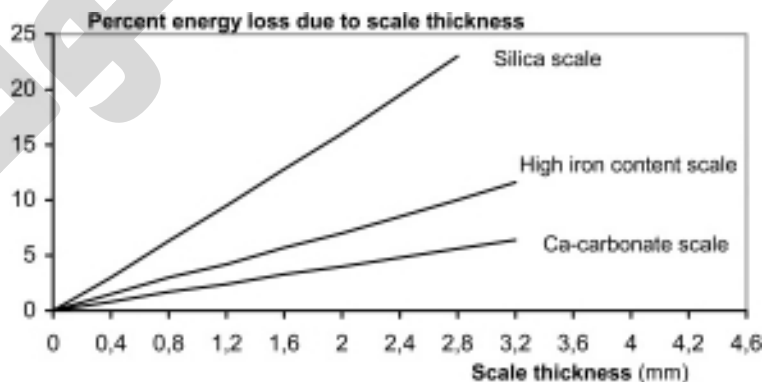


Figure 1.6 Increase in energy as a function of the type of scale.

When $a = 1$, P is experimentally close to 90% instead of 100% for the majority of waters. This practical result is connected to permanent hardness (which does not contribute to scale) and to the dispersed precipitate (not adherent to the surface). The equation is applicable to waters having bicarbonate as the predominant constituent.

When a surface is smooth and clean, scale does not immediately form, and an induction time is observed before scale formation. The delay is related to the time from the nucleation of insoluble salts to their adhesion and growth on the surface [16]. Hydrophobic surfaces (e.g., plastic) and hydrophobic materials (e.g., quaternary ammonium compounds or oily materials adsorbed on the surface) delay deposition [17]. However, after the first adherent nucleation, the rate of crystal growth rapidly increases. This is observed for phosphates, carbonates, sulfates, and calcium soaps. Calcium soaps, for instance, can take more than a week to become evident inside polyamide pipelines delivering lubricant, but only a day to increase in volume sufficiently to clog filters and pipelines.

Precipitation is accelerated both by adding crystals of salts already dissolved in the system [18] and by leaving the surface dirty. This means that, if cleaning and descaling are incomplete, precipitation (scale and soil) takes place more rapidly and increases in volume.

Hasson [19] demonstrated that the rate of scale deposition is controlled by the diffusion of Ca^{2+} and HCO_3^- ions to the deposit/water interface. A rise in the velocity of the fluid flow normally increases the rate of calcium carbonate and soil deposition, but sometimes may reduce it. This is caused by a boundary layer which forms next to the pipe or the equipment wall [16]. The boundary layer behaves as a relatively stagnant area. In the field, however, an increase in scale growth is always to be expected as a consequence of increased flow rate of water and processed liquid foods. Conversely, the rate of soil removal increases in direct proportion to the flow rate of the cleaning solution (see Section 8.2).

1.1.2.2 Sequestration

Sequestration describes the event of binding metal ions in water-soluble complexes and, thereby, of preventing undesirable precipitates [14].

Ions are divided into cations and anions. Cations, such as calcium and magnesium, bear a positive charge. They include both metallic ions and all the organic molecules bearing a total positive charge (e.g., quaternary ammonium compounds) or a partial positive charge such as the peptide group of proteins. Both metallic and organic cations can be mono- or polyvalent, where the polyvalence of the organic matter can also mean more charges in the same molecule. The differentiation between a mono- and polyvalent charge is not of merely theoretical interest. Actually, the polyvalent cations have negative effects on the cleaning process, while the monovalent ones help detergency. Defining the quantity of polyvalent cations often is the key to good cleaning results. The concentration of a detergent is frequently calculated as a function of the water hardness to which the polyvalent cations of the contamination (expressed as calcium) have to be added.

Anions bear a negative charge. They can be inorganic (e.g., chloride, carbonate) or organic (e.g., tartrate, oxalate, fatty acids). All react with cations and form salts. Anions giving insoluble salts cause precipitation unless another type of anion, more competitive and able to form soluble complexes, is present. Anions forming insoluble salts are defined as precipitants. Anions forming soluble complexes constitute the group of sequestrants. Thus, sequestration is the ability of some anions to keep the polyvalent cations soluble or to re-solubilize them if they are in a precipitate.

The chemistry of coordination governs the chemistry of sequestrants. All atoms except hydrogen and carbon are able to give or accept electrons and form coordination bonds as well as the normal bonds expected from the covalence rules [20]. Ligands link the central metal by a coordinated covalent bond in which all the electrons participating in the bond derive from the ligands. Therefore, the central atom acts as an electron acceptor and each ligand acts as an electron donor according to Lewis's acid-base reaction. Molecules and ions with pairs of free electrons form complexes, the strength of which depends on their ability to share those electrons [21]. The coordination number indicates the number of bonds with the metal ion and can vary from 2 to 9. The most frequent numbers are 2, 4 and, still more frequent, 6 (octahedral structure ML_6). Multi-ligand sequestrants are able to build a ring structure, which has higher stability when 6 bonds are present [20, 22].

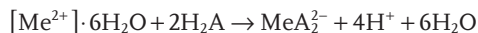
Werner's theory of coordination affirms that [20, 23]

- Most elements show two types of valence. The primary valence corresponds to the oxidation state of the element and the secondary one to its coordination number.
- These elements tend to satisfy both valences.
- The secondary valence is directed toward fixed positions in space.

The directional bonds are explained by the theory of atomic orbitals overlap. The atomic orbitals determine the formation of a stable bond only if they have the greatest electronic density. While the type s orbital gives spherical nondirectional symmetry, the p and d types show the electronic density along the xyz axis ($3d_{x^2-y^2}$, $3d_z^2$, and hybrid $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$) [22]. From these postulates a complex can be represented with spatial geometry. Examples are given in Figures 1.7 and 1.8.

A coordination reaction is likewise described as shown in Figure 1.9 [24].

The reaction is based on the following general reaction:



Octahedral, tetrahedral, trigonal and the other spatial structures as well as the theory and principles of coordination bonding are comprehensively reviewed by Cartmell and Fowles [22] and Schläfer and Gliemann [27].

Sidgwick's EAN (Effective Atomic Number) theory proposes that the central metal ion tends to surround itself with as many ligands as are necessary to

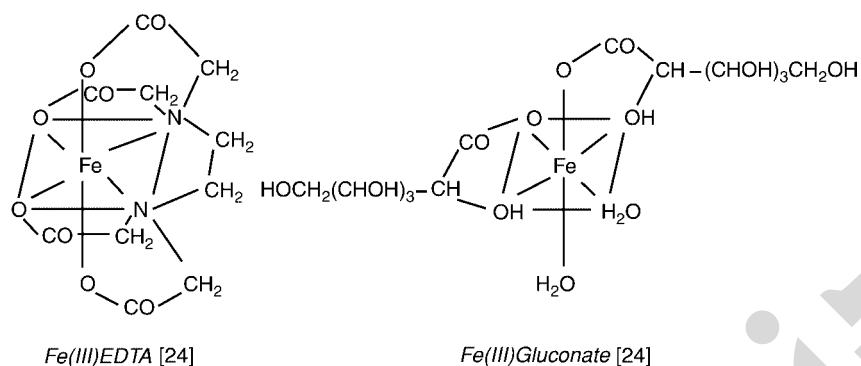


Figure 1.7 Iron complexes with EDTA and gluconate.

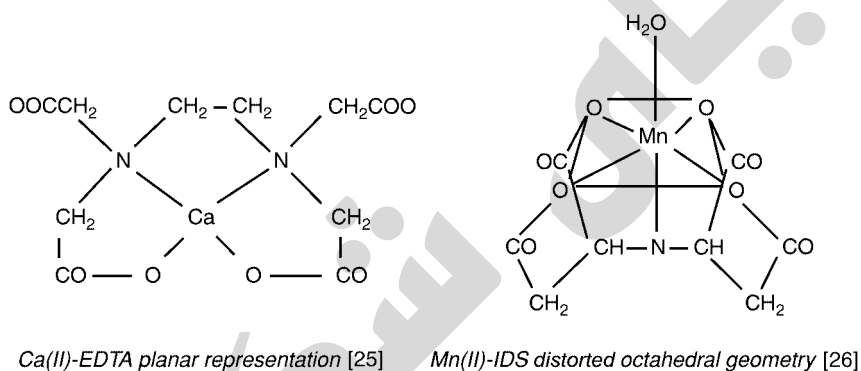


Figure 1.8 Complex structure for Cu-EDTA and Mn-IDS.

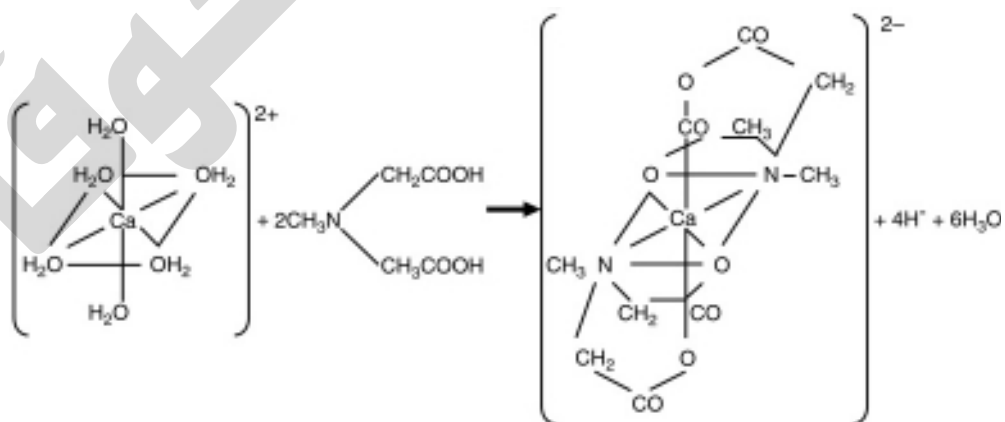


Figure 1.9 Coordination reaction.

achieve a number of electrons equal to the nearest inert gas. This is said to be the *effective atomic number* of the central ion. If the central metal ion affects the stability of the complex as a function of its electronic configuration, the smallest ions should form the strongest bond as a consequence of their stronger magnetic field. As far as the bivalent hydrated ions are concerned, the fact that the heat of hydration is a function of the reciprocal of the atomic radius confirms this (Figure 1.10) [22, 28].

As the ionic radius increases, the strength of the ion-dipole bonds decreases. Thus, stronger bonds are to be expected in complexes with magnesium than in complexes with barium. Since the ionic radius also decreases from Ca^{2+} to Zn^{2+} because of the contraction of the electronic cloud from 0.99 to 0.72 due to the increase in the nuclear charge of the elements, a similar trend should be found in the heats of hydration of the bivalent ions of the first transition series. The experimental data actually reveal a slope with two peaks (Figure 1.11) [22, 28]. The extra stability is explained by the stabilization energy of the Crystal Field Theory, which supports the electronic configuration theory of the central metal ion. The crystal field theory assumes that the ligands of a coordination compound are the source of an electrostatic field (negative charges) which perturbs the energy level of the d orbitals of the central metal ion (positive charge). This subjects the metal ion to an electric field analogous to the field of an ionic crystal lattice (ionic bonds). Thus, the crystal field theory connects the stability of the

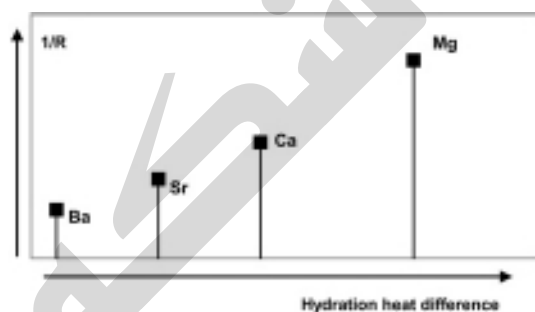


Figure 1.10 Heat of hydration as a function of the reciprocal of the atomic radius.

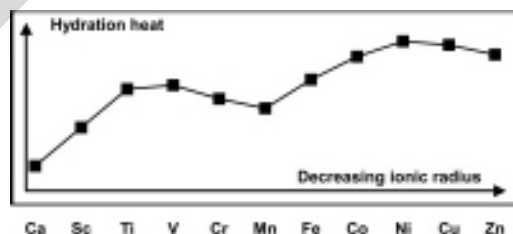
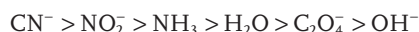


Figure 1.11 Heats of hydration of the transition elements.

complex not only to the positive central metal ion but also to the anionic ligands. Thus, the actual stability depends on a combination of the properties of the metal ion and the ligands.

Strong bonds due to a smaller ion do not always ensure higher stability of the metal-sequestrant complex. Actually, the ambient species [hydrogen, hydroxyl ion, and water (H^+ , OH^- , and H_2O)] compete as ligands and take part in the complex. It follows that the competition between hydration, protonation, hydroxylation, and sequestration can sometime lead to a reversal of the order and make the stability of bigger ions superior to that of smaller ones. Examples of stability constants are given in Table 1.10 [13, 29].

It is possible to determine the perturbation of the energy levels from the alteration of the adsorption spectrum of the central metal ion [30]. Thus, it is possible to list ligands according to the strength of their influence on the energy level. As strength also means bond stability, ligands are arranged according to their stability. The order of strength of the ligands is known as the spectrochemical series. The position of the absorption band of a compound moves toward the blue (shorter wavelength) when one ligand is replaced by another giving a stronger bond. The strengths of the bonds formed by the following ligands tend to be in the order shown [20, 31].



Van Uitert and Fernelius [24, 32] suggest the following order of affinity to the central metal:



Besides this series, sulfonic ($-\text{SO}_2\text{OH}$) and phosphonic [$-\text{PO}(\text{OH})_2$] together with hydroxyl ($-\text{OH}$) and sulfhydryl ($-\text{SH}$) groups are often combined with amino and aminocarboxylic groups in order to obtain molecules whose the structure is increasingly suitable for providing stability to the complex in every medium.

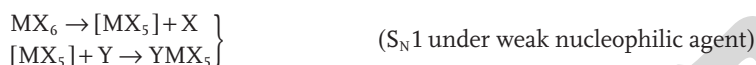
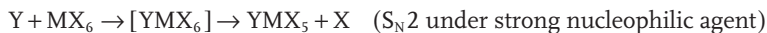
Investigating complex compounds with radioactive ions, Basolo and Pearson [33] demonstrated that complexes exchange ligands independently of their stability. So, the central metal ion is not blocked and fixed to a ligand, but ligands may

Table 1.10 Examples of stability constants.

Metals	HEDP	ATMP	EDTMP	DTPMP	STP	EDTA	NTA	PBTC
Ca^{2+}	5.74	6.68	9.33	7.11	5.36	10.59	6.41	4.4
Mg^{2+}	6.39	6.49	8.63	6.40	5.81	8.69	5.41	5.6
Fe^{3+}	33	28.9	19.6	—	—	25.1	15.87	13.3
Cu^{2+}	19	13	18.95	19.47	8.70	18.79	12.7	10.1

HEDP, Hydroxyethylidenediphosphonic acid; STP, Sodium tripolyphosphate; ATMP, Aminotrimethylenephosphonic acid; EDTA, Ethylenediaminetetracetic acid; EDTMP, Ethylenediaminetetramethylenephosphonic acid; NTA, Nitrilotriacetic acid; DTPMP, Diethylenetriaminopentamethylenephosphonic acid; PBTC, Phosphonobutanetricarboxylic acid.

be continuously replaced in binding metals. The interchange rate is related to the electronic configuration of the complex rather than to the nature, charge, and radius of the metal. The rate does not usually depend on the nature of the ligands but follows the reaction of nucleophilic substitution S_N2 or S_N1 according to the strength of the nucleophilic reagents [22]:



For instance, cyanide (CN^-), still used as sequestrant in galvanic processes, shows the following rate of exchange (Table 1.11) [22]:

The competition concerns a number of ligands for a single metal rather than a number of metals for a single ligand [18]. The mobility of ligands [11] can be used to explain the ability of blends of sequestrants to keep the polyvalent cations soluble. In actual fact, the stoichiometric¹⁾ sequestrants (e.g., EDTA, NTA, MGDA and GLDA) precipitate only when all their charge is saturated by ions of polyvalent metals. Consequently, if one still-free charge of EDTA is sufficient to keep all the complexes soluble, it is also proved that multivalent cations above the stoichiometry will precipitate all the remaining complexes. Besides this, the stoichiometric sequestrants show stability constants and reaction rates generally higher than the threshold sequestrants. This means that the stoichiometric sequestrants first react and are saturated by polyvalent cations when they work together with the threshold sequestrants. In spite of this, the stoichiometric sequestrants do not precipitate and keep their sequestering ability even in sub-stoichiometric conditions in the presence of threshold sequestrants. The reason is simply due to the huge amount of intra- and extramolecular coordination bonds sustained by the threshold sequestrants. Some of these are always sufficiently free to allow the stoichiometric ones to exchange ligands and help them to remain soluble. Of course, thresholds have not the same ability to provide a suitable configuration to help stoichiometrics to remain soluble. Thus, mixtures of sequestrants must be tailored to the expected field of application (pH and type of contamination). Experience proves that the best performing blends include a stoichiometric EDTA, NTA, MGDA, GLDA, and IDS (order of result) combined with a threshold ATMP, PBTC, and DTPMP (order of preference).

Table 1.11 Rates of exchange of the cyanide group.

Complex ion	Stability constant	CN^- exchange rate
$[Ni(CN)_4]^{2-}$	10^{22}	Very fast
$[Fe(CN)_6]^{4-}$	10^{37}	Very slow
$[Hg(CN)_4]^{2-}$	10^{42}	Very fast
$[Fe(CN)_6]^{3-}$	10^{44}	Very slow

1) See Chapter 3 for a detailed explanation of stoichiometric and threshold sequestrants.

The complexity of the different phases involved in the reactions of sequestration is also revealed by comparing conductance measurements of the solution of sequestrants in acidic form in the course of their neutralization with caustic soda and calcium hydroxide respectively. The addition of caustic soda or calcium hydroxide gives different trends of conductivity. The initial part of the slope is similar for both bases (approximately up to 40–70 mL in Figure 1.12), and is explained as a simple neutralization, which involves purely covalent bonds. After the first step, sodium hydroxide follows the typical curve of conductivity, where conductivity immediately rises at the end of the neutralization of the acidity. On the other hand, calcium hydroxide keeps up a constant conductance because it forms coordination complexes after neutralizing the acidity and before going back into solution. As each sequestrant expresses coordination bonds in its own structure, the second portion of the curve is able not only to identify anions revealing chelating property but also to highlight their different behavior as sequestrants. The determination of the EDTA conductance shows the same trend, as reported in Chaberek and Martell (Figure 1.13) [24].

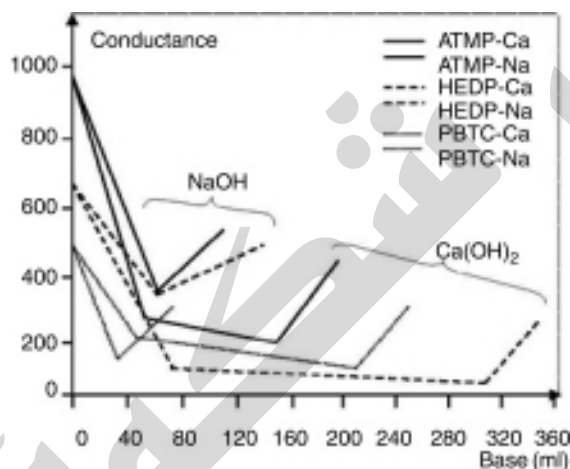


Figure 1.12 Addition of bases (1 M) to sequestrant (5 g L^{-1}); conductance in μS .

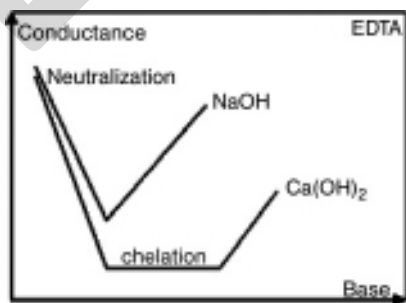


Figure 1.13 Conductance of EDTA.

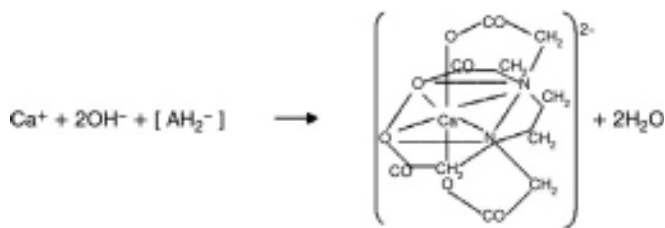
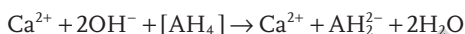


Figure 1.14 Coordination reaction.

The first segment in the Figure 1.13 corresponds to the hydrogen ion neutralization of two carboxyls:



The second (chelation) corresponds to the formation of coordination bonds (Figure 1.14). After adding the second mole, the EDTA complexing power is saturated. The amount of calcium exceeding the EDTA stoichiometry becomes free to increase the conductivity of the solution again (third segment in the Figure 1.13).

The stationary conductivity indicates sequestration, but it is a negative event if phosphoric acid, for instance, is used to add conductivity to peracetic acid. As a matter of fact, no conductivity is observed until phosphoric acid completes the reaction with the polyvalent metals of the water hardness. Thus, the conductivity of disinfectants based on peracetic acid comes from nitric or sulfuric acid. These have no sequestering power, and thus prevent a void of conductance, the width of which depends on the concentration of metals (hardness).

1.1.2.3 Flocculation

In terms of detergency, flocculation can be considered to be a different physical form of precipitation. It is positively desired in the cleaning process because the material, made inert in the form of light fluffy flocs freely moving in solution, is prevented from becoming an adherent deposit. Flocculation is the term used to indicate the destabilization of the system when colloidal organic ions and inorganic ions are simultaneously neutralized and linked together to achieve a macroscopic size. Coagulation is the further irreversible process when aggregates change to a much denser form and separate out. As electrostatic forces are mainly responsible for repulsion, the aggregation is accomplished when the properties of the system are modified by suitable chemicals able to minimize such forces. Flocculation, therefore, concerns the modification of the physical structure of the particles and their inclusion in an inert matrix. Further polymeric chemicals gather the coagulated particles and form inert larger agglomerates [6]. Then, if flocculation defines the moment of destabilization, coagulation describes the final agglomeration.

A caustic medium promotes flocculation. Organic and inorganic matter such as calcium carbonate, calcium phosphate, starch, and casein is sensitive to alka-

linity. The higher the concentration of hydroxyl ions, the more the substance tends to acquire negative charges. Hydroxylation increases electrostatic repulsion and disperses the agglomerated flocs. For this reason, a critical pH has been identified (Section 1.1.4), which represents the physical change from salt coagulation in hydroxylated agglomerates to their precipitation as adherent crystals. In systems such as bottlenwashing and recovered cleaning solutions, it is more convenient to promote a controlled flocculation rather than to arrive at stoichiometric sequestration.

1.1.2.4 Dispersion

Dispersion is also referred to as deflocculation. Its purpose is to prevent the lumping together of crystals and dispersed particles. When an insoluble material becomes part of a system (e.g., sand, limestone, dolomite, clay, pigments, insoluble inorganic and organic salts... [16]), it can cause agglomeration, precipitation, and scale generation. In order to prevent this negative development, the single particles have to be kept separated by modifying their surfaces through the adsorption of repelling substances. Keeping soil particles finely divided means keeping them dispersed.

The process is the result of competition between forces of Van der Waals attraction and Born electrostatic repulsion, according to the classical description of the interaction widely reported in the literature and represented in Figure 1.15 [34–38].

Dispersion can be attained by adjusting the charges on the particles and making the attractive energy weaker than the repulsive energy (see also Section 1.1.2.6). The adsorption of negatively charged chemicals (dispersants) generates a negative layer on each particle, which increases the zeta potential. The more the repulsive energy barrier (r.e.b.) increases, the more the particles remain stably

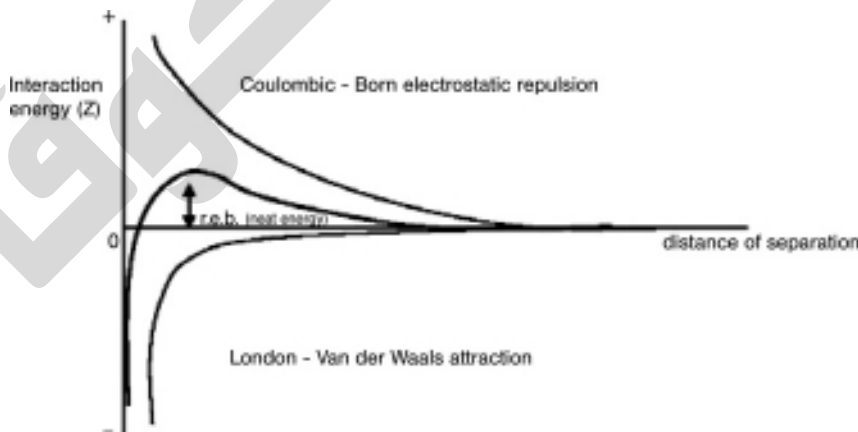


Figure 1.15 Competition between Van der Waals attraction and Born electrostatic repulsion.

Table 1.12 Influence of sequestering agents on drop in zeta potential when hardness increases from 0 ppm to 300 ppm CaCO_3 . Courtesy of Witiak, Ref. [39].

Additive	Change in zeta potential (mV)	
	Hardness (ppm CaCO_3)	
None	0	300
Detergent + polyphosphate 1500 ppm	–40	–6
Detergent + polyphosphate 1500 ppm and polyacrylate 25 ppm	–65	–41
	–68	–45

dispersed. The r.e.b. is the sum of the Van der Waals attraction and the electrostatic repulsion (central line of the graph). Hardness (calcium ion) has a dramatic effect on the surface charge. Witiak's investigation [39] demonstrates that, when CaCO_3 content increases from 0 to 300 ppm, the zeta potential drops from –40 to –6 mV in a laundry formulation free of sequestering agents, while the drop is well controlled in the presence of polyphosphate and polyacrylate (sequestrants) (Table 1.12).

Verwey and Overbeek [40] and Sonntag and Strenge [41] reversed the same concept of flocculation, coagulation, deflocculation, and dispersion to show the mechanism of soil removal from a surface [42]. They observed that the smaller the potential barrier, the more the detergent is adsorbed and the more the cleaning is promoted.

Dispersion is a property normally developed by high-polymer sequestrants (e.g., acrylic and maleic compounds). It is also claimed for all the threshold sequestrants, inclusive of phosphonates [43–45]. As described, sequestrants work by adsorption, involving simple electrostatic forces, rather than by forming true covalent bonds [5]. The surface is modified to an extent that the neighboring particles are repelled and the structure responsible for the aggregation is broken down. Therefore, if adsorption occurs early in the growth of a particle, it will prevent its further growth [5, 14]. As dispersion depends on the adsorption of a substance on a surface, sequestrants vary considerably in their ability to keep solid materials dispersed in a supersaturated system. For instance, polyacrylates represent typical dispersants, but only those of high molecular weight have good dispersing properties. On the other hand, different insolubilized materials react in different ways to the action of dispersants. It is more difficult to keep calcium carbonate dispersed than calcium sulfate [16].

Dispersion is the typical treatment of systems subjected to concentration such as cooling towers and re-used solutions of detergents. In these systems, keeping the precipitated salts dispersed is more effective and more convenient than endeavoring to prevent precipitation.

1.1.2.5 Suspension

Suspension is the opposite to precipitation and sedimentation. Applied to insoluble particles, suspension is more similar to dispersion and gives similar bene-

fits. It embodies the ability to keep insoluble particles free to move inside a solution without adhering to the surface. Suspending sequestrants are able to prevent both growth of deposits and consolidation of insoluble matter on flat surfaces. Scale is generated not only by direct growth of crystals but also by the action of gravity on inert flocs, e.g., calcium hydroxide/carbonate sedimentation in stagnant caustic solutions. For this reason, bottlewashing and recovered solutions of CIP (cleaning in place) do not form scale if detergents are formulated to contain suspending sequestrants. Electrostatic forces and hydrogen bonds between particles reduce the speed of sedimentation and flattening.

It is known that substances normally considered components of contamination (e.g., casein and starch) develop suspending ability in alkaline media. Their functional groups and polymeric structure make them quite similar to a sequestering agent, so that they actually assist the primary sequestrants in inertizing salts and keeping soil suspended as a soft mud. Keeping the caustic sections of the bottlewasher free of mineral deposits is a well-known benefit deriving from starch and casein (glue on recovered bottles). Although aluminates cannot be thoroughly conditioned by the presence of the label glue (starch-casein), this glue reduces the gluconate concentration needed to prevent aluminum oxides from forming hard deposits in the bottlewasher.

Acrylic polymers prove to be a typical example of a suspension agent, whether they are homo- or co-polymers. The suspending efficacy of the homopolymers series is illustrated in Figure 1.16. As in the dispersion process, the graph confirms that high-molecular weight compounds are the best suspension agents.

The pH affects the suspension activity. As pH increases, suspending power decreases. Figure 1.17 shows the suspending ability of polyacrylates of molecular weight between 2×10^3 and 1.5×10^5 . For each pair of lines, the lower one represents low molecular weights and vice versa.

The best suspending sequestrants do not always prevent scale. Salts in contact with a surface can actually adhere even if the suspension agents reduce sedimentation due to gravity. pH affects the apparent difference between suspending

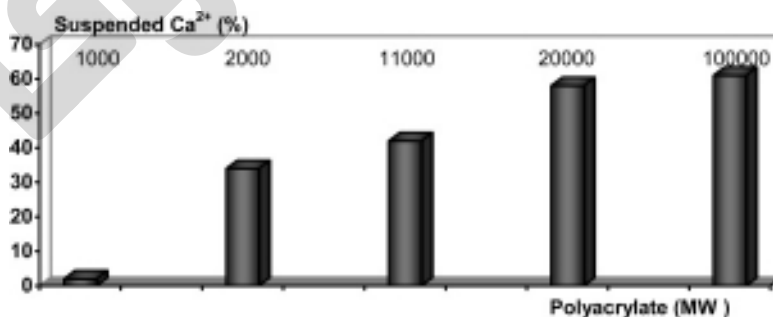


Figure 1.16 Suspending ability of polyacrylates: pH 11, Ca²⁺ 830ppm, 25 °C, 70h of rest.

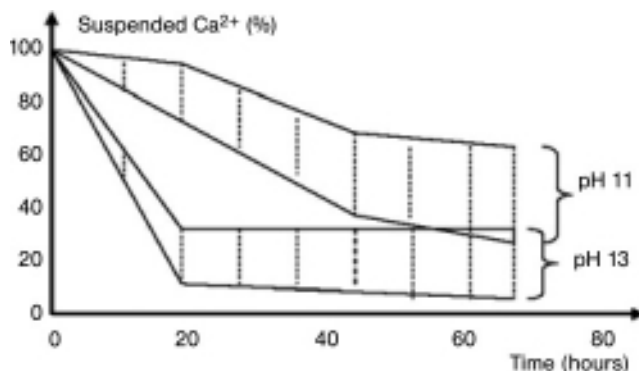


Figure 1.17 Suspending ability of polyacrylates as a function of pH.

power and scale control. The higher the pH, the less effective are the suspension agents. However, incrustation is less evident in caustic solutions than in less alkaline ones.

1.1.2.6 Anti-redeposition

Anti-deposition and anti-redeposition result from the dispersing and suspending efficiency of a washing solution. Undesirable deposition and redeposition could take place during the washing process. Detergents are expected to remove soil from the surface, prevent salts from precipitating, and prevent contamination from redeposition. Washing time, temperature, movement, rinsing conditions, surfactant type and concentration, water hardness, particle size, shape of the particulate and its charge of surface, viscosity, liquid-soil surface tension, and nature of the surface are variables involved in redeposition.

The theory of colloid stability is commonly applied to explain the process of soil redeposition. The most common definition of a colloidal dispersion is a system where particles from 1 nm to 1 μ m of any nature are dispersed in a continuous phase of different composition. In such systems, the particles are continuously undergoing brownian motion, colliding with each other. The stability of the colloid is determined by the interactions between the particles during these collisions, which is decided by a combination of attractive and repulsive forces [46]. If the repulsive forces are dominant, the dispersion will be stable. There are three basic mechanisms to stabilize colloids: steric, electrosteric and electrostatic effects.

Steric and electrosteric stabilization occur when macromolecules are adsorbed at the particle surface.

Electrostatic stabilization is explained by the DLVO theory based on the zeta potential (ζ). The theory, developed in the 1940s by Derjaguin, Landau, Verwey and Overbeek, states that the stability of a particle in solution depends on the total potential energy function V_T [46, 47], also known as the repellent energy barrier or neat energy (see also Section 1.1.2.4):

$$V_T = V_A + V_R + V_S$$

where

V_A = attractive contribution [$A/(12\pi D^2)$]

A = Hamaker constant,

D = distance between two particles

V_R = repulsive contribution [$2\pi\epsilon a\zeta^2\exp(-\kappa D)$]

a = particle radius,

ϵ = dielectric constant,

κ = Debye-Hückel parameter,

ζ = zeta potential,

π = solvent permeability

V_S = potential due to the solvent

V_S is not considered when water is the solvent.

The zeta potential is the factor that has the greatest effect on V_R . Consequently, high values of zeta potential prevent soil from redeposition. The concentration of the potential-determining ions (high charge on the particles) and a large electrical double layer length (as predicted by the Debye-Hückel theory) will generate a high zeta potential. Thus, dispersion will resist flocculation, and sedimentation (redeposition) will be prevented.

The point of the highest colloid instability is the point of electroneutrality or the isoelectric point (zero zeta potential). Therefore, in order to avoid soil redeposition, the potential needs be made more negative by keeping a high pH during washing [46]. As well as pH, carefully selected surfactants, sequestrants, and organic polymers act on the steric and electrostatic behavior of the particles, keep them suspended and dispersed, and prevent salts from depositing and soil from redepositing.

1.1.3

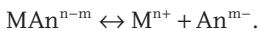
Stability Constant

1.1.3.1 Theoretical Meaning

The ratio defined as the solubility product is the factor which determines precipitation or solubility:

$$K_{sp} = \frac{[M^{n+}][An^{m-}]}{[MAn^{n-m}]}$$

It is the equilibrium constant of the reaction



Analyzed in terms of precipitants, the solubility product gives the quantity of substance in solution at equilibrium. Hence, the solubility product determines the precipitating action. For this reason, K_{sp} is also referred to as the instability constant [20] because its value becomes higher as salts become more dissociated,

that is as salts become less stable. Solubility product (or instability constant) is reported with a negative exponential. That of calcium carbonate, for instance, is

$$K_{sp} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{CaCO}_3]} = 1.7 \cdot 10^{-8}$$

Conversely, when the solubility product is related to complexes of sequestration, the aforementioned ratio is inverted so as to emphasize the thermodynamic stability of the soluble complex [20]. The inverse ratio is known as the stability constant and is reported with a positive exponential. The stability constant for Ca-EDTA, for instance, is [13]

$$K_{st} = \frac{[\text{Ca EDTA}^{2-}]}{[\text{Ca}^{2+}][\text{EDTA}^{4-}]} = 3.9 \cdot 10^{10}$$

It shows the equilibrium constant of the reaction



Stability constants are usually written in logarithmic form for ease of handling. Examples of stability constants are reported in Tables 1.13 and 1.14.

1.1.3.2 Practical Meaning

The competition between precipitants and sequestrants is one of the most important aspects of the detergency process. Detergency is often satisfactory or not according to the winner of this competition. The stability constant proves to be one of the parameters that predicts in advance which competitor will be the winner among precipitants and sequestrants. The complexing ability of a sequestering agent must fight with the insolubilizing power of a precipitant, from which it attempts to remove the metal. As a consequence, it is possible to deduce whether a precipitant is controlled by a sequestrant simply by comparing its solubility product with the stability constant of the sequestrant. Only the anions with higher stability constants will be primarily and permanently linked to the metal. In order to graphically show the concept, Figure 1.18, reported from Cutler and Davis [14], explains the competition well.

Table 1.13 Examples of stability constants.

a)	HEDP	ATMP	EDTMP	DTPMP	STP	PBTC ^a
Ca ²⁺	5.74	6.68	9.33	7.11	5.36	4.4
Mg ²⁺	6.39	6.49	8.63	6.40	5.81	5.6
Fe ³⁺	33	28.9	19.6	—	—	13.3
Cu ²⁺	19	13	18.95	19.47	8.70	10.1

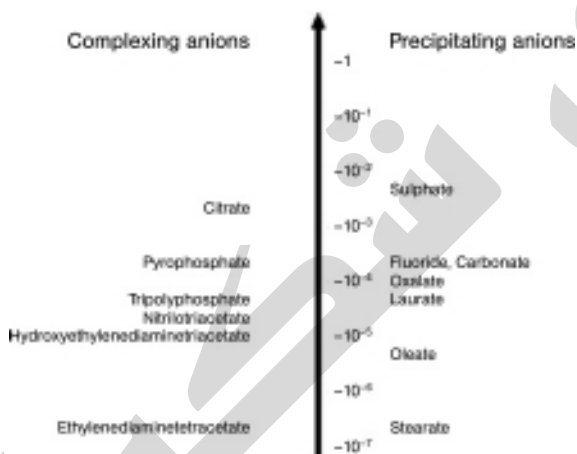
a) Adapted from Ref. [13].

Table 1.14 Examples of stability constants.

a)	NTA	EDTA	DTPA	HEDTA
Ca^{2+}	6.4	10.6	10.8	8.2
Mg^{2+}	5.5	8.8	9.3	7.0
Fe^{3+}	15.9	25.0	28.0	19.8
Cu^{2+}	12.9	18.7	21.4	17.5
Al^{3+}	11.4	16.5	18.7	14.4

a) Adapted from [48].

HEDP, Hydroxyethylenediphosphonic acid; EDTA, Ethylenediaminetetracetic acid; ATMP, Aminotrimethylenephosphonic acid; NTA, Nitrilotriacetic acid; EDTMP, Ethylenediaminetetramethylenephosphonic acid; DTPA, Diethylenetriaminopentacetic acid; DTPMP, Diethylenetriaminopentamethylenephosphonic acid; HEDTA, Hydroxyethylenediaminetriacetic acid; STP, Sodium tripolyphosphate; PBTC, Phosphonobutanetricarboxylic acid.

**Figure 1.18** Competition between complexing agents and precipitants.

Any sequestering agent shown on this figure dissolves all the precipitates located higher on the scale [14]. It means, for example, that EDTA is the only anion able to compete with stearate for calcium. For this reason, it is thoughtless always to use the same sequestrants in detergents and hope for good cleaning results. A deep knowledge of the chemistry of both sequestrants and precipitants is essential.

Soap-based lubrication is a typical example of the aforementioned competition. This competition was first observed during the study of the solubility of calcium

soaps (salts of linear carboxylic acids) [49]. The higher the stability constant, the more effective is the competition, as seen from inspection of the constants in Table 1.15 [13]. EDTA will be able to keep calcium oxalate soluble but will not prevent the precipitation of copper sulfide. Polyphosphates do not keep iron soluble in a strong caustic medium [12], but they will use their dispersing capacity in preventing the basic iron salt from sedimenting and scaling. The success of sodium tripolyphosphate (STP) as a scale prevention agent proves that the simple description of the stability constant as the reverse of the solubility product does not exactly represent what really happens in practical scale prevention. While the solubility product is only related to the quantity of dissolved salt, the stability constant is connected to a soluble complex. In terms of chemistry, salt and complex are different in structure [50]. Unlike salts, complexes change their structure according to the medium and keep their solubility. In many cases a suitable concentration of sequestrants (ionic strength) cannot be determined by a simple comparison between stabilities. Moreover, scale prevention has often to be attributed to a sort of complex between sequestrant and insolubilized salt rather than between sequestrant and metal ion. In other words, deposit prevention depends on the synergism between sequestration, dispersion, and suspension. Furthermore, scale control is often achieved by preventing adhesion rather than by keeping ions soluble. Dispersion and suspension confirm their crucial importance in detergency. They assist and complete the ability of a sequestrant to form the overall framework of the complexes [51, 52]. Going back to Table 1.15, polyphosphates (STP in particular) will not keep iron hydroxide soluble and cannot re-solubilize it in caustic medium. However, STP performs sequestration by dispersion and anti-redeposition of solid molecules and is able to prevent deposits even in this unfavorable condition. Phosphonates and polyacrylates perform likewise. Since one single chemical manifesting these three properties to the full does not exist, judicious blends of sequestrants should be applied to every process.

As carefully examined by Chaberek and Martell [24], sequestration depends on many factors. Concentration, temperature, pH, and ionic strength are parameters able to affect the stability constant. Therefore, constants are correctly compared only when determined and reported under the same conditions.

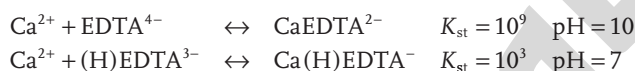
Table 1.15 Example of stability constants.

Ca-EDTA	3.9×10^{10}
Calcium oxalate	3.8×10^8
Cu-EDTA	2.4×10^{18}
Cu-Sulfide	1.2×10^{44}
Fe(OH) ₃	1.6×10^{36}
Fe-Pentapolyphosphate	3.2×10^6 [12]

Sequestration depends on pH, whereas the stability constant (chemical behavior) is independent [13] of it or only indirectly connected to it. In actual fact, the stability constant is not associated with a sequestering anion and its sequestered metal but is an attribute of the complex. The stability constant remains the same over the whole range of pH within which that complex exists. If the stability constant appears to change, the type of complex is actually changing, usually as a function of pH. Every new complex is characterized by its own different stability, which is linked to a different constant.

The influence of hydrogen ion on replacing ligands is well known [53]. Generally speaking, a decrease in pH weakens the stability of a complex, as hydrogen replaces one or more ligands of the complex. Sequestrants containing carboxylic groups prove to be the most sensitive. Their stability constants are remarkably strong when they are deprotonated and drastically change when pH decreases. Examples with EDTA and NTA are given below.

EDTA [13]



NTA [18]



Conversely, the hydroxyl complexes of many metals offset their stability in alkaline conditions. The hydroxyl ion is such an effective ligand that it competes with sequestrants. For this reason, it is reported a conditional stability constant [48]. The conditional stability constant takes into consideration the influence of both hydrogen and hydroxyl ions, being defined as

$$K_{\text{conditional}} = \frac{K_{\text{MX}}}{\alpha_{\text{X}}\alpha_{\text{M}}}$$

where α_{X} is a coefficient which describes progressive protonation of the ligands with decrease in pH while α_{M} represents the tendency of the metal to be hydroxylated.

Plotting the conditional stability constant versus pH in a graph, it is possible to identify the peak of performance for each sequestrant toward the metal ions. Examples are given in Figure 1.19 [48].

The hydroxyl-hydrogen competition is clearly evident from the change in stability of the complex as a function of pH. The value of $K_{\text{conditional}}$ also indicates the peak of activity where the sequestrant shows the best control on each single metal.

When a solution contains equal concentrations of two or more metal ions, sequestrants will form complexes preferentially with the metal ion giving the higher stability of the complex [18]. The reaction follows the order of priority and virtually waits until it has gone to completion with the most stable ion prior to any reaction with the second ion on the list.

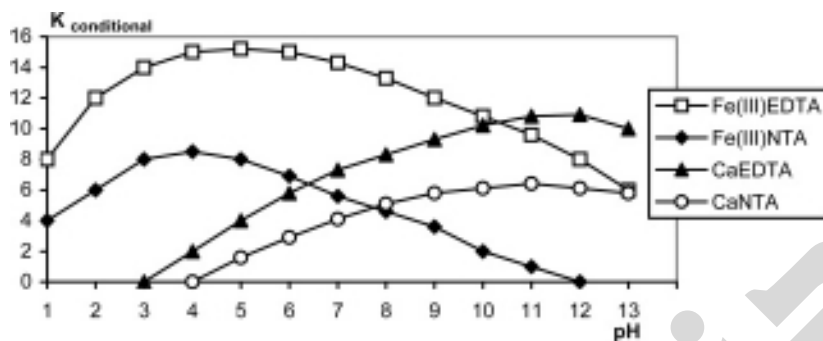


Figure 1.19 Peak of performance for different sequestrants.

1.1.4

Critical pH

The literature confirms the primary importance of the pH effect on sequestration because of the hydrogen-hydroxyl ions competition with the sequestering agents for ligands. Actually, at high pH a ligand generally exists in the fully ionized state, which provides the most effective bonds for complexing. Lowering the pH means adding protons to the ligand stepwise until there is no ionic species capable of sequestration [14]. Investigation of the sequestering power at different pH values and different concentrations of sequestrant shows two non-linear relations:

- the increase in pH and the quantity of adherent precipitate
- the pH giving the highest volume of scale and the concentration of sequestrant necessary to prevent it.

Deposition on every surface (flat and vertical) shows a peak between pH 8.5 and pH 10.5, diminishing above pH 12 and changing into nonadherent agglomerates freely moving in the system. Concentrations of caustic soda above 0.5% (pH > 12.4) change the salt structure from hard crystals into hydroxylated inert flocs. These hydroxide flocs settle on flat surfaces where they set like stone in the absence of dispersants.

Sequestrants increasingly have difficulty in preventing precipitation within the pH range 10–12.5 with a peak between 11.5 and 12. Table 1.16 shows the lack of control.

This trend is successfully applied, for instance, to determine the concentration of the most suitable sequestrant for the rinse section in bottliewashing. The bottle-washer rinse is a typical system where pH progressively decreases from ca. 12 to neutrality.

Donnel and Lin [54] clearly noticed this critical range of pH in their method for the assessment of detergent builders in water hardness control.

The critical zone of pH depends both on the chemical composition of the water (hardness salts) and the concentration of the sequestrant. In both cases, the more

Table 1.16 Difficulty in preventing scale within the pH range 11.0–12.5.

pH	10.0				11.0				11.5				12.0				12.5			
ppm	100	200	300	400	100	200	300	400	100	200	300	400	100	200	300	400	100	200	300	400
ATMP	–	++	+++	+++	–	++	+++	+++	–	+	+++	+++	–	–	+	++	–	–	++	+++
STP	–	–	+	++	–	–	–	++	–	–	–	–	–	–	–	–	–	–	–	++
PA ^{a)}	–	–	–	+++	–	–	–	++	–	–	–	–	–	–	–	–	–	–	–	–

a) Partially neutralized polyacrylic acid 20 000 MW.

Rating: – insufficient + sufficient ++ good +++ excellent hardness control.

Conditions: 40dF, 60°C, 20h of rest, sequestrants adjusted at 40% of active matter. Deposit assessment on glass slides.

the water hardness or the sequestrant concentration increases, the more the peak of the critical pH moves to higher value. However, the volume of deposit decreases when the concentration of sequestrants rises. The critical pH is also revealed by the higher concentration of sequestrant required to keep the salts soluble, or, as Ashcraft affirms [55], an increase in pH needs higher dosages of sequestrant to stabilize hardness.

The critical pH identifies the transition zone where scale changes from sticky adherent crystals to amorphous material. Below the critical pH, scale grows everywhere on vertical and flat surfaces. Above the transition zone, alkalinity (OH^-) changes the precipitate into a sludge which, in time, compacts itself like marble on flat surfaces. Dispersants keep the sedimented precipitate in sludge form. Many techniques are available in the laboratory to make the solution suitable for every condition in the field. Hundreds of detergents have been developed to answer the purpose. The graph in Figure 1.20 illustrates what happens.

The first line shows the quantity of deposit on the surface after rinsing with deionized water. The second shows the concentration of sequestrant required to prevent scale. The range between pH 13.00 and pH 13.40 (rapid increase in scale) shows what happens without dispersants: the settled deposit becomes as hard as marble after lying undisturbed for a few hours.

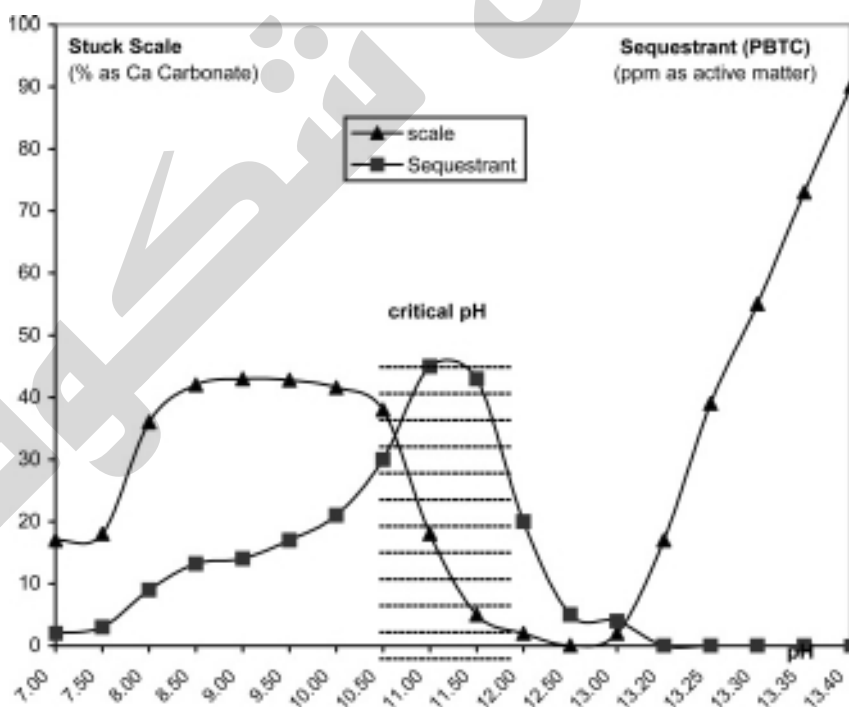


Figure 1.20 Effect of dispersant on deposits. Conditions: 40dF, 70°C and 20h of rest. Ca determined with EDTA.

Several metals (e.g., aluminium and iron) form hydroxy-complexes that polymerize as the pH increases. The polymer reaches its maximum size when the charge of each complex unit is zero, that is, when the number of hydroxyl groups per metal ion is equivalent to its charge. This is schematically represented in Figure 1.21 [24].

What is described for metals can also be applied to the ligands linking metals, whether they are precipitants or sequestrants. Thus, pH affects the behavior of both ligands and metals. When complexes co-ordinate molecules of water, they partially or totally replace them with hydroxyl ions. Moreover, the metal chelate can disproportionate to give metal hydroxide and the formation of larger complexes, as shown in the equation for bivalent metals (Figure 1.22) [24].

The metal hydroxide is usually insoluble and settles out. The change from a 1:1 to a 2:1 metal chelate compound and the disproportionation to give a free insoluble metal hydroxide can explain the partial loss in activity of some sequestrants having an insufficient number of donor groups to satisfy their coordination requirements, mainly when an effective ligand, such as the hydroxyl ion, increases in the system. Thus, the competition of the hydroxyl ion explains the reduced complexing efficiency of most sequestrants at high pH ($K_{\text{conditional}}$, as in Section 1.1.3.2).

The pH effect on polyphosphates clearly demonstrates the presence of a critical pH between 10 and 12. As Rudy's work shows [56], the concentration of sequestering agents required to thoroughly soften a fixed volume of hard water increases only within the pH range 10–12. Above and below this, the concentration of polyphosphates remains unchanged, as shown in Figure 1.23 adapted from Rudy's investigation [24, 56].

Detergent solutions whose pH is in the transition zone need a mixture of sequestrants carefully chosen in type and concentration to run smoothly.

1.1.4.1 Effect on Bicarbonates

The critical pH identifies the transition phase from carbonate to hydroxycarbonate schematically shown in Figure 1.24.

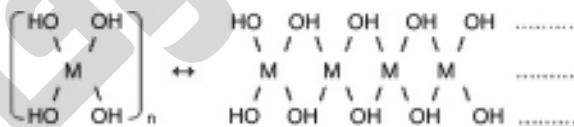


Figure 1.21 Hydroxylated complex with geometry extended to three dimensions.

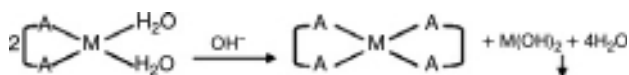


Figure 1.22 Disproportionation reaction.

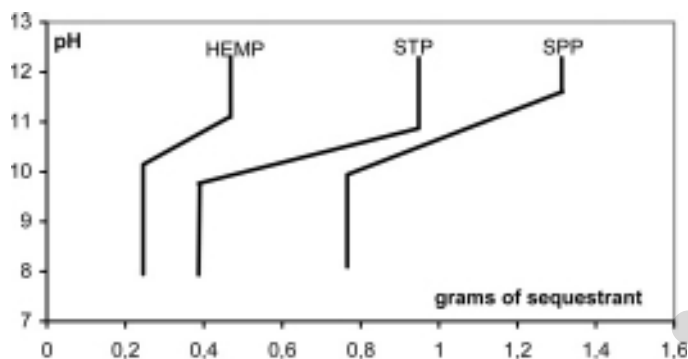


Figure 1.23 Grams of sequestering agents necessary to soften 1 L of water containing 64.8 mg L^{-1} hardness.

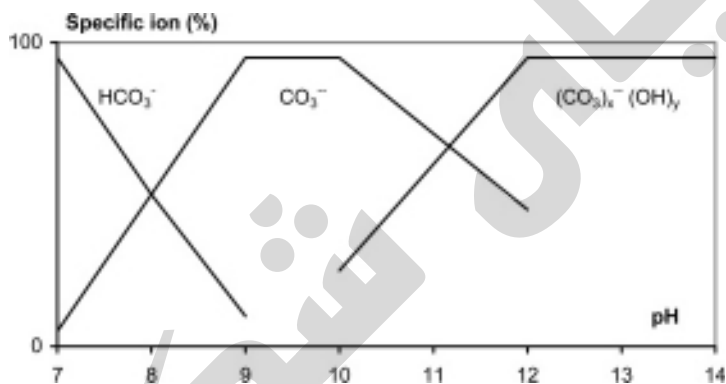


Figure 1.24 Ionic species as a function of pH.

When the alkalinity P is zero (phenolphthalein end point $\text{pH} \approx 8.2$), bicarbonate (HCO_3^-) is the main ionic species. Bicarbonate does not show a pink color at the P point. It is therefore determined at the methyl orange (M) point ($\text{pH} \sim 3.6$). On the contrary, 50% of carbonate (CO_3^{2-}) is checked at the P (phenolphthalein) point and the remainder at the M (methyl orange) point. Above pH 10, the ionic species consists of hydroxycarbonate. The caustic pH completes the hydroxylation. The second intersection in the graph falls in the critical zone of pH. It separates the crystalline adherent precipitation from nonadherent flocculation (see Section 1.1.4). Calcium hydroxycarbonate $[\text{Ca}_2(\text{OH})_2\text{CO}_3]$ in a caustic medium ($\text{pH} > 12$) coagulates into flocs sedimenting by gravity or floating in a stirred solution. Below the critical pH (< 12), calcite or aragonite crystals (CaCO_3) grow everywhere. A higher concentration of sequestrant is mandatory to prevent deposits.

1.1.4.2 Effect on Phosphates

The pH effect on phosphates has been well known since 1849 [57], and from then on has been exploited in several treatments of industrial water. When trisodium

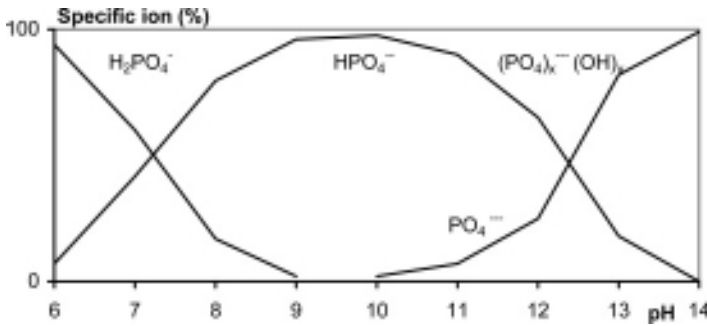
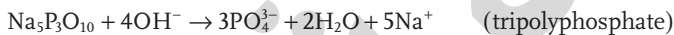


Figure 1.25 Phosphate species as a function of pH.

phosphate is added to water, it raises the pH to 12 and coagulates hardness into soft agglomerates [5]. Flocs adsorb metals, prevent deposition, and allow the insoluble materials to be removed as sludge. However, the chemistry of phosphates is quite complex, varying according to the degree of polymerization of the monomer PO_4^{3-} , whose polymers are chemically unstable, eventually becoming monomers again through aqueous hydrolysis. The reaction rate depends on temperature and alkalinity [58–25].



Unfortunately, only the phosphate monomer ion is sensitive to change in pH. Protonation and hydroxylation modify the physical form of its precipitate. The graph in Figure 1.25 schematically indicates the ionic species at different values of the pH.

Calcium hydroxyphosphate [poly-hydroxyapatite $n\text{Ca}_5\text{OH}(\text{PO}_4)_3 \cdot (\text{OH})_m$] forms in caustic solution and precipitates as an inert soft sludge. Below pH 12, a hard deposit of calcium phosphate crystals $[\text{Ca}_3(\text{PO}_4)_2]$ grows everywhere if not controlled by suitable sequestrants. Thus, phosphates behave like carbonates (Section 1.1.4.1). An example of calcium phosphate growth can be seen in Figure 1.26. This shows the progressive clogging of the drain holes of a cheese mold.

Calcium phosphate is one of the most chemical-resistant deposits. Nitric acid and EDTA are the only reagents able to pull the calcium out of orthophosphate and resolubilize it. Dairies in particular suffer from phosphate precipitation. Milk pasteurization, sterilization, and whey crossflow filtration are the processes most affected.

1.1.4.3 Effect on Sequestrants

According to Lewis's definition of acids and bases, metals behave as acids (electron acceptors) and ligands are considered to be bases (electron donors). The combination of the two constitutes is an acid-base reaction in every respect. The competition of the sequestering agents for metals, hydrogen ions, and hydroxyl ions has been discussed in Sections 1.1.3.2 and 1.1.4. Thus, hydrogen ions

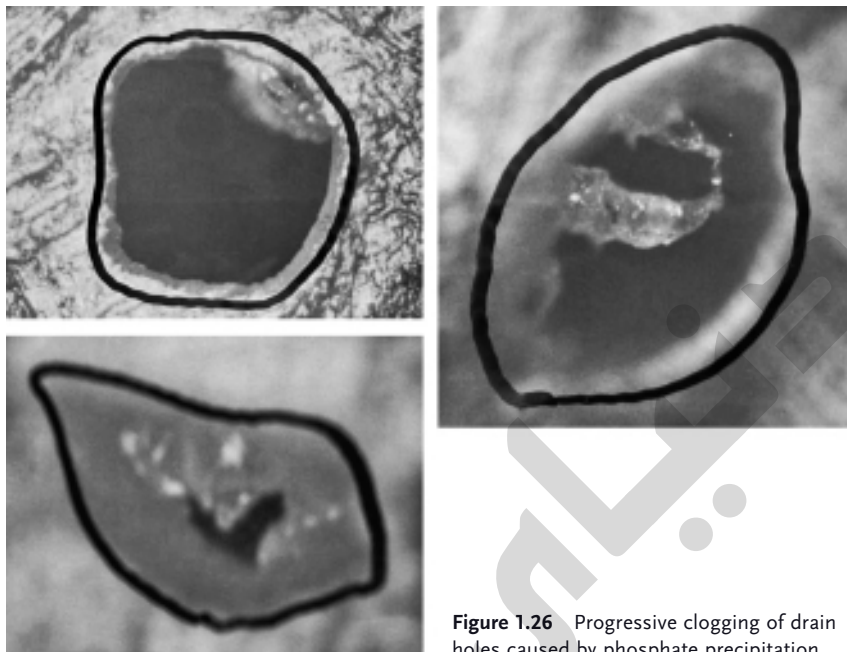


Figure 1.26 Progressive clogging of drain holes caused by phosphate precipitation.

compete with metals for ligands. The addition of hydrogen ions to a system (decrease in pH) displaces the metal ions from the metal complex [24]. According to this concept, the ionization constant of the acid and the dissociation constant of the chelate are comparable:

$$K_a = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} \quad K_c = \frac{[\text{M}^{2+}][\text{A}^{2-}]}{[\text{MA}]}$$

Their negative logarithms, pH and pM, are comparable as well. Hence, it is possible to describe the above concepts by plotting pM against pH (Figure 1.27) in order to highlight the displacement of ligands from the metal by the decrease in the complex concentration (decrease in pM) as a function of the hydrogen ion concentration [24].

The hydrogen ion competition weakens the complex, its stability, and the chelating power of the sequestrant. Thus, chelate dissociation (pM) and conditional constant ($K_{\text{conditional}}$) are different terms describing the same event (Section 1.1.3.2).

The critical pH divides sequestrants into two groups. The former performs better at caustic pH, the latter below the transition zone (neutrality). Phosphonates, for instance, are very sensitive to the transition zone of the pH. Some of them develop the best efficiency in a caustic medium (e.g., ATMP), others at neutrality (e.g., HEDP), and some others equally well in both systems (e.g., PBTC). Moreover, the gluconate group (gluconate, glucoheptonate, boroheptonate...) are linearly dependent on the increase in pH. The more the alkalinity

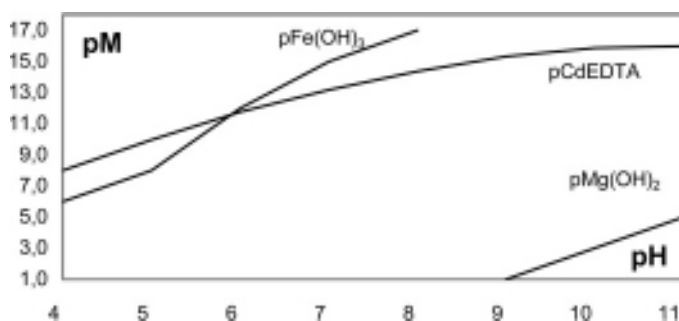


Figure 1.27 Equivalent quantities of some metal complexes as a function of pH.

increases, the more the OH structure moves to enolate (O^-) and the more the hardness is controlled. It is interesting to note that both precipitants (carbonates and phosphates) and sequestrants show the same zone of critical pH.

Although deposition can be easily prevented in the laboratory by the use of a suitable concentration of sequestrants, the cost of chemicals is a serious issue in practice. Softening the water or lowering the pH to neutrality with acid is often more sustainable than increasing the concentration of the sequestrant. As an example, the addition of acid (sulfuric) to the bottlewasher rinse enables the concentration of sequestrant to be reduced and hence leads to a reduction in the overall cost of the treatment.

1.2

Inorganic Competitors

Anionic substances forming insoluble salts are referred to as precipitants. Anionic compounds forming soluble complexes are termed sequestrants. Precipitants and sequestrants always compete for possession of the polyvalent metals. Precipitants cause the formation and usually the deposition of insoluble salts, while sequestrants endeavor to keep the polyvalent cations in solution.

1.2.1

Bicarbonates

Most natural waters consist of a solution of bicarbonate. Carbonates, however, are the main constituents of scale. Chemical and physical mechanisms trigger the change from bicarbonate to carbonate.

1.2.1.1 Chemical Mechanism

Bicarbonate shows behavior quite similar to that of amphoteric compounds. It can behave both as an acid and as a base, reacting with hydroxide and hydrogen ions as follows:



The acidic behavior lowers pH and gives carbonate. Carbonate reacts with calcium and precipitates calcium carbonate. Adding alkalinity to hard water produces incrustations if not prevented by using the correct sequestrants.

The basic behavior leads to a rise in pH. Even if incrustation is prevented, the change could affect the efficacy of systems based on pH stability. The amino-lubrication of tracks is an example. High concentrations of bicarbonates in the dilution water (high hardness) disturbs the weakly acidic buffer of the lubricating solution. If the pH exceeds 7, precipitation of insoluble amino-carbonate salt occurs.

1.2.1.2 Physical Mechanism

Temperature induces the water salinity to change. The reaction on heating is the sum of the previous two chemical reactions:



The solubility of carbon dioxide in water depends on temperature and pressure. In open plants the CO_2 solubility only depends on temperature. An increase in temperature diminishes the carbon dioxide solubility and the equilibrium moves to the right, where the carbonate precipitation occurs.

Thus, calcium carbonate deposition is to be expected whenever alkalinity is added to hard water or hard water is heated, unless sequestrants prevent insolubilization.

1.2.2

Silicates

Silicon is the second most abundant element in the earth's crust. Its compounds [silica (SiO_2) and silicates] consist of complex molecules assembled around the $(\text{SiO}_4)^{4-}$ tetrahedral structure, which can occur singly or in groups [16]. Silicate exists in raw water, having been dissolved out of silicate-containing minerals by the water running through the strata. There is probably a balance between silica in colloidal form and hydrogen silicate anions (HSiO_3^-) [6]. Silicate associates with several different metals, some of which are even able to replace silicon in the crystal. The combinations forming molecules are infinite. For this reason silicates are usually described in terms of the ratio between the silicon dioxide and the metal oxide. The occurrence of silicate is rare in the dissolved salts in raw waters. Except for certain specific cases, silicate content does not exceed 50 ppm and is much lower than carbonate content. Its deposits are insoluble in acidic and alkaline solutions at reasonable concentrations, times of contact and with safe applications. Luckily, the thermodynamic instability of calcium carbonate to acids succeeds also in removing the unreacted crystals of silicate at the same time as the limestone dissolution with acids.

Silicate reacts with cations of calcium, magnesium, and polyvalent metals, and forms different complex salts. Their precipitation is relatively slow. However, it occurs even at moderate temperatures because of the long contact time [16]. Magnesium reduces silicate solubility. The formation of magnesium silicate, nevertheless, gives a remarkable effect in inhibiting corrosion. Its cathodic protection cannot be actually exploited, being effective only within a narrow range of pH [60]. The boundary between the establishment of corrosion-inhibiting films and the formation of scale is practically uncontrollable.

The deposit of silicates is detrimental, being hard to dissolve. Treatments with highly concentrated caustic solutions (even 30% alkalinity) and acids (inclusive of hydrofluoric) should be alternated and repeated. This procedure is not easy to handle and unsafe to use in the food industry [59]. Therefore silicate (also sulfate) must be prevented from precipitating.

Aluminium gives even the more problematical alumino-silicates. Precipitation occurs, for instance, in alkaline sections of bottlewashers (aluminium labels and foil) by misapplication of sequestrants and dispersants, gluconate in particular.

Boiler treatments have to allow for the volatility of silica in steam. When carried along by steam, silica can either reach the saturation point and precipitate (scale) or form hydrosilicic acid and corrode. As sequestrants cannot be added to steam, keeping SiO_2 below the threshold level ($<0.02 \text{ mg L}^{-1}$) is crucial to prevent problems.

Silicate shows a peculiar reactivity with ferrous (stainless steel) and vitreous (glass and ceramic) materials [61] when it dries on. The chemical reaction of drying on such surfaces yields silicate crystals that include surface ions as well. When the silicate deposit is descaled, the loss of surface ions makes the surface corroded. The corrosion is irreversible and can only be manually masked by filling the micro-holes of corrosion by physical treatment, e.g., with hydrocarbon oil or silicone (brighteners). Hence,

- Detergents containing silicates must be carefully rinsed off in order to prevent corrosion of stainless steels, glasses, and ceramics.
- Raw waters containing high concentrations of silicate leave behind a corrosive saline solution. More frequent maintenance is needed to remove or mask the whitish deposits and the corrosion.

1.2.3

Sulfates

Sulfates are salts containing the SO_4^{2-} group, and are dissolved in water from gypsum minerals and by sulfide oxidation. They can reach hundreds of milligrams per liter. The sulfate ion reacts with polyvalent cations and forms low-solubility salts. Calcium and magnesium sulfate are the most common salts in industrial processes. Barium sulfate is the most insoluble and chemically inert compound, but its occurrence is negligible in common raw waters. There are three naturally occurring forms of calcium sulfate:

- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ dihydrate (gypsum, alabaster, selenite);
- $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ hemihydrate (formed on heating the dihydrate);
- CaSO_4 anhydrite (soluble or insoluble depending on the duration of heating).

The chemistry of sulfate deposition is complex and essentially depends on temperature. Calcium sulfate dihydrate proves to be more soluble and easier to remove. Hence, it is crucial to prevent anhydrite formation. Experiments on the solubility of gypsum and anhydrite show that gypsum will normally deposit first from saturated solutions when evaporation takes place below 42°C . Anhydrite is the stable form above this temperature [16].

The temperature at which anhydrite formation occurs also depends on the type of ions forming the water salinity. Sodium chloride [62] and potassium sulfate [63] decrease the temperature of nucleation. Thus, anhydrite is formed not only by dissociation of gypsum [59] but directly by chemical reaction. Consequently, deposition is mainly on heat exchanging surfaces, where the first layer generally consists of anhydrite; this is followed by gypsum, as seen in Figure 1.28. Bianucci [64] reports occurrence of the calcium sulfate species as a function of temperature in Figures 1.28 and 1.29.

Calcium and magnesium sulfate are more soluble than the carbonates and hydroxides. In the presence of both, sulfate can exchange cations and increase its solubility. Conversely, the exchange leads other species to precipitate according to the following reactions [65]:

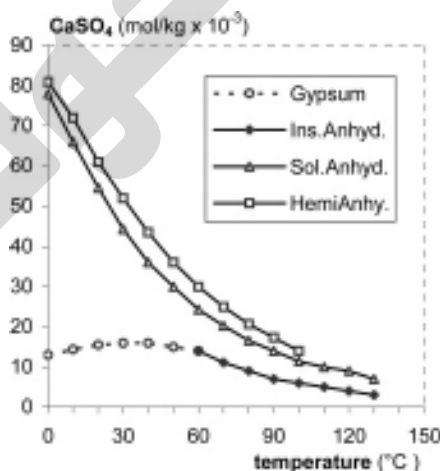
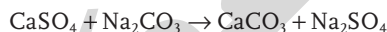
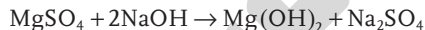


Figure 1.28 Solubility of calcium sulfate species (courtesy of Bianucci [64]).

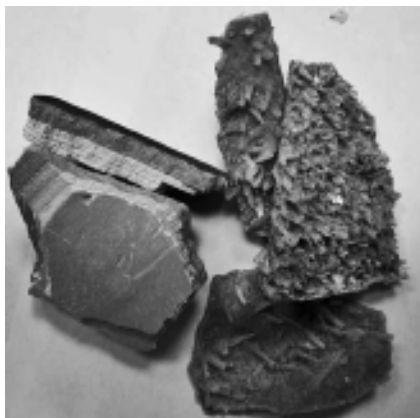


Figure 1.29 Types of deposition.

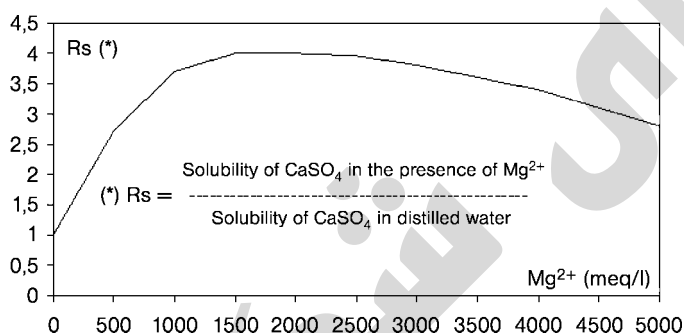


Figure 1.30 Effect of magnesium ions on the solubility of calcium sulfate, (courtesy of Cowan and Weintritt [16]).

Magnesium ions in strata enhance the sulfate solubility. For this reason, the higher the concentration of sulfate in water, the higher is the concentration of magnesium ions found. Graphs from laboratory tests prove the magnesium effect on calcium sulfate solubility as Cowan and Weintritt [16] report in Figure 1.30.

Problems of calcium sulfate scale are particularly expensive and troublesome. Its chemical inertia even toward strong alkaline or acidic treatments is evident from Figure 1.31 [66, 67]:

The usual content of sulfate in raw waters precipitates onto the limestone deposit. Acids dissolve limestone and, at the same time, remove the inert deposit of sulfate. Sequestrants easily prevent the precipitation of sulfate. Thus, sulfate scale is a typical deposit relatively easy to prevent but very hard to remove.

Besides being a scale-forming material, sulfate takes part in microbial metabolism (sulfate-reducing bacteria) and generates hydrogen sulfide (H_2S). Hydrogen sulfide corrodes ferrous materials and releases disagreeable odors. The biological pathways of the sulfate evolution involve different bacteria such as *desulfovibrio*,

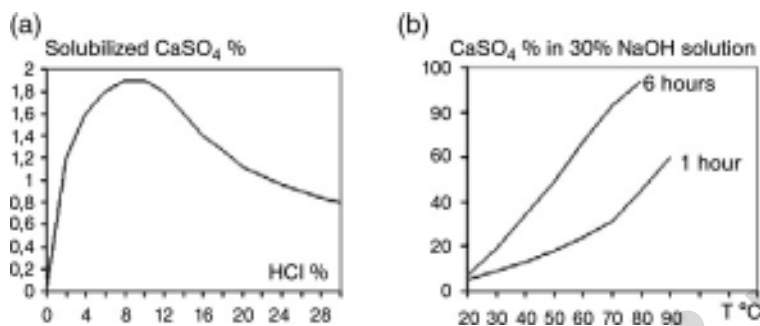


Figure 1.31 (a) Calcium sulfate solubility in hydrochloric acid (courtesy of Ryss and Nilus [66]). (b) Calcium sulfate solubility in caustic soda, (courtesy of Posnjak [67]).

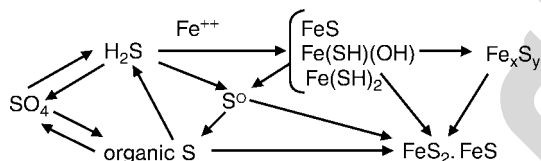
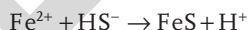
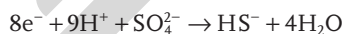


Figure 1.32 Biochemical reactions of sulfur compounds.

clostridium, *thiobacillus*, and *ferrobacillus*. Fiorentini Potenza summarizes the biochemistry of sulfur in Figure 1.32 [4].

Besides the offensive smell from hydrogen sulfide, a black film of iron sulfide coats the surface and ends the bio-reaction:



The stability constant of FeS is one of the highest. Strong acids are needed to dissolve the deposit. If sulfates are present, the water should be maintained in an aerobic condition to prevent sulfide formation by preventing precipitation and bacterial growth.

Lubricants based on cationic chemicals (fatty diamines and imidazoline) are claimed to be insensitive to hardness. The insensitivity, actually, is to cations (e.g., Ca^{2+} , Mg^{2+}). The anionic hardness affects the solubility of the cationic lubricating molecules and causes precipitation of their salts. Sulfate is one of the worst anions as regards interference. It reacts with fatty diamines and imidazoline both in alkaline and acidic pH. The resulting salts clog filters and spray nozzles of the delivery equipment over time. Hence, lubricants based on fatty amines include specific dispersants for sulfate.

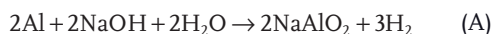
1.2.4

Aluminates

Aluminates are salts formed from the reaction between aluminium and alkaline chemicals. The aluminium surface is corroded in contact with caustic soda, caustic potash and alkaline salts (e.g., carbonate, polyphosphates, chloride...) unless specific corrosion inhibitors protect it from being damaged. Silicates act as inhibitors, form a cathode barrier, and stop corrosion.

Several industries use aluminium and its alloys for labels and foils in bottle-washing, aluminium mold cleaning, surface treatment, and finishing. Moreover, foods can directly release aluminium into the system (Table 1.17) [7]:

Aluminium chemistry is not easy to manage in the field. The most risky reactions occur in recovered and static solutions where the aluminium concentration continuously rises. The dissolution or precipitation of aluminate essentially depends on the caustic soda concentration. The sequestering additives can only prolong the life of the solution. They keep aluminate temporarily soluble or dispersed in a concentration higher than caustic soda would bear. The main reactions are given below [68].



As water immediately converts sodium aluminate into aluminium hydroxide (B), reaction (A) is only the transition phase to (B). Reaction (B) represents the real critical phase on which either solubility or precipitation depends. The equilibrium really is:



Reaction (D) proves caustic soda to be crucial in keeping aluminates soluble. Aluminium hydroxide $[\text{Al}(\text{OH})_3]$ cannot exist as such. Hence, either it remains soluble, evolving to (D) or precipitates as crystalline alumina, moving to (C). For instance, 30 g L^{-1} of aluminates in 1.5% NaOH solution at 80°C already causes problems of precipitation without an adequate concentration of gluconate. Figure

Table 1.17 Aluminum-releasing foods.

Food	Al (~mg/kg)
Meat and fish	20
Egg, milk, wine, fruit juice, oil	50
Cereals, cheese, sugar	200
Vegetables and fruit	250

1.33 relates to the process of aluminium etching, and shows the increase in caustic soda concentration indispensable for keeping aluminium soluble.

Etching is a process in which dissolved aluminium accumulates and caustic soda is increased as necessary. However, increasing the caustic soda is a limited tool. The usual method of preventing the deposition of alumina consists in using sequestering agents, gluconate in particular [69, 70]. A typical composition of 'soaker scale' in a brewery bottleshwasher is given in Table 1.18.

Aluminium scale is feared, since chemicals do not remove the aluminate deposit in reasonable time and using safe systems. If dissolved aluminium is known to be present in a process, detergents should be formulated to contain a good sequestering system in which gluconate plays the leading role.

Temperature affects aluminium solubility, as illustrated in Figure 1.34.

As the kinetics of aluminium dissolution significantly slow down at room temperature, applications of mildly alkaline cleaners can be carried out at room temperature without evident corrosion even in the absence of inhibitors (e.g., silicates). Low-caustic self-foaming detergents for OPC are an example.

Silicate stops corrosion, phosphates and nitrate accelerate it, and gluconate controls and prevents deposition. It follows that in those systems where aluminium dissolution is required to be as fast as possible, detergents cannot include silicate. Thus, detergents with silicate should not be used in bottleshwashing.

According to the stoichiometry of the reaction $(2\text{Al} + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow 2\text{NaAlO}_2 + 3\text{H}_2)$, 1 kg of dissolved aluminum

- needs 1.48 kg of caustic soda;
- releases 0.11 kg of hydrogen;
- produces 3.07 kg of aluminate (NaAlO_2).

Owing to hydrogen generation, plants are designed to be open in order to prevent explosion. For this reason, bottleshwashers are provided with ventilating ducts.

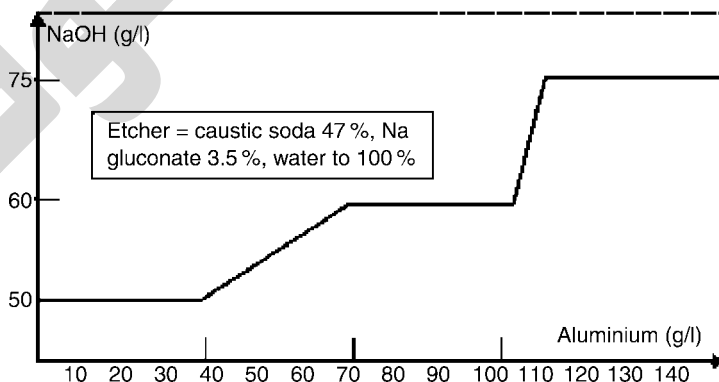
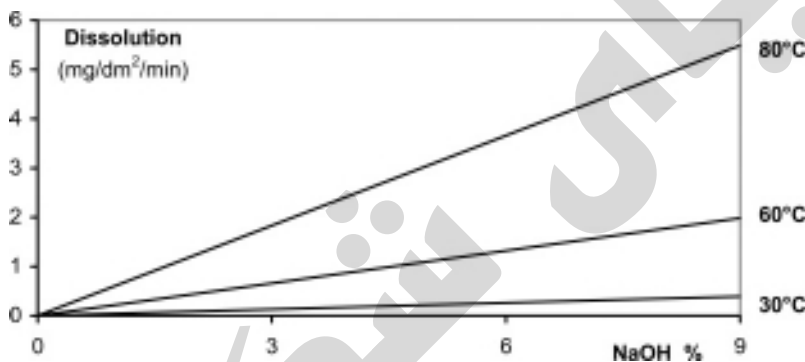


Figure 1.33 Increase in caustic soda concentration required to keep aluminum soluble.

Table 1.18 Metal concentrations in scale (ignited, then digested in HCl/HNO₃).

Metal	Metal content (%)
Al	8.41
Ca	8.89
Mg	0.14
Na	6.48
Si	0.24
Zn	0.02
Mg	0.14
Fe	0.72
Loss on ignition	14.8%

**Figure 1.34** Aluminum solubility rate in caustic soda at different temperatures.

1.2.5

Phosphates

The literature reports the use of phosphate and polyphosphate as softeners and agents preventing deposits [71–73]. This system first found favor after the discovery of the effectiveness of phosphate in controlling polyvalent cations at a time when nothing else was known to be suitable to solve scale problems. The risk of precipitation of calcium phosphate was disregarded in view of the benefits achieved. However, the current advanced technology of sequestration and provisions of the law make phosphates no longer essential to solve scale problems.

Phosphates are salts containing the group PO_4^{3-} . When present in raw water, these are pollutants. On the other hand, phosphates can be found as process residues coming either directly from food (e.g., milk and whey), from food additives (e.g., polyphosphate in sausages and processed cheese, phosphoric acid in soft drinks) or as components of detergents.

Phosphorus occurs in

- polyphosphates [hexametaphosphate (6P), pyrophosphate (4P), tripolyphosphate (3P)]
- mono-, di-, and trisodium phosphate
- phosphoric acid
- phosphono derivatives (phosphonate and phosphonoacrylate)
- phosphine derivatives.

The monomeric phosphate (PO_4^{3-}) is the only species responsible for deposits. The insolubility of its salts has been described in Sections 1.1.4, 1.1.4.1 and 1.1.4.2. For instance, the solubility of calcium orthophosphate $[\text{Ca}_3(\text{PO}_4)_2]$ is roughly 0.02 g L^{-1} [58]. In practice, all the phosphate precipitates out in the presence of hard water. Figure 1.35 shows the percentages of all the chemical species during the hydrolysis of STP [58].

As the polymers are destined to hydrolyze to the monomer, phosphate precipitation can occur even when polyphosphates are involved. Therefore, the use of polyphosphate quite often causes the insoluble calcium orthophosphate to precipitate instead of preventing scale.

The rinsing of descaling detergents based on phosphoric acid adds another element to the discussion. The concept of rinsing is based on an infinite dilution up to water neutrality. When acidity is rinsed off, phosphoric acid is gradually neutralized. Thus, the hardness in the rinse water causes phosphate to insolubilize and form a deposit unless suitable sequestrants are coformulated. Phosphoric acid has difficulty in re-solubilizing di-calcium and tri-calcium phosphate. Nitric acid is effective. These behaviors justify the customary use of nitric and phospho-nitric acid as the acidic step in CIP.

Aside from nitric acid, EDTA is the only sequestrant able to pull calcium out of the orthophosphate structure. The single-step cleaning technology (alkaline cleaning without a further acidic step) is based purely on the complexing power of EDTA.

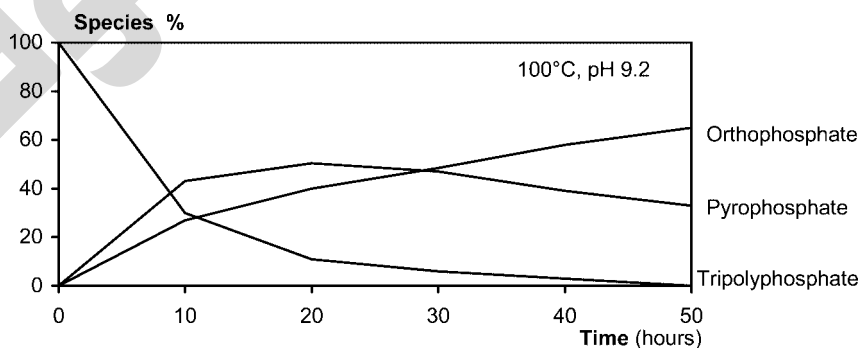


Figure 1.35 Chemical species during hydrolysis of STP (sodium tripolyphosphate).

1.3

Organic Competitors

According to the Lewis definition, a base is any ion or molecule able to form bonds sharing electrons, and an acid is any ion or molecule able to form bonds accepting electrons. Thus, polyvalent metal ions behave as acids and react with most organic compounds by accepting their electrons. Total electric charge (e.g., fatty acids) or partial charge, such as one or several poles in the same molecule (e.g., proteins and starches), are potential competitors for polyvalent cations with which they form simple coordination bonds, complexes, and salts. The ability of the organic material to link up with metals and its sensitiveness to changes in temperature and pH produce insolubilization, denaturation, and close-packed contamination hard to remove. The following organic substances show chelating activity:

- proteins
- starches
- fatty acids
- specific carbohydrates derived from the processing.

Although all of these sometimes behave like dispersants, mostly they are effective precipitants.

1.3.1

Proteins

Proteins (Greek 'proteios', i.e., 'primary') derive their name from their great importance in all forms of living matter. They invariably contain nitrogen (16–18%) and usually also sulfur and phosphorus [74]. Two groups of proteins are mainly involved in the detergency process. The first group includes fibrous proteins, insoluble in water and used as structural materials by animals. Fibroin, collagen, and keratin belong to this group. Globular proteins form the second group, and are soluble in water and in aqueous solutions of acids, bases, and salts. Egg albumin, casein, plasma proteins, and cereal seed glutelins are members of this group.

Proteins consist of giant molecules with molecular weights from ~5000 to several million. The building units are joined together through peptide links ($-\text{CONH}-$) formed from carboxyl and amino groups of aminoacids as represented in Figure 1.36.

The structure of a protein is actually much more complicated. The lateral chains of the aminoacids have functional groups able to affect their spatial configuration and reactivity such as

- $-\text{OH}$ serine, threonine
- $-\text{SH}$ cysteine
- $-\text{CONH}_2$ asparagine, glutamine.

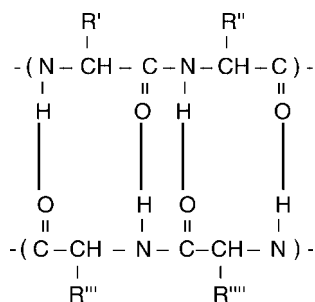


Figure 1.36 In order to visualize the sequestering capacity, proteins can be simply represented as a chain of aminoacids linked by hydrogen bonds.

Table 1.19 Proteins and enzymes in milk (courtesy of Cappelli and Vannucchi, Ref. [7].)

Casein (74%)	Whey	
	Proteins	Enzymes
- α	- β -lactoglobulin	- Protease
- β	- α -lactoalbumin	- Lipase
- κ	- Whey albumin	- Lysozyme
- γ	- Immunoglobulin	- Peroxidase
- Traces of others	- Proteose-peptones	- Phosphatase

The structure of the assembled protein consists of [7]

- **Primary structure:** the aminoacids sequence;
- **Secondary structure:** the spatial configuration of α helix and β pleated sheet portions stabilized by hydrogen and sulfur bridges (S–S);
- **Tertiary structure:** the spatial configuration of α -helix and β pleated sheet portions stabilized by all the bonds available in a protein: hydrogen bonds (between, e.g., hydroxyl, amide, and phenol), hydrophobic bonds (aliphatic chains and aromatic groups), covalent bonds of sulfur bridges, ionic bonds between groups positively and negatively charged (carboxyl and amino);
- **Quaternary structure:** the association of different chains of polypeptides that already show a tertiary structure.

Milk Proteins constitute ingredients of many foods both in milk products and in the huge number of food and beverage derivatives. Proteins in milk form macromolecular complexes (micelles) together with mineral salts of calcium, magnesium phosphate, and citrate. Casein is only one of many proteins. A summary is given in Table 1.19 [7].

Dried micelles contain proteins (92–93%) and minerals (7–8%) consisting of calcium phosphate (90%), with citrate and magnesium as the remaining fraction. The native micellar structure is therefore known as acidic calcium phosphoca-

seinate, which, on average, contributes casein (27 g), combined CaO (0.37 g), and colloidal calcium phosphate (1.7 g) to one liter of cow's milk [75]. As percentages free of the whey constituents, the following is the average composition [76]:

	g/100 g
• casein	93.4
• calcium	2.9
• organic phosphorus (PO_4 -casein)	2.2
• inorganic phosphorus (PO_4)	2.9
• magnesium	0.1

Ter Horst [77] considers the binding of calcium and phosphate to casein as a combination of phosphate ions with its cationic parts (e.g., epsilon amino group of lysine) and calcium with anionic groups (e.g., carboxyl groups and the phosphoric acid ester group of casein). The calcium-phosphate-casein chemistry is responsible for the growth of 'milkstone', which is one of the hardest contaminations.

Egg Proteins form a second group of proteins. Lipids (lipoproteins), phosphorus and iron as well as a small amount of calcium characterize the yolk proteins. The albumen proteins add thio-aminoacids to the system. When overcooked, sulfur compounds lose -SH groups and lead to iron sulfide precipitation.

Meat Proteins The last group of proteins involved in detergency comes from meat (Figure 1.37). Among these, blood proteins attract specific attention since they are sources of ammonia (NH_3) in static anaerobic fermentation. Ammonia resists the usual sewage treatments and harms the environment. Slaughterhouses are particularly involved in this. Oxidation (blowing air into the static zones of the sewage flow stream) prevents anaerobic bio-reactions and ammonia generation.

Water adsorption, swelling, solubility, viscosity, gel formation, foaming, and emulsification constitute the basic behavior of proteins. The extreme sensitivity to chemicals and temperature limits the stability of proteins and can lead to an irreversible change known as denaturation. In denaturation, the primary



Figure 1.37 Blood from pigs (courtesy of Italcarni), and rabbits.

structure is maintained and the secondary, tertiary, and quaternary structures are modified. Water plays an important role in denaturation. It promotes the substitution of stronger hydrogen bonds ($C-N-H-O=C$) according to the reaction illustrated in Figure 1.38 [78].

Muscular proteins, for instance, start to coagulate at 55 °C and complete this process at 65 °C. Collagen proteins shrink at around 65 °C and turn into gelatin at higher temperatures. Heating of denatured proteins of whey and caseins leads to polymeric aggregates [79]. A denatured protein loses its electrochemical behavior and hydration capacity. In many cases, free sulfhydryl groups increase [74, 76]. A denatured protein is less soluble than the native protein because of an increase in hydrophobic groups. Heating, freezing, ultrasonic waves, ionizing rays, and mechanical treatments induce denaturation.

In a group where oxygen is connected to nitrogen via carbon, a strong electronic shift can be expected. This polarization is confirmed by X-ray investigation, where the $C-N$ group proves to behave like a double bond [80]. The polarization of peptide groups and phosphoryl and sulfhydryl components causes proteins to be precipitants directly competing with sequestrants for calcium, as shown diagrammatically in Figure 1.39.

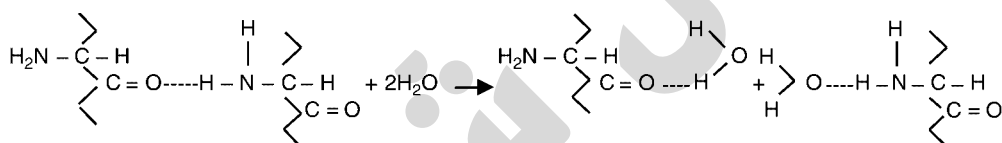


Figure 1.38 Example of reaction with water in denaturation.

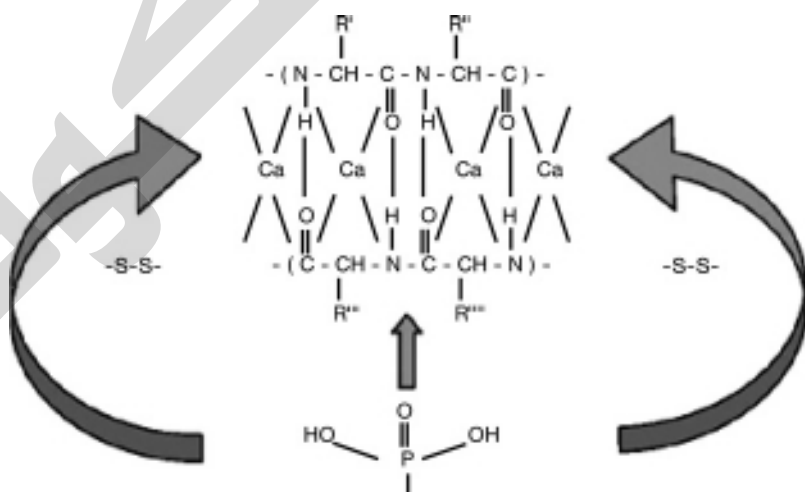


Figure 1.39 Peptide, phosphoryl, and sulfhydryl groups cause proteins to be precipitants

Because of their cross-linking function, metal chelation and thermal denaturation lead to the development of deposits so hard and nonreactive that they resist both acids through the organic structure and caustics through the lattice of inorganic salts. Thus, the overall denatured structure consists of a self-protected deposit. The deposit in milk pasteurizers and sterilizers is a well-known example of such hard-to-clean contamination. Organically bonded calcium and calcium phosphate provide the denaturation with a mineral skeleton by incorporating sub-micelles of casein into a largely closed self-protected macrostructure [81].

COO^- and S^- help PO_4^{3-} group to link to Ca^{2+} ions and contribute to the cementation and stabilization of the deposit.

Heating, cooling, and pH are the main factors causing change in stability. Temperature improves the hydrophobic interactions, cooling promotes the hydrogen bonds, and sulfur bonds stabilize the protein gels [7]. This intricate behavior affects the cleaning process and explains the foam generation in solutions containing proteins. Proteins form very efficient foaming systems. Various distributions of charge and hydrophobic areas inside the peptide chains confer surfactant properties on them [75]. Since proteins incorporate hydrophobic and hydrophilic groups, they are readily adsorbed at gas-water and gas-oil interfaces, and hence stabilize foam [82–84]. For this reason, detergents used to clean up proteic soil usually need the addition of defoamers.

The proteic structure contains a balance of positive and negative charges, one of which predominates according to the pH of the solution. These charges are equal in strength at the isoelectric point. At the isoelectric point, proteins have the highest stability and resistance to hydrolysis. Resisting hydrolysis means resisting cleaning in the detergency process. As the isoelectric point of the most important proteins in the food industry lies in weakly acidic range, cleaning will be attained at the extreme limits of pH, usually at caustic pH. Figure 1.40 schematically represents this.

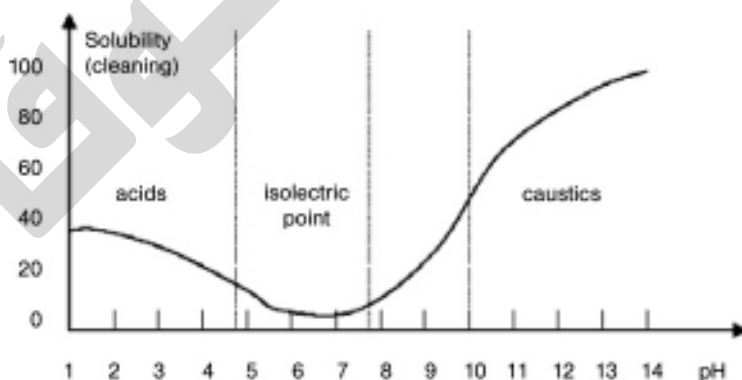


Figure 1.40 Proteins are stable at the isoelectric point.

The point of effective solubilization is achieved above pH 12.5. As 0.5% caustic soda reaches such a pH, 0.5% alkalinity is taken as the lowest concentration able to give good solubilization of proteins in the cleaning process.

1.3.2

Starches

Starch is the reserve carbohydrate in the majority of plants. As amylase enzyme and mineral acids break down starch to maltose, starch would at first seem to consist of a chain based on maltose units [74], although starch is actually considered to be a polymer of α -(D)-glucose (Figure 1.41).

Starch should be not treated as a single chemical compound but rather a naturally formed structure with a roughly spherical shape (starch granule), the main components of which are amylose and amylopectin, forming linear and a branched polymers of glucose respectively [85]. Granules are of varying size and shape, small for rice (5–7 μ) and bigger for wheat and potato (40–50 μ). Nevertheless, the physical and chemical attributes are identical [3]. Starch can be separated into two fractions: [74]:

- 1) A soluble component [amylose (10–20%)] with chains of molecular weight up to 5×10^4 . It forms a blue-colored complex with iodine.
- 2) An insoluble fraction [amylopectin (80–90%)] with branched chains of molecular weight up to 1×10^5 . Amylopectin has a globular, finely spongy structure, and is responsible for swelling in aqueous solution [7].

The starch granule is insoluble in cold water. It swells when heated and eventually bursts with a gelatinization effect. Amylose and unbranched components are responsible for the gelling property [86].

The cleaning process has to deal with starch either as insoluble granules (flour) or an aqueous gel-forming viscous layer which changes to amorphous adherent soil when dried. The presence of large amounts of ether and hydroxyl groups makes the starch molecule multipolarized and prone to adsorb both hydrophilic and lipophilic compounds. Starch can therefore establish ligands with multivalent cations and can adsorb oil. Even if less of a problem than the proteic deposit, its bonds provide the contamination with a lattice slow to clean. Figure 1.42 diagrammatically represents the adsorption of calcium ions on starch.

Calcium adsorption and especially gel formation in contact with water give rise to a barrier which prevents further hydration underneath. As calcium stiffens the

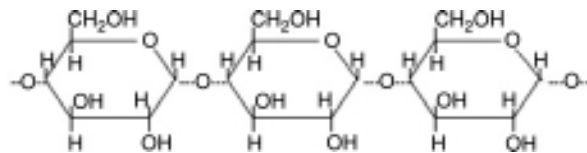


Figure 1.41 Starch chain.

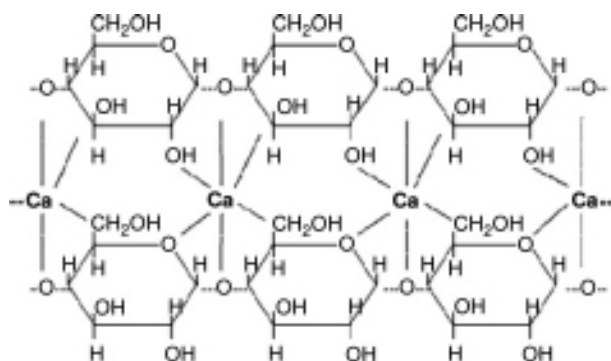


Figure 1.42 Starches behave as precipitants.



Figure 1.43 Mold adhering to surface with mucopolysaccharides and glycoproteins (courtesy of JohnsonDiversey; adapted from Ref. [87].).

structure and gel does not allow the cleaning solution to penetrate in depth, time and difficulty in cleaning increase in the presence of starch contamination. Acids prevent starch from gelling, so that acid cleaning is sometime preferred as a first step.

Cellulose is the polysaccharide which provides the supporting framework for vegetables. Cellulose, a type of β -(D)-glucose polymer, forms rigid and insoluble fibers sensitive to water. Water is adsorbed by capillary attraction and stabilized by polarization forces. Speed of cleaning is greatly influenced by the moisture content of the soil. Cellulose fibers take a long time to be re-hydrated, often far longer than the time available in a normal cleaning operation. This is in accordance with another fundamental rule in detergency which asserts that the soil should not be allowed to dry in order to achieve satisfactory cleaning within the planned procedure.

Heteropolysaccharides, mucopolysaccharides, and glycoproteins receive particular attention in the cleaning process. Their association with calcium forms the matrix anchoring molds to the surface, as shown in Figure 1.43.

Adhesion is so strong that a high concentration of alkalinity supplemented by an oxidant (chlorine or hydrogen peroxide) and sequestrants (e.g., EDTA, NTA, STP, IDS, GLDA) is needed to detach molds from the surface. The problem of mold removal is typically found in bottling. Milkstone in milking machines usually originates from the growth of mold spores (see Section 13.3).

Pectins, alginates, and gums (e.g., carrageenan, tragacanth) form the group of carbohydrates present as deposits in fruit and vegetable processing. However, many industries make considerable use of them as additives to foods (e.g., ice cream, cheese, mayonnaise, jam, pudding, jelly...) and clarifiers in the wine stabilization process. Their polymerization, drying, and reactions with metals lead to glassy deposits tenaciously anchored to the surface. Alkaline cleaning needs oxidants (usually hydrogen peroxide) to get a satisfactory result. Crossflow filtration, carried out during the processing of fruit and vegetables (e.g., juices, essences, water, and wine) cannot perform cleaning without hydrogen peroxide.

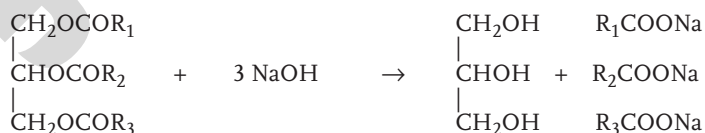
1.3.3

Fatty Acids

A hydrocarbon chain $[-CH_2-]_n$ is defined as fatty when it has a length of between 7 and 25 nm. A fatty chain ending in a carboxylic functional group is known as a fatty acid. Fatty acid chains are said to be short when n does not exceed 10. The chain length is a critical factor in detergency. The longer the length, the higher is the stability constant of calcium soaps (inductive stabilization). Competition with sequestrants proves that a chain length of 10 carbon atoms is the point above which the only sequesterant able to completely overcome the competition is EDTA.

Fatty acids form lipids with glycerol. These are produced by plants and animals, which use them as an energy reserve. Lipids are classified as saponifiable (glycerides, phospholipids, glycolipids, waxes) or unsaponifiable (terpenes, steroids). Glycerides are synonymous with fats in food detergency. Figure 1.44 illustrates the sources of fatty materials.

Alkaline and acidic solutions readily hydrolyze the ester group. The hydrolysis of triglycerides releases fatty acids and glycerol respectively.



Instead of three identical acids [R], fats invariably consist of a mix of esters incorporating two or three different fatty acids, and the position of the fatty acids in the molecule and their saturation may affect the result of cleaning as well as the mass of fat per volume of meat. Saturation and unsaturation ratio together with the position in the structure influence the melting point of fat. The lower the melting temperature, the easier is the cleaning. If, for instance, similar structures containing the same fatty acids in different positions are considered,

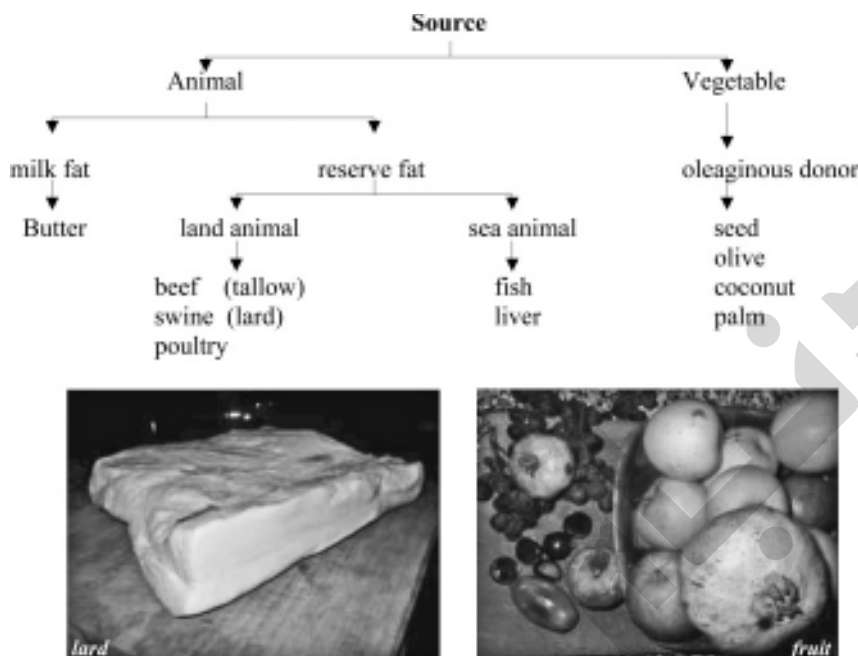


Figure 1.44 Sources of fatty material.



where: S = stearic acid, P = palmitic acid

their melting points differ in spite of the fact that they are formed from the same mixture of acids (S and P). More precisely, even though the liquidizing temperature of the mixture of fatty acids is the same (ca. 55°C), the melting point of the (A) structure is 68°C whereas that of (B) is 63.5°C.

Esters hydrolyze releasing their constituents both in acidic and caustic media. Acid hydrolysis gives free fatty acids, which are hydrophobic substances insoluble in water. Alkaline hydrolysis leads to salts of the fatty acids known as soaps. Soaps of monovalent cations (e.g., Na and K) and alkanolamines are soluble foaming and cleaning agents. Conversely, soaps of polyvalent cations (e.g., Ca and Mg) are hydrophobic, insoluble, and defoaming and constitute one of the most detrimental contaminations. Thus, alkaline hydrolysis proves to be ideal for achieving cleaning in food detergency, and detergent based on acid alone is inadequate to accomplish thorough cleaning and leaves a hydrophobic residue. Acids must be formulated with wetting agents (surfactants) effective on fatty matter.

The stability constant characterizes the chemical attraction between anions and cations. As far as calcium soap is concerned, the shift of electron density from

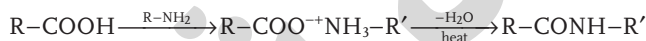
the hydrocarbon chain to the carboxyl group (inductive effect) increases and stabilizes the negative charge on the carboxyl group. Moreover, calcium links two molecules of fatty acid:



The resulting salt is more hydrophobic and stable. Only concentrated acids and EDTA pull calcium out. However, acids do not accomplish detergency (all remain hydrophobic). Thus, EDTA in alkaline solution is the effective chemical system for cleaning.

A further complication is oxygen absorption by the unsaturated fatty acids (oxidation) whether they are free or in the form of esters. Light, heat, and traces of heavy metals promote the reaction. The final compounds are alcohols, aldehydes, ketones, hydrocarbons, and derivatives of radical polymerization. Dimers and polymers linked by calcium generate a sticky, hard-to-remove deposit. Quaglia [82] reports reaction sequences and degradation compounds produced by the radical reactions. These are schematically summarized in Figure 1.45.

It follows that complex glycerides with double, triple, and higher molecular weights can be formed [88]. As well as undergoing radical polymerization, fatty acids react with amines and give salts that yield amides after losing water on heating. [80]:



When the proteic nitrogen is involved, the reaction denatures the protein, increases its hydrophobic sites, and produces less reactive derivatives such as lipoproteins [88]. Thus, the original compounds are converted into less emulsifiable and washable materials.

Another type of detrimental behavior of calcium soap concerns its melting point. As the original fats (triglycerides) come from living things, they become

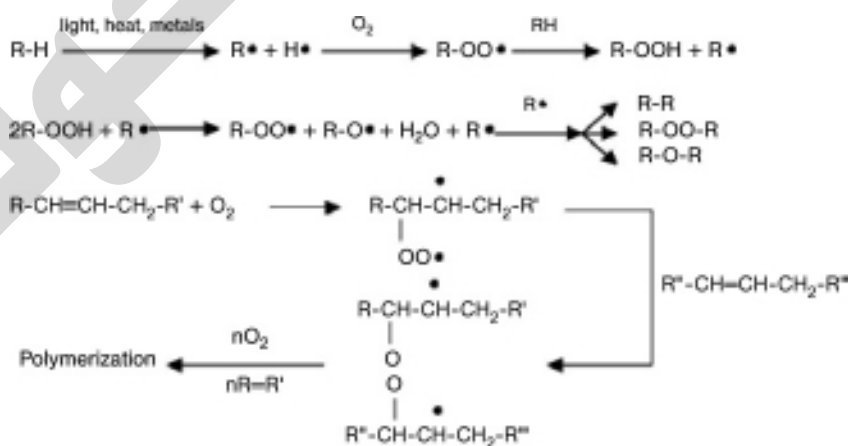


Figure 1.45 Scheme of radical reaction.

Table 1.20 Water, protein, and fat contents for different animals (courtesy of Lorusso *et al.*, Ref. [89]).

Animal	%		
	Water	Proteins	Fats
Veal	70.0	19.9	5.0
Beef	69.0	19.5	11.0
Pig	58.0	16.4	25.0
Lamb	65.0	18.6	16.0
Horse	72.0	21.7	3.0
Rabbit	70.0	21.0	8.0
Chicken	74.8	21.5	2.5

sensitive at the physiological temperature of life (ca. 35 °C for animals). This means that triglycerides are pasty and tend to liquefy above that temperature. However, hydrolyzed fatty acids behave differently with temperature as a function of

- **Type of hydrocarbon chain:** Saturated lauric (C_{12}) and stearic (C_{18}) acids, for instance, are solid at room temperature, pasty above 35 °C and liquid above 45 °C.
- **Type of soap:** Potassium and alkanolamines produce soaps that are liquid at lower temperatures than sodium soaps. Calcium increases the melting temperature even above 60 °C (e.g., saturated coconut C_{12} calcium soap).

At room temperature the behavior can be roughly summarized as follows:

- R-COOK and alkanolamines generally liquid and soluble;
- R-COONa usually solid and soluble;
- $R_1\text{COO}-\text{Ca}-\text{COOR}_2$ always solid and insoluble.

Lorusso and Porcu report the average composition for different animals Table 1.20 [89]:

When fat is part of contamination, the selection of suitable sequestrants and builders is the key factor in attaining a good detergency result. EDTA should always be in the list of sequestrants for detergents for fat removal. Chlorinated detergents should contain STP and PBTC. Where EDTA is not permitted, NTA, MGDA, GLDA, IDS, STP, and anionic surfactants help to achieve cleaning (e.g., linear alkylbenzene sulfonate, ethylhexyl sulfate, lauryl ether sulfate).

1.3.4

Other Carboxylic Compounds

Hydroxylated and carboxylated compounds are used in a considerable number of food industries. Citrate, tartrate, and oxalate belong to this group of carboxylate

chemicals (hydroxycarboxylic compounds). The concurrent presence of carboxylic and hydroxyl groups (except for oxalate) makes them react with cations as stoichiometric sequestrants. For this reason, some of them (e.g., citrate, gluconate, and tartrate) are also employed for sequestration in detergents. The higher the number of hydroxyl groups available in the molecule, the more the sequestering power rises in alkaline solutions (enolate development). Unfortunately, such molecules behave strictly as stoichiometric agents. This means that the reaction is strictly quantitative and relates to the single molecule. Every surplus of polyvalent cations precipitates them as components of the scale. Therefore, their use in detergents derives from benefits not strictly attributable to simple sequestration. For instance:

- Gluconate governs aluminate precipitation and promotes label removal in bottling.
- Tartrate and citrate adjust pH in the tunnel pasteurizer for aluminium cans, help bottles to drain water in the bottlewasher rinse, and remove the residual salinity on glass bottles, jars, and tins in the process of tunnel pasteurization.
- Hydroxyacetic acid adds disinfection to the acid cleaning process.
- Oxalate enhances the derusting efficiency of mineral acids.

Conversely, when these substances come directly from the food process, they are considered to be contamination. The typical residue in a winery (potassium and calcium tartrate) can be seen in Figure 1.46.

The following industries deal with hydroxylated and carboxylated carboxylic compounds in their processes:

- **Winery:** Tartrates constitute the main deposit. Tartrates have variable solubility according to whether they are calcium or potassium salts. Calcium tartrate is soluble in acids, potassium tartrate in caustics.
- **Vegetable processes (e.g., spinach, pea):** Oxalates form deposits together with cellulose fibers and clay.
- **Brewery:** oxalates are included in the organic contamination precipitated from the fermentation and clarification processes.

Oxalic acid is the most critical component of the group. Its solubility can be thoroughly controlled in solution, but calcium oxalate is hard to re-solubilize once precipitated. Cleaning is more easily achieved through detachment from the surface instead of solubilization. Thus, the cleaning procedure needs the help of oxidants (hydrogen peroxide and chlorine). The re-solubilization of calcium oxalate in the presence of clay (blanching) demands prolonged time of contact with acids, oxidants, and strongly sequestered detergents



Figure 1.46 Potassium calcium (bi)tartrate. (a) photomicrograph of deposit in empty bottle, (b) in maturing tank, and (c) in wooden barrel.

1.3.5

Humic Substances

Humic substances form an extremely complex and diverse group of organic materials whose structure is not well defined [18]. They normally occur in raw water and increase in concentration in strata close to rivers and marshes. The structure is an amorphous polydisperse substance (colloid) which, when coagulated, filtered, and concentrated, appears as a brown or yellow-brown material having different solubility in dilute acid and base. This solubility difference differentiates between the two main groups of humic substances:

- fulvic acids, soluble in dilute acid and base
- humic acids, soluble in dilute base and precipitated by dilute acid.

Fulvic acids are of lower molecular weight than humic ones even though both consist of large molecules having a molecular weight from several hundreds to tens of thousands [18, 90]. Carboxyl, carbonyl, ether, ester, hydroxyl, methoxyl, and phenolic groups are distributed in a large structure which also includes nitrogen and sulfur. Every functional group mentioned is involved in coordination bonds and competes with sequestrants. This enormous structure behaves as

sequestrant, acid, base, and dipole according to the medium and the material in contact with it. For this reason, humic substances can include clay, metals (usually iron and aluminum oxides), sulfide, proteic colloids, and peat trapped inside, and are deposited on filters (Figure 1.47).

Sulfide usually forms part of the deposit and releases the typical disagreeable smell of hydrogen sulfide in contact with acid. Aquatic humus influences the biological productivity in natural water [18]. Metals weakly linked to the humic and fulvic structure are available as nutrients for the growth of organisms. However, specific detrimental microorganisms may also be found in ideal conditions (e.g., iron bacteria, sulfate-reducing bacteria, and algae) where such compounds exceed the safe concentration.

Humic substances influence several processes in the food industry. Destabilization and coagulation occur soon after the change in the pressure, temperature, and oxidation state of raw water coming out of the strata. Coagulation causes an unstable deposit on pipeline walls, and water hammer can release flakes of such deposits, which can then enter the food production process. When colloids are noticeable (Kübel oxidation $>3 \text{ mg L}^{-1} \text{ O}_2$), the combination of water chlorination and/or filters installed in the early stage of water treatment prevents pollution. Chlorine (0.4–4 ppm) accelerates coagulation and agglomeration. Filters (cross-flow microfiltration or sand filtration) hold back the agglomerate before the manufacturing process is reached. An example is shown in Figure 1.48.



Figure 1.47 Colloid substances on 100 μ filter for well water.

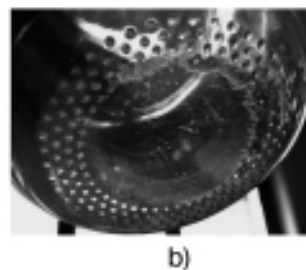
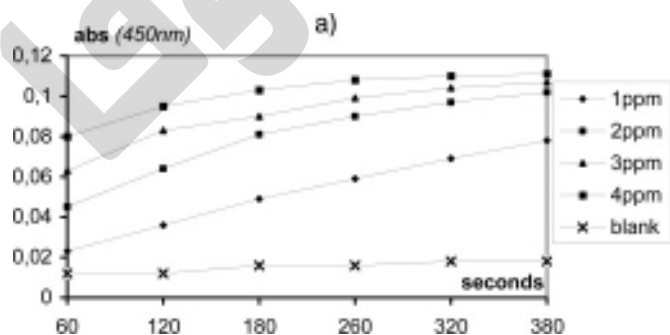


Figure 1.48 Chlorine destabilizing colloids a) and coagulated colloids in bottle b).

Humic substances influence the lubrication of conveyors. Humic and fulvic acids (anionic) react with the lubricating fatty polyamines (cationic) and precipitate as insoluble salts on the nozzles until they clog the spray (see Section 7.3.2).

1.4

Self-Protected Contamination

Contamination reacts in different ways to acidic and alkaline agents. As a rule, alkaline solutions readily dissolve the organic matter, and acids solubilize the inorganic matter. It follows that the chemical attack is weakened and made difficult when both types of contaminations are combined. This happens with dairy, brewery, and vegetable contamination. Denaturation and precipitation of casein along with calcium phosphate on heating make the deposit so hard to remove as to need a dedicated technology, based on EDTA and/or peroxides, to succeed in the cleaning. Calcium oxalate in hops, resins, carbohydrates, and proteins from beer fermentation; calcium oxalate in cellulose fibers and clay from processed vegetables make deposits equally hard to remove. Dried, polymerized, and oxidized soil offers further resistance to cleaning. The radical-induced polymerization and cross-polymerizations of fats have already been described in Section 1.3.3. Ionic chain polymerization provides a viable alternative to free-radical polymerization. This kind of process can take place when the reactive center at the growing end of the chain is ionic in character. Cationics containing electron-releasing substituents (e.g., $-OR$, vinyl, and phenyl groups) and anionics containing electron-attracting substituents (e.g., $-COOH$, $-COOR$ and $-CN$) are involved in polymerization [91].

The organic and inorganic cross-reaction and deposition identify a sort of self-protected contamination. The mixture of organic and inorganic material protects itself from acidic and alkaline cleaners. This self-protected contamination can be treated by the third way of cleaning based on sequestrants and their ability to strip calcium away from soil. Sequestrants take part directly in both preventing the insolubilization of salts and cleaning. Therefore, besides the rough force of caustics and the more gentle activity of surfactants (wetting and emulsifying properties), detergency is accomplished through the robust contribution of sequestrants. These exploit their ability to strip calcium away (carrier effect), uprooting the stability of the soil structure and enabling the strong caustic to attack the remaining organic deposit, as schematically illustrated in Figure 1.49:

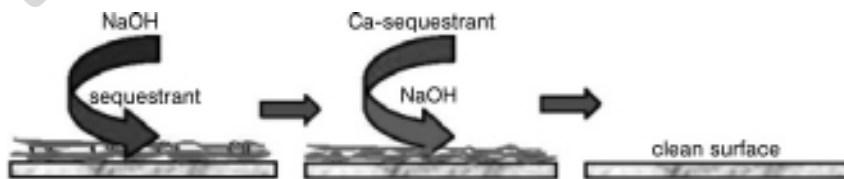


Figure 1.49 Carrier activity of sequestrants in the cleaning process.

Organic matter is sensitive to oxidizing agents. Detergents frequently rely on chlorine to enhance cleaning (chlorinated detergents). When chlorine cannot be used (corrosion at temperatures $>50^{\circ}\text{C}$) or is unacceptable (food quality and safety), hydrogen peroxide takes its place. Oxidants break up oxidizable molecules, release micro-bubbles of gas, and remove the contamination through what may be described as micro-explosions from its interior. Hard deposits are loosened (dairy and brewery), pectins, gums and polymeric carbohydrates are detached (wine, vegetable, and fruit industry), and cooking residues are broken up (deposits on saucapans).

Hydrogen peroxide replaces chlorine for several reasons. Chlorine generates a risk of

- stainless steel corrosion (pitting) when not thoroughly rinsed (chloride residue)
- corrosion whenever temperature increases. Chlorine and chlorinated detergents must run below 50°C (head space corrosion).
- medicine-like unpleasant taste from the reaction with polyphenols
- mold and cork taste from the reaction with anisole
- formation of chlorinated hydrocarbons responsible for environmental pollution and ozone holes
- formation of chloramines, whose bactericidal activity persists in the presence of dirt, can arrive at the biological treatment of sewage, and can endanger the biodegradation process. Moreover, some chloramines are even suspected of carcinogenic activity.

Hydrogen peroxide is free of the aforementioned risks and provides cleaning with the same efficacy as that of chlorine. Hydrogen peroxide bases its efficiency as a cleaner on its instability in alkaline media and at elevated temperatures. It releases oxygen, which performs oxidation and mechanical detachment. It is unstable in liquid detergents, and is therefore separately added to in-use alkaline solutions.

Hydrogen peroxide is fast-acting and rapidly leaves the solution. Therefore, consecutive short injections are necessary to maintain the steady efficacy of the cleaning solution (injection in the early and halfway stages of the cleaning, at least). The graphs in Figure 1.50 show the decrease in hydrogen peroxide with time.

1.5

Modifiers Affecting Deposits

Physical events able to modify the structure of the organic substance can lead to the precipitation of hard contamination. Heating, dehydration, and polymerization harm the structure of the food macromolecules. Several such modifications are appreciated since they enhance the quality of foods. However, in terms

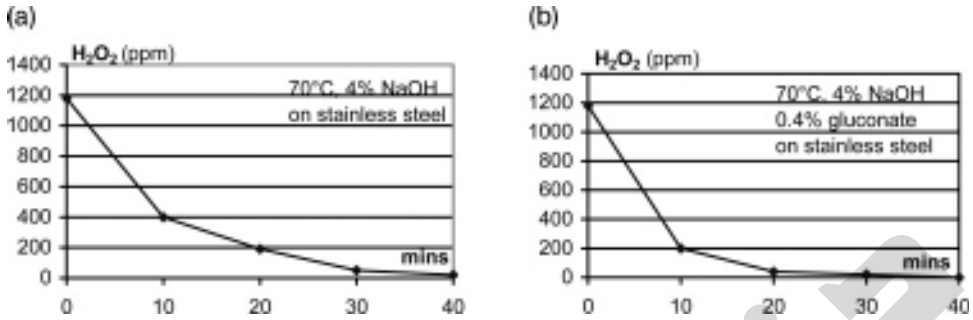


Figure 1.50 (a) Alkalinity and (b) temperature destabilize hydrogen peroxide.

of detergency, they usually prove to be quite detrimental. Destructuring and consolidation of the organic matter, adsorption of inorganic salts, dehydration, and polymerization make soil harder and harder to clean off.

1.5.1

Heating

As a general rough rule, the rate of chemical reactions doubles with every 10°C rise in temperature [92, 93]:

$$Q_{(\Delta T=10)} = \frac{K_{T+10}}{K_T} = 2$$

where

$Q_{(\Delta T=10)}$ = temperature coefficient

K_{T+10} = reaction rate at temperature $T + 10$

K_T = reaction rate at temperature T

However, an excessive temperature (>60°C) could be deleterious if fresh contamination which has not been thermally treated is involved. Excessive temperature causes undesirable reactions between soil and surface [59]:

- High temperature causes calcium bicarbonate to lose carbon dioxide and precipitate limestone (Section 1.2.1).
- Thermal denaturation of proteins causes their original properties to be modified, gel to be formed, and adsorption of metals to be made easier (Section 1.3.1).
- Heating (>60°C) decreases the soluble calcium and phosphate in milk. Precipitation rapidly increases at higher temperature. Although Evenhuis and de Vries [94] conclude that the precipitation of apatite crystals leaves milk unsaturated with respect to calcium and enhances the milk stability, in terms

of detergency the removal of calcium phosphate from milk by heating means deposition of hard soil.

Structural modification and deposition are considerable in the heat-exchanging processes (e.g., cooking, pasteurization, and sterilization) where the molecules in contact with the exchange surface are adsorbed, accumulated, and overheated.

The effects of heating are summarized below.

- starch amalgamation and plasticization, gelatinization
and solubilization
- protein denaturation and insolubilization
- microorganisms and enzymes destruction and inactivation
- fragrances modification and neutralization
- color browning
- humidity drying.

More extreme events are described as caramelization and carbonization.

1.5.1.1 Caramelization

One component of caramelization basically is the initial loss of hydrogen and oxygen from organic molecular structures and progressive concentration of carbon. Carbon enrichment, Maillard reaction [7], between amine groups and reducing sugars (e.g., maltose, lactose), polymerization, and oxidation (e.g., ascorbic acid and quinones) make the organic compounds yellow-brownish in color and increasingly hydrophobic and less compatible with aqueous systems. Whatever happens, caramelization chemically remains a noncritical modification in terms of cleaning. The caramelized molecules actually maintain their original behavior and reactivity toward aqueous solutions and remain sensitive to the usual detergents.

1.5.1.2 Carbonization

Intense and prolonged heating causes such a loss of hydrogen and oxygen from the molecular structure as to leave nothing but its carbon skeleton. Substances take on a dark brown color and are said to be carbonized.

Percentages of C, H and O in cellulose and amorphous carbon (carbonized cellulose) are given in Table 1.21 [4].

Table 1.21 Change in composition of cellulose on intense heating.

	C	H	O
Cellulose	46.95	6.23	43.20
Carbonized cellulose	93.50	2.81	2.72

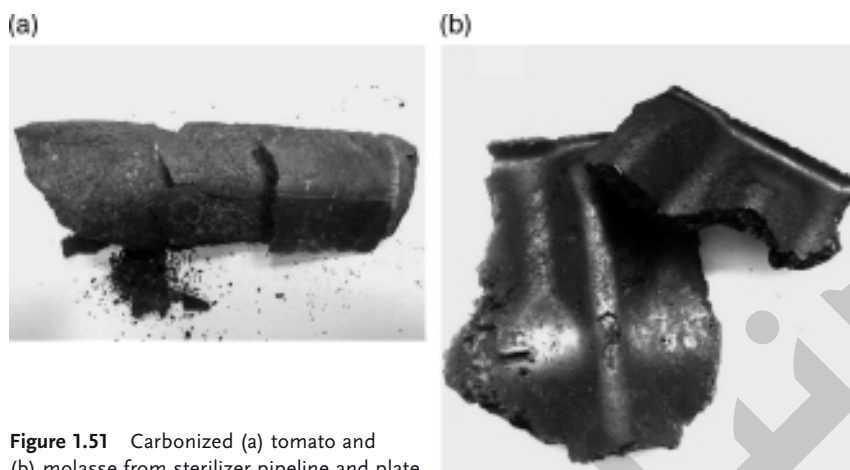


Figure 1.51 Carbonized (a) tomato and (b) molasse from sterilizer pipeline and plate.

Carbonization does not allow the individual molecules to be identified. It forms an amorphous material, essentially made up of carbon. The more intense and prolonged the thermal action, the more indeterminate is the residue. Examples of carbonized residues are shown in Figure 1.51.

When the organic material undergoes carbonization (prolonged or repeated heating), it behaves as a hydrophobic material, and aqueous solutions no longer solvate, swell, or dissolve it. Soil becomes inert to aqueous detergents except for highly concentrated caustic solutions. Thus, in order to make the removal of carbonized residues easier, the technology of the chemical attack shifts to solvents. However, environmental and safety issues tend to exclude technologies based on chlorohydrocarbon solvents. As good alternatives to such effective cleaning solvents are not available, it is mandatory not to force the heating processes and not to repeat baking without cleaning. It is advisable to plan more frequent washing of baking pans, trays, and molds in order to prevent hard carbonization of the residue and allow easier cleaning with aqueous detergents.

1.5.2

Dehydration

Dehydration (drying) means water removed from a substrate. Water in food can be found in three structural systems [82]:

- water molecules linked to ionic groups (e.g., carboxyl and amino groups)
- water molecules linked to hydroxyl and amido groups by hydrogen
- free water inside the capillary interstices.

Drying leads to significant physical modifications to the structure of matter and involves

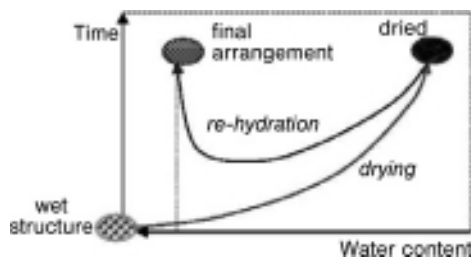


Figure 1.52 Irreversible modification of the food structure by drying.

- volume reduction of the animal and vegetable substrate
- migration and redistribution of solids originally present as gel
- polymerization
- formation of semipermeable membranes
- precipitation of inorganic salts.

The attractive forces decrease in proportion to the square of the distance so that closer packing increases them and increases the difficulty in removing and dispersing soil [92]. Some of those modifications prove to be partially or totally irreversible. Even though the rise in the cleaning temperature increases the rate of rehydration and solvation, rehydration is actually never so complete as to restore the original structure and chemical composition, as schematically illustrated in Figure 1.52.

Precipitated salts and polymerized matter suffer irreversible alteration, which demands more time than is required for the usual cleaning procedure. The contamination needs only a few minutes to be washed off when in a fresh condition (hydrate). When dry, it needs at least 3 h of pre-soaking to be satisfactorily removed in a tunnel machine.

The process of cooking fruit and vegetables is another example. Calcium oxalate and clay precipitate together with cellulose fibers and organic matter and constitute a sort of self-protected deposit which needs a long time of contact with caustic and acidic solutions strengthened with oxidizing additives to be rehydrated and removed.

1.5.3

Polymerization

Polymerization of lipids, proteins, and carbohydrates can occur naturally through oxygen, temperature, light, and contact with acids, aldehydes, and phosphates if sufficient time is available (see Sections 1.3.3 and 1.4). Polymerization follows two main processes [82]:

- thermal polymerization, where C–C bonds are involved
- oxidative polymerization promoted by oxygen and characterized by C–O–C bonds.

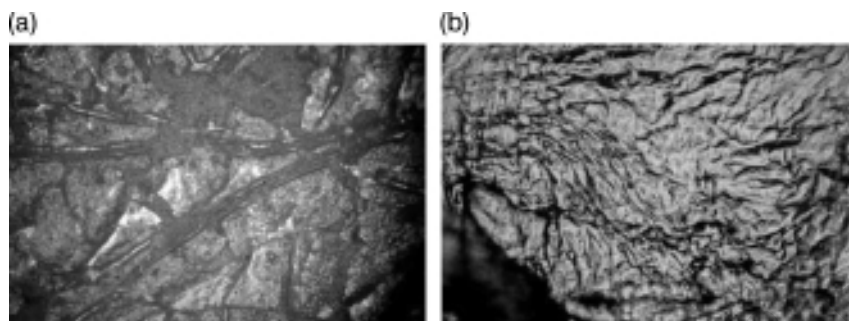


Figure 1.53 (a) Glass-like organic matter deposit on membrane used for microfiltration of apple juice, and (b) fatty amines in a lubricant solution insolubilized and polymerized to give a plastic-like film (photomicrograph).

Both cause detergency to run into trouble. Polymerized proteins behave like stretched fibers by converting the globular material into a long-chain structure. Proteins can copolymerize with peroxidized polyunsaturated fatty acids to give insoluble and dark-colored reaction products [95]. Heating causes two- and three-dimensional cross-linking of (poly)unsaturated fats [92]. Polymers of unsaturated fatty acids, cross-linked with metal ions, are water-repellent and solid when dry. Polyethers of cellulose are practically insoluble in water [74]. The polymerization of the soil promotes the restructuring of the processed material into larger molecules with a varnish-like property [59] (Figure 1.53).

If deposits are not immediately cleaned off, drying and polymerization increase with time. Detergency demands cleaning of the contamination and rinsing of the detergent before they are dry.

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2

Chemical-Physical Treatment

Calcium, magnesium, sodium, iron, barium, bicarbonate, sulfate, chloride, and silicate are usually found in raw water. All of these can be removed by absorbing them on solid materials able to exchange one ion for another. For over a century technology has endeavored to optimize ion exchange resins, increasing their efficiency. These resins consist of a hydrocarbon structure provided with charged functional groups bonded to ions. The ion exchange occurs when the salts in the water diffuses into the capillaries of the resin beads. The ions of the dissolved salts (either positive or negative) displace the ions on the resin and remain absorbed inside the bead structure (Figure 2.1).

The softening process exchanges cations. Deionization or demineralization removes both cations and anions.

2.1

Softening

An anionic resin exchanges cations and softens water. The functional group on the resin can be sulfonate ($-\text{SO}_3^-$) to give strongly anionic resin or carboxylate ($-\text{COO}^-$) to give a weak one. The weak resins are more associated with the concept of dealkalinization, targeted at sodium bicarbonate and carbonate removal (Section 2.3). When the sulfonic group is involved, the following reaction describes the exchange (Figure 2.2) [1]:

The reaction is reversible. After saturation, resins are regenerated either with brine (saturated NaCl solution) or acid, depending on whether the resin configuration is preferred in the sodium ion form or in the acidic form. Regeneration by acids yields soft acidic water, which could cause corrosion. Thus, brine treatment is the usual means of regeneration.

The ion-exchange efficiency depends on the ion size, its hydration, and the temperature. Magnesium is a typical example. Though smaller than a calcium ion, the magnesium ion is more highly hydrated. As a result, its increased size makes calcium adsorption preferred. The mechanism of ion exchange differs from that of sequestration. Sequestrants bind metals and form complexes, while ion exchange binds metals and forms salts.

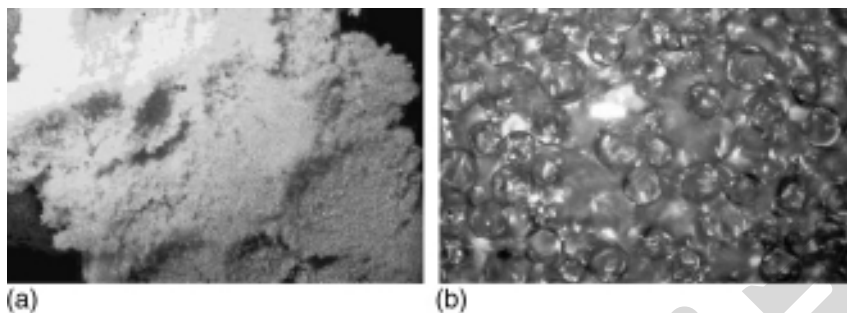


Figure 2.1 (a) Example of an anionic resin (cation exchanger) and (b) a photomicrograph of the resin.

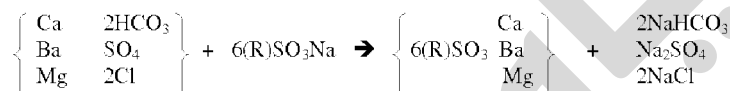


Figure 2.2 Examples of cation exchange reactions. (R) = resin matrix, for example, styrene co-polymers sulfonate.



Figure 2.3 A water softener, showing the brine tank and microfiltration system.

A softener consists of a vertical tank through which water and brine run alternately via nozzles sited above the resin bed.

Figure 2.3 shows the simplest and the most utilized type of softener in the food industry. The use of soft water enables the detergent concentration to be much lower and facilitates the cleaning process.

2.2 Deionization

Cationic resins remove anions. The positive charges on the resin are at quaternary nitrogen groups (R_4-N^+) in the case of a strong cationic resin, or primary, secondary, or tertiary amine groups with weak ones. If the anions on the resin are chloride ions, the reaction in Figure 2.4 describes the exchange [1].

The reaction is reversible. The saturated resin is regenerated either with brine or caustic soda, depending on whether the resin is preferred in the chloride or hydroxide form.

The removal of all the salinity is accomplished by a combination of cation and anion exchange. If deionized water is required, the resin regeneration must be carried out through acid (usually hydrochloric) and caustic soda in order for the resin to releasing the ions of water (H^+ and OH^-).



The sequence of processes is to remove the cations before removing the anions in order to prevent the hydroxyl groups on the resin from reacting with cations and precipitating their hydroxides (Figure 2.5).

Conductivity (below $10 \mu S$) and silicic acid concentration are used to assess the demineralization process. A strong basic resin and low water flow are needed to retain weakly ionized silicic acid, according to the reaction

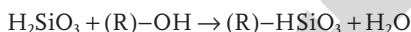


Figure 2.4 Examples of anion exchange reactions. (R) = resin matrix, for example, *N*-alkyl polystyrene.

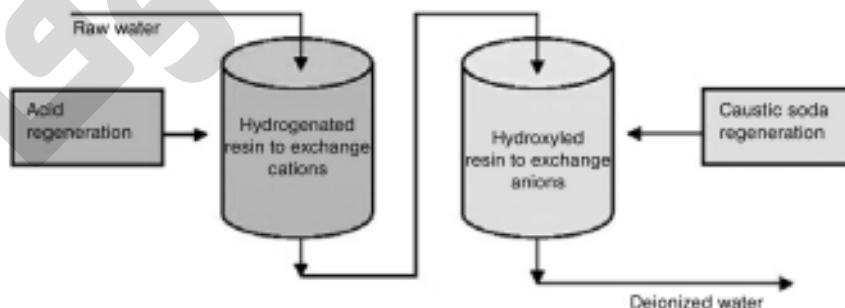


Figure 2.5 Resin regeneration scheme.

Nevertheless, some silicic acid escapes the ion exchange process, even running with very efficient columns.

The ion exchange resins are sensitive to suspended colloids and oxidizing agents. Resins do not adsorb colloids but filter them out. The filtered-out colloids coat the resin beads and decrease their absorption efficiency. Biofouling gives the same effect. Oxidizing agents (e.g., chlorine) have a harmful effect on the functional groups, slowly corrode the hydrocarbon structure, and shorten its shelf life. However, chlorine is the main disinfectant commonly used. The benefit in preventing the growth of biofilm counterbalances the damage to the resin.

Deionized water is like distilled water in every way. The solvent activity of water is so efficient as to require a small residual conductivity ($<10 \mu\text{S}$) to prevent pipelines from being corroded.

Deionization is widely used in pharmaceuticals manufacture, research laboratories, electronic production, high-pressure boiler feedwater, and even to reduce the hardness of very hard waters to a level suitable for any particular manufacturing process (e.g., soft drinks).

2.3

Dealkalinization

Applications sensitive to M alkalinity benefit from the removal of carbonate and bicarbonate (e.g., glass cleaning). Even in the absence of polyvalent metals, glass undergoes hazing from dried-on sodium carbonate after a hot rinse. The usual softeners based on strong anionic resin remove the multivalent metals, replacing them with sodium (brine being used for regeneration) but leave M alkalinity unchanged. Conversely, softeners based on a weak anionic resin that is regenerated with acid $[(R_e)\text{COOH}]$ exchange cations (calcium, magnesium, and sodium, associated with M alkalinity) for hydrogen ions, according to the reaction given in Figure 2.6.

A decarbonator (air blower in countercurrent) gives a low residual level of carbon dioxide in the water. Thus, dealkalinization is also known as decarbonation (carbonic acid removal). It only partially deionizes. As dealkalinization only removes the carbonate and bicarbonate anions, other anions such as sulfate, chloride, nitrate, and silicate pass through the resin column unaffected [1]. The anionic hardness exceeding M alkalinity remains in the water. Weak resin needs a weak acid for regeneration (e.g., citric acid).

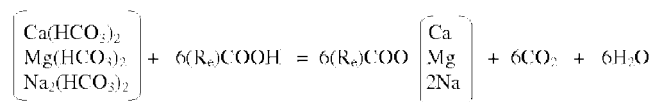


Figure 2.6 Examples of dealkalinization reactions.

Dealkalinizers are ancillary equipment. Even though original equipment manufacturers (OEMs) recommend setting the dealkalinizer before the softener, decarbonation, usually after the softener, offers the most economic option.

2.4

Reverse Osmosis

The foregoing sections describe the chemical approach to deionizing water. The alternative physical process is based on filtration, but the filter must be so highly effective that it will succeed in removing matter of Angstrom size (ions). The reverse osmosis process (RO) answers the purpose.

When a semipermeable membrane divides two salt solutions of different concentrations, the solutions tend to homogenize. Water moves from the less concentrated solution to the higher one. Hydrostatic pressure, known as osmotic pressure, can be generated in this process, which is called osmosis. Conversely, when the water stream is forced to move from the more concentrated solution to the less concentrated one, the process is called reverse osmosis, and this can be used to separate water from its salinity (Figure 2.7).

High pressure (20–70 bars) drives the process. The early method based on cellulose acetate membranes was sensitive to temperature, pH, and cleaning chemicals. The second generation of composite polymers (TFC) tolerates more drastic restoration (chemicals), extends shelf life, and widens applications.

Reverse osmosis produces pure water and concentrates salts, but these salts could precipitate on the membrane. Dispersants in running plants play a positive role in keeping the RO efficiency high for longer (e.g., 1000 ÷ 2000 MW acrylic homopolymers, PBTC and HEDP). Membranes are discussed in detail in Chapter 12.

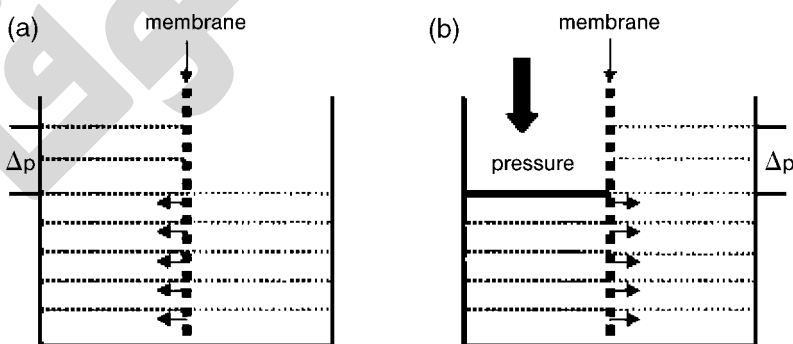


Figure 2.7 Osmosis (a) means flow of water toward higher salinity. Reverse osmosis (b) means flow of water from high salinity toward clean water.

Reference

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3

Sequestrants

3.1

Definition

Sequestrants are chemical agents forming water-soluble complexes with metals. The binding process sequesters or inactivates the metal ions and prevents them from reacting with anions that give a low solubility product, such as carbonate, sulfate, and phosphate. Competition is the most important feature of the sequestering reaction. Two types of anions compete for polyvalent cations. The first type (precipitants) cause insolubility, and the second (sequestrants) endeavor to pull the metal out of the precipitated material and keep it soluble. As already mentioned, the result of the competition depends on several variables which depend on the metals involved: concentration, pH, temperature, stability constant, and ionic strength. For this reason, a significant number of molecules with functional groups suitable for forming coordination bonds have been synthesized in addition to the traditional polyphosphates, EDTA, NTA, citrate, and gluconate. The molecular engineers continue to investigate new combinations of functional groups in new structures, aiming at finding out new categories of sequestrants and making the already existing classes perform better.

The words 'ligand' and 'chelant' are used to describe sequestrants, and 'chelation' and 'complexation' are adopted as synonyms of sequestration. However, ligand denotes the type of functional group able to form bonds with metals. The term ligand should be used to identify the single coordinating group instead of the whole sequestering molecule. In the same way, chelant should refer to the stoichiometric sequestrants. Sequestrant is intended as a general name defining molecules suitable for forming coordination complexes.

The primary distinction among sequestrants concerns stoichiometric and threshold behavior.

A sequestrant is defined to be stoichiometric when, excluding the coordination bonds, it is able to react with a number of positive charges (metals) exactly equal to the sum of its negative valences. When the amount of metal causes this number to be exceeded, all the complexes are inactivated and the sequestrant itself precipitates and contributes to scale.

A sequestant is defined as threshold when it is able to keep the multivalent cations soluble in a quantity exceeding the simple sum of its valences. This means holding a large concentration of multivalent metals on the threshold of crystallization. The stabilization of metals is possible since the threshold sequestrants can stop or, at least, delay the crystal growth by being adsorbed or inserted as impurities into the structure of the crystal nucleus of the starting scale. Therefore, the stabilization is described as distortion or prevention of further growth of the crystal after nucleation [1]. Threshold behavior would prevent scale in two ways: by producing smaller crystals easier to disperse and by loosening the adhesion of the crystal to the surface. Given that no solid can be isolated even after $0.45\text{ }\mu\text{m}$ filtration, the sequestant adsorption occurs on sub-microscopic crystal nuclei and involves kinetic rather than thermodynamic interactions [2, 3]. The concentration of scale inhibitor required to stop the crystal growth is much lower than that needed to sequester the metal ions. Thus, the threshold sequestant would be related to the number of the crystal nuclei rather than to the number of ions. Nevertheless, detergency needs absence of crystals or no adhesion of crystals. In terms of detergency it is no use using a chemical which permits crystal formation, even if the crystals are distorted. Detergency rigorously requires agents able to prevent adhesion, crystal growth, and nucleation. Currently, scale inhibition and sequestration are considered to be synonymous. Some authors differentiate between their meaning and relate scale inhibition to the ability to stop crystal growth and sequestration to the efficiency in preventing the crystal nuclei from forming. It is difficult to compare these definitions as dissimilar and noninteracting. In reality, a threshold-sequestering molecule can also form external bonds and set up a complex lattice where the excess of cations, singly or in the form of crystal nuclei, contributes to interface remaining trapped as in one soluble macro-complex. If the threshold effect only depends on the adsorption of the sequestering agent onto the growth sites of crystals, every sequestant should act as threshold, at the beginning of nucleation at least. This seems to be supposed by Dowson and Pritchard's mathematical model [4]. The model tries to describe specific interactions of polymers with crystal nuclei. It is affirmed that the most efficient inhibitors of crystals are those having the highest diffusivity and the highest molar concentration per volume. This means that, if the mechanism of the crystal inhibition involves the hindering of the growth of the agglomerates below a critical size, inhibition would happen when the sequestering molecules diffuse into a volume which also contains a sufficient number of precipitants and reach the sub-critical agglomerates faster than the precipitants [5]. All the small sequestrants with high diffusivity should comply with the model. What happens seems rather different. For instance, EDTA, NTA, gluconate, citrate, tartrate, and iminodisuccinate do not show any threshold behavior. However, when the EDTA carboxylic groups are replaced with phosphonic ones (EDTMP), the molecule changes from an absolutely nonthreshold sequestration to one of the best. As the threshold effect proves to be a mechanism which does not reduce the activity of the calcium ion (the activity of a ion diminishes only when the ion is blocked into a precipitate [6]), Bradley [2] affirms that the threshold

agents (hexametaphosphate) will inactivate the nucleating sites rather than distorting the precipitated crystals and retarding their growth [7]. Consequently, considering that

- phosphate-phosphonic-phosphinic groups possess the most suitable structures for bearing polar and dative bonds facing the outside of the molecules (multi-linked complexes), and
- the presence of phosphorus and a long sequence of carboxylic groups (co-poly-acrylate-maleate) induce and improve the threshold behavior,

both stopping-modifying-distorting the crystal growth and building a soluble macro-complex with metal ions and a macro-frame with crystal nuclei, amorphous and colloidal agglomerates [8] are responsible for the whole threshold effect. In these terms, stopping-modifying-distorting the crystal growth should be considered the final activity of a threshold effect near the threshold limit of the scale growth. Conversely, the overall complex frame, which prevents any precipitation of salts, establishes the effective threshold behavior in progress. The same graph of the activity of threshold sequestrants is better explained as the establishment of a sort of macro-complex framework (threshold zone) followed by destabilization and formation of undissolved salts of the sequestrant (turbidity zone) [3] and the final zone of mono-complexes (like stoichiometric sequestration) in which the molar concentration of the sequestrant is higher than the concentration of the polyvalent cations. Figure 3.1 shows the behavior described [9].

The turbidity zone does not depend on the addition of calcium to a fixed concentration of sequestrant but on the addition of sequestrant to a fixed hardness. The rise in sequestrant should increasingly stabilize the system. A dramatic loss in efficiency actually occurs, the peak of which changes as a function of each threshold agent. The failure is more easily explained as collapse of the

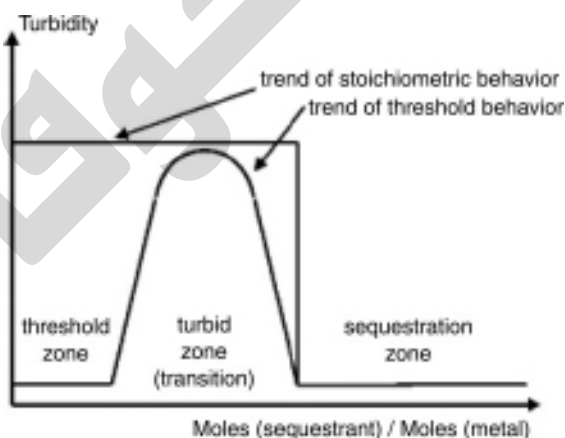


Figure 3.1 Stoichiometric and threshold behavior.

comprehensive macro-complex (moment of transition from threshold to stoichiometry) rather than loss of activity on the crystal nuclei. As it is possible to observe distorted crystals rather than the molecular framework, the advanced phase of distorted crystals is described as an indication of threshold activity, as shown in Figure 3.2 adapted from Ref. [10]. The ability of polymaleic sequestrant to distort calcium carbonate is also reported [11].

In a different way, the threshold capacity can be traced by checking the quantity of hardness stabilized before precipitation occurs in the turbidity zone. An example is given in Figure 3.3 [12].

Polyaldehydecaboxylic acid of MW 1500 (POC HS 2020) becomes effective at 0.5 ppm and changes into the turbidity zone at 5 ppm. ATMP (2 ppm) inhibits the precipitation of 6500 ppm of calcium sulfate for 7 days. In this case the molar ratio between Ca^{2+} and ATMP is 10000:1, while the normal solubility of calcium sulfate is 2500 ppm, and 2:1 should be the theoretical molar ratio between Ca^{2+} and ATMP [13].

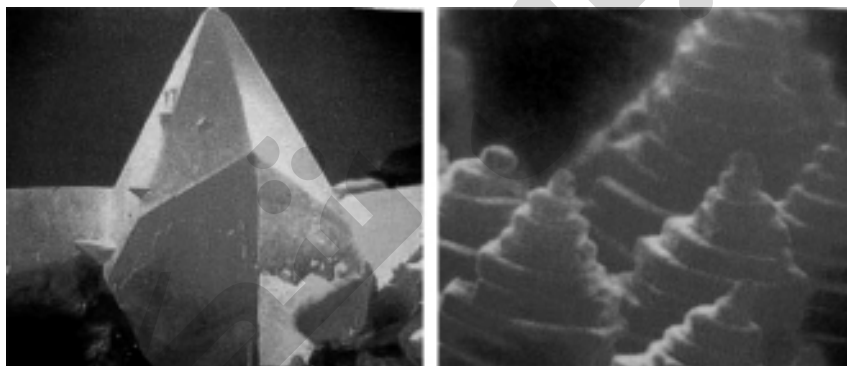


Figure 3.2 Calcite and its distorted crystals with polyaspartate salts (Baypure DS100–Bayer trademark) (SEM picture reprinted by courtesy of John Wiley & Sons, Inc. [10]).

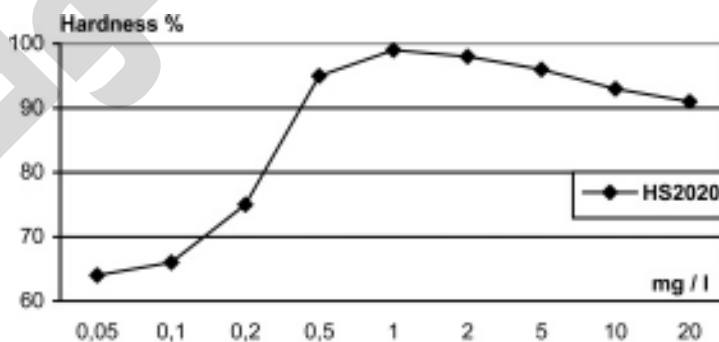


Figure 3.3 Checking threshold capacity. Conditions: hardness 12 dG, 90°C, neutral pH. Rating: soluble hardness after 28 h. HS 2020 = POC HS 2020 (Degussa trademark).

In a different investigation, the concentrations of both sequestrant and hardness are kept unchanged and the solution is recycled in a coil immersed in hot water. Figure 3.4 shows the result of laboratory tests.

Acrylic homopolymers show an evident loss of threshold activity when they increase in molecular weight. However, they balance the loss through their suspending and dispersing power. Suspension and dispersion really are the main properties of the high-molecular weight polyacrylate compounds (Section 3.4.4).

The stability of complexes formed by threshold agents is weaker than it is in the case of stoichiometric ones. Threshold agents do not succeed in competing for strong precipitants. Thus, threshold agents alone can be applied in the treatment of slightly contaminated systems such as raw water (rinse, tunnel pasteurizer, cooling water, and boiler). For high ionic strengths (caustic media), mixtures of thresholds and stoichiometrics are always recommended in order to get the benefit of the stoichiometric strength for cleaning and the threshold efficiency to keep all contaminants soluble. This concept is the basis of sequestration practice in the field. Threshold and stoichiometric sequestrants complement each other in detergency performance.

This synergistic mechanism is known as the carrier function. When calcium is trapped in a deposit of insoluble salts, complexing strength and steric hindrance of sequestrants are involved. The steric hindrance takes on a task comparable to the stability constant and affinity with metals. The sequestrant must succeed in entering the contamination, reacting with the calcium, and being desorbed in the form of a calcium complex. Sterically smaller and stronger sequestrants (stoichiometric) can more readily reach calcium ions inside, react with them, and leave the soil carrying the calcium with them. Once soluble, the carrier exchanges calcium with another sequestrant (threshold assistant) sterically less favorable. The carrier mechanism contributes to loosening the

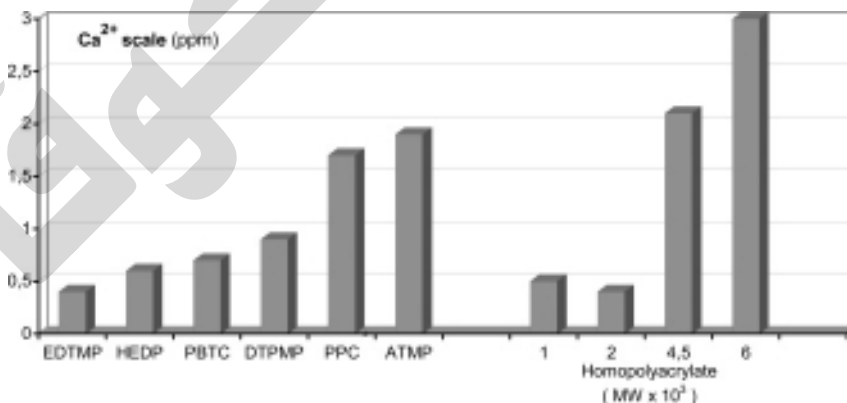


Figure 3.4 Condition: 2 ppm of sequestrant, cold water hardness 120 dF recycled in 3 m coil soaked in water at 80 °C, flow rate 140 L h⁻¹, 6 h of recycling. Limestone is re-solubilized with HCl and calcium titrated with EDTA. (*) PPC = Phosphinopolycarboxylate.

soil structure and aiding cleaning [8]. It is schematically represented in Figure 3.5.

EDTA, NTA, MGDA, EDG, HEDTA, IDS, GLDA belong to the group of carrier sequestrants. Temperature decreases the calcium-binding capacity and the efficacy of the sequestering agents. Jakobi *et al.* have reported the influence of temperature in various tables [14, 15], including the dramatic loss of sequestering activity of citric acid. These results are shown in Table 3.1.

Acrylic (co)polymers confirm the negative dependence on both temperature and pH. Table 3.2, adapted from BASF technical information [16, 17], shows these effects.

Table 3.1 Sequestration as a function of temperature.

Chemical name ^{a)}	Calcium binding capacity (mg CaO/g)	
	20 °C	90 °C
STP ^{a)}	158	113
HEDP ^{a)}	394	378
ATMP ^{a)}	224	224
NTA ^{a)}	285	202
EDTA ^{a)}	219	154
Citric acid ^{a)}	195	30
Ion exchanger (polyacrylic acid) ^{b)}	310	260
Ion exchanger (polyacrylic acid-co-maleic acid) ^{b)}	330	260
Ion exchanger (polyacrylic acid-co-allyl alcohol) ^{b)}	250	140
Ion exchanger (Na-Al silicate) ^{b)}	165	190

a) Adapted from Jakobi [14].

b) Adapted from Jakobi [15].

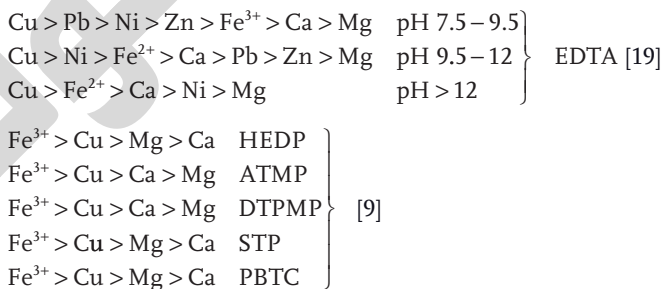


Figure 3.5 The carrier mechanism of sequestrants makes the cleaning easier.

Table 3.2 Acrylic (co)polymers sequestration as a function of temperature.

Chemical name (molar mass)	Calcium binding capacity (mg CaCO ₃ / g active matter)			
	pH 9		pH 11	
	25 °C	90 °C	25 °C	90 °C
(a) Methyl-vinyl-maleic copolymer (70000)	425	525	600	450
(b) Acrylic-maleic copolymer (70000)	350	425	500	450
(c) Olefin-maleic copolymer (12000)	350	200	575	100
(d) Modified polyacrylic acid (4000)	800	400	950	525
(e) Polyacrylates (2000)	475	300	725	450
(f) Polyacrylate (4000)	475	350	725	475
(g) Polyacrylate (15 000)	450	400	650	475
(h) Polyacrylate (70000)	425	400	650	575
(i) Polyacrylate (100 000)	425	425	600	525
(j) Polyacrylate (250 000)	575	450	700	625
(a) Sokalan CP2	(e) Sokalan PA 20		(i) Sokalan PA 80	
(b) Sokalan CP5	(f) Sokalan PA25PN		(j) Sokalan PA110S	
(c) Sokalan CP9	(g) Sokalan PA 40			
(d) Sokalan CP10	(h) Sokalan PA70PN [Sokalan® is a BASF trademark]			

Sequestrants have varying affinity with metals and form complexes in competition with each other. According to the rule of the stability constant, a sequestrant will not chelate another metal until the most stable is totally complexed [18]. Competition due to varying affinity with metals confirms once again that the use of a single sequestrant could not prevent deposition in the detergency process. Examples of preferential sequestration are given below:



Although the sequestering capacity is the primary parameter to establish the effectiveness of a sequestrant, the choice of the blend of sequestrants cannot be simply decided on the base of sheer sequestration. It also depends on how the sum of sequestrant properties can globally improve the cleaning process. Thus,

knowledge gained through as many laboratory tests as possible together with practical experience enable sequestrants able to solve any cleaning problem to be selected.

3.2

Coordination Groups

Electrons in σ and π symmetry orbitals not directly involved in binding are available to participate. Atoms can use these electrons to establish coordination bonds in addition to the covalent ones. Molecular rings and cages represent configurations of soluble complexes with metals deriving from the combinations of one or several groups bonding to these atoms. Nitrogen and oxygen satisfy these requirements and enter into most coordination complexes, singly and combined. The coordination groups are generically drawn up as follows:



Some authors [20] include groups as enolate ($-O^-$), azo-ions ($-N=N-$), and N-ring-N and list the following affinities with metals:



Even though the evaluation of a single affinity is theoretically correct, it takes on a fairly practical meaning. In practice, the effectiveness of sequestering depends on the molecular framework rather than on the single coordination group. The sequestering power and the stability of the complex indicate an efficacy based on the combination of groups and their spatial arrangement rather than on an absolute single value of affinity with metals. For instance, the carboxylic group completely changes its chelating properties according to its association with hydroxyl (e.g., gluconate), amino (e.g., EDTA) or phosphonic (e.g., phosphonate) groups. Hence, the most significant differences between the chelation powers of metal ions have to be attributed to the molecular structure, which denotes the various clusters of sequestrants. For this reason, it is more profitable to list the possible combinations of the coordination groups as in Table 3.3.

One structure cannot be theoretically preferred to another. Each molecule makes its own contribution in preventing precipitation as a function of the application and operating conditions, which suit one structure rather than another. Thus, the best choice implies both knowledge of the sequestering, dispersing, suspending, and anti-redeposition ability of a sequesterant and knowledge of the chemistry of the contamination which the sequesterant is being used to remove.

Table 3.3 Combination of the coordination groups.

$-N-R-COOH$	Amino carboxylic acid
$HO-R-COOH$	Hydroxy carboxylic acid
$HO-R-NH-R'-COOH$	Hydroxy amino carboxylic acid
$R-O-R'-COOH$	Ether carboxylic acid
$-RCOOH-R'COOH-$	Polycarboxylic acid
$R-O-R'-OH$	Ether hydroxy framework
$-R-CONH-R'-CONH-R''-$	Polyamide framework
$R-PO(OH)_2$	Alkyl phosphonic acid
$-N-R-PO(OH)_2$	Amino phosphonic acid
$HOOC-R-PO(OH)_2$	Phosphocarboxylic acid
$HOOC-R-P(OH)_2$	Phosphinocarboxylic acid
$(HOOC-R)_n-[PO(OH)_2]$	Polycarboxy polyphosphono framework
$HO-R-PO(OH)_2$	Hydroxy phosphonic acid
$-(NaPO_3)_n^-$	Polyphosphate

3.3

Sequestration Data

Sequestrants compete with other anions for calcium. It follows that the appropriate methodology for assessing the sequestering power of a chemical entails the presence of a competitor. As the choice of the competing agent should be made as a function of the precipitants related to the contamination in the field, it is possible to create procedures suited to each application. On the other hand, it is equally profitable to take an interfering competitor able to mediate the strength of the precipitating anions. Oxalate is one of the competing agents satisfactorily attaining practical goals. Field experience confirms the sequestration data in its presence. Thus, the result, mainly from stoichiometric agents, is directly transferable to applications in the field. The data in Table 3.4 are derived from the turbidimetric procedure based on oxalate.

The table relates to sequestration in three typical conditions reproducing neutral, critical, and caustic pH. The result is expressed in mg $CaCO_3$ sequestered per gram of raw material as supplied (to assess the cost-in-use as well). Calcium is added as $CaCl_2$ (0.2 M). A complete description of the methodology is given in Section 4.1.1.

The sequestering efficiency is a linear function of the concentration. The linear relationship allows a direct comparison among sequestrants when they are used on the same soil and under the same operating conditions. The graph for ATMP (Figure 3.6) is given as an example of linearity.

The result is considered to be pure sequestration. The more the application moves to raw water (neutrality), the more the values of the table describe the reality (e.g., bottlwashing rinse, tunnel pasteurizers, cooling water, and boiler). Conversely, only the data from stoichiometric sequestrants assume a practical

Table 3.4 Condition: sequestrant 1 g and 20 mL of 0.2% Na oxalate solution to 1000 mL distilled water, 20°C.

Sequestering agent	pH 7	pH 11	NaOH 1%
Na hexametaphosphate	350	350	350
Na tripolyphosphate	165	295	330
K pyrophosphate	105	195	95
Trisodium phosphate	25	15	10
ATMP (40%)	85	205	295
HEDP (60%)	360	665	635
EDTMP (17%)	35	145	230
HDTMP (22%)	40	60	210
DTPMP (25%)	60	165	270
PBTC (50%)	80	225	285
EDTA 4Na (80%)	230	250	305
HEDTA-3Na (43%)	65	100	145
NTA 3Na (80%)	115	340	350
MGDA-3Na (40%)	40	160	210
DTPA (40%)	50	75	105
IDS-4Na (34%)	75	104	145
EDG-2Na (28%)	95	105	170
GLDA-4Na (38%)	125	130	175
Citric acid	120	125	135
Tartaric acid	20	25	65
Na gluconate	10	15	105
Sorbitol	8	10	55
Alkylpolyglucoside	10	15	90
Acrylic homopolymer (54%–1 000 MW)	90	100	105
Acrylic homopolymer (50%–1 500 MW)	80	85	105
Acrylic homopolymer (54%–2 000 MW)	135	170	180
Acrylic homopolymer (40%–2 500 MW)	95	150	155
Acrylic homopolymer (53%–3 400 MW)	115	150	160
Acrylic homopolymer (40%–4 000 MW)	105	115	160
Acrylic homopolymer (48%–4 500 MW)	135	175	180
Acrylic homopolymer (50%–6 000 MW)	135	170	165
Acrylic homopolymer (35%–9 000 MW)	70	115	130
Acrylic homopolymer (25%–10 000 MW)	60	110	135
Acrylic homopolymer (91%–20 000 MW)	205	215	255
Acrylic homopolymer (45%–40 000 MW)	180	190	260
Acrylic homopolymer (25%–60 000 MW)	95	145	185
Acrylic homopolymer (30%–70 000 MW)	75	125	135
Acrylic homopolymer (37%–100 000 MW)	165	190	205
Acrylic homopolymer (37%–125 000 MW)	105	180	230
Acrylic homopolymer (25%–240 000 MW)	80	130	170
Acrylic copolymer (40%–4 000 MW)	105	115	160
Acrylic copolymer (25%–12 000 MW)	20	70	165
Acrylic copolymer (35%–60 000 MW)	65	255	385
Acrylic copolymer (40%–70 000 MW)	110	255	385
Phosphono polyacrylate (40%–2 000)	150	165	195
Phosphono polymaleate (40%–2 000)	165	165	180
Phosphino polyacrylate (40%)	150	190	200
Polymaleic acid (50%)	110	175	230
Polyaspartic acid (41%)	78	90	115

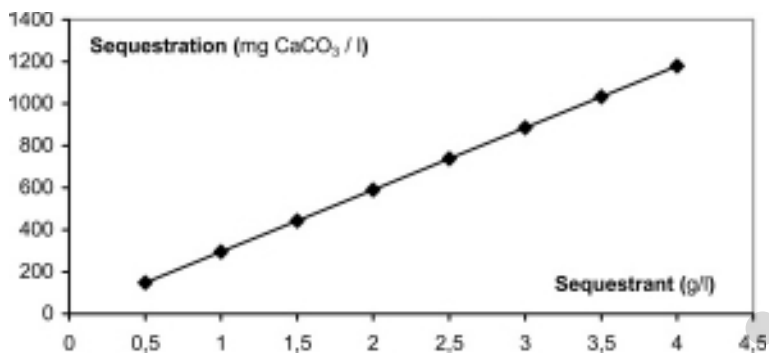


Figure 3.6 Example of a linear sequestration graph. Conditions: 20°C, 1% NaOH, 20 mL L⁻¹ Na oxalate 0.2%, Ca added as CaCl₂ 0.2 M.

meaning in alkaline cleaning. The suspending, dispersing and threshold capacity involves properties unobtainable from simple sequestration. Therefore, specific investigations are tailored to assess the overall performance of each sequestrant. Polyacrylates are a typical example. Their value for pure sequestration is clearly insufficient to indicate the huge potential they really reveal. They cover the whole range from sequestration close to stoichiometry (<2000 MW) to predominantly suspension and dispersion (>40000 MW). Molecular weights between 3000 and 20000 provide the best compromise. For this reason, 2000–4500 MW polymers are the ones most used as sequestrants, while polymers above 40000 MW are used to disperse and suspend in processes concentrating salinity (e.g., boiler and cooling water).

3.4

Food Cleaning Sequestrants

Detergency is the result of several interconnected reactions such as solubilization, wetting, emulsification, peptization, adsorption, detaching, desorption, suspension, dispersion and antiredeposition. Most of these cannot operate without sequestrants. Sequestrants control compounds that disturb cleaning (metals and anionic precipitants) coming from both hardness and residues of the process. The next chapters analyze the sequestrants entering the technology of food detergency both as builders and ancillary compounds.

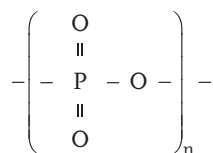
3.4.1

(Poly)phosphates

Rather a lot of literature is devoted to the use of phosphate and polyphosphates as water softeners and deposition inhibitors [2, 21–24]. The original enthusiasm was generated by the discovery of the efficacy of the phosphate group in

preventing deposition of hardness salts in an age when other chemicals able to solve the scale problem were unknown. As a consequence of the benefits achieved, a blind eye was turned toward the risk of depositing calcium phosphate. Phosphate is long-established, safe, cost-effective, and resource-efficient ingredient for detergents. Their peptizing property together with good threshold and dispersing ability still make the polyphosphates one of the most interesting groups of sequestrants, especially when they work together with the current advanced sequestrants that counterbalance the negative effect of the hydrolysis of polyphosphates. Unfortunately, because of their potential impact on eutrophication, phosphates are becoming less accepted as sustainable detergency agents. Thus, they are often replaced with mixtures of other sequestrants low in phosphorus, always aiming to achieve equal performance.

(Poly)phosphates are salts derived from the PO_4^{3-} monomer and have a polymeric structure:



Phosphates are rarely found in raw waters. They enter the process as residue coming either directly from food (e.g., milk) or from food additives (e.g., polyphosphates in sausages and soft cheese, and phosphoric acid in soft drinks) or as components of detergents. Cleaning products include phosphates in the following form:

- Polyphosphates: hexametaphosphate (6 P)
pyrophosphate (4 P)
tripolyphosphate (3 P);
- Monosodium–disodium–trisodium phosphate;
- Phosphoric acid.

The problems with polyphosphate arise from its monomer, orthophosphate. It is the monomer that is really responsible for deposits, its behavior being very sensitive to pH, as described in Sections 1.1.4, 1.1.4.1 and 1.1.4.2. The solubility of calcium orthophosphate $[\text{Ca}_3(\text{PO}_4)_2]$ is roughly 0.02 g L^{-1} [7, 25]. This means that all the monomer phosphate existing in the system precipitates as scale in the presence of hardness. As polyphosphates are unstable in aqueous solution, they inevitably change to orthophosphates by hydrolysis, the rate of which depends on temperature and pH. Figure 3.7 [25] shows the ratio of the chemical species during the hydrolysis of STP.

The pH of the solution affects the hydrolysis of polyphosphate considerably. At pH 4.7 and 70°C , for instance, hydrolysis of STP is 87.4% complete in one day, while at pH 12 it is only 29.5% complete after 10 days [25]. Thus, polyphosphate is sufficiently stable in an alkaline medium. The glassy phosphate (hexametaphosphate) has actually been widely used as a water softener (neutral pH).

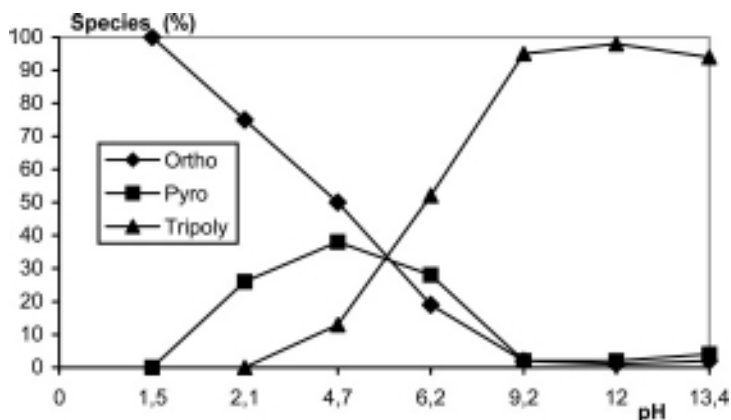


Figure 3.7 Species found at different pH after 24 h at 70°C starting from STP (figure adapted from Ref. [25]).

Softening neutral water, however, is a less demanding technology than the re-use of solutions of alkaline detergents.

Algae, bacteria, and their enzymes represent another factor affecting the hydrolysis rate. Rates 10^5 – 10^6 faster in their presence have been reported [7]. Most micro-organisms possess enzymes capable of interacting with inorganic condensed phosphates and promoting hydrolysis. Pyrophosphate phosphohydrolase catalyzes the hydrolysis of pyrophosphate to 2 moles of orthophosphate [26].

Detergents are sold in concentrated form and are warehoused for long periods. Shen and Dieroff [27] found that the rate of degradation of polyphosphates in aqueous solution increases exponentially with their concentration. A liquid detergent prepared with polyphosphate and stored for months before use would therefore have undergone hydrolysis of the polyphosphate to orthophosphate with consequent deterioration of its performance.

As polymers are totally or partially destined to become monomer, phosphate precipitation may occur whenever one of the poly-species is present. Also, when acidic detergents and descalers are based on phosphoric acid, precipitation occurs in the course of the rinse, rinse being defined as an infinite dilution (up to pure water). On passing from acidity to neutrality, the multivalent cations of the water hardness neutralize and precipitate the final traces of phosphoric acid. Scale is generated unless threshold sequestrants (e.g., phosphonates) are co-formulated in the acidic detergent.

As the hydrolysis rate decreases at caustic pH, polyphosphates last long enough to provide a useful aid to the alkaline cleaning. STP is stable to chlorine and can thus be included in chlorinated products with no problems. Figure 3.8 shows the progress of chlorine loss in the presence of tripolyphosphate.

The chlorine is regarded as acceptably stable if over 50% of the starting concentration is still detectable after 6 months in a cold environment or after 3 months in a hot one. Both formulations in Figure 3.8 pass the stability test.

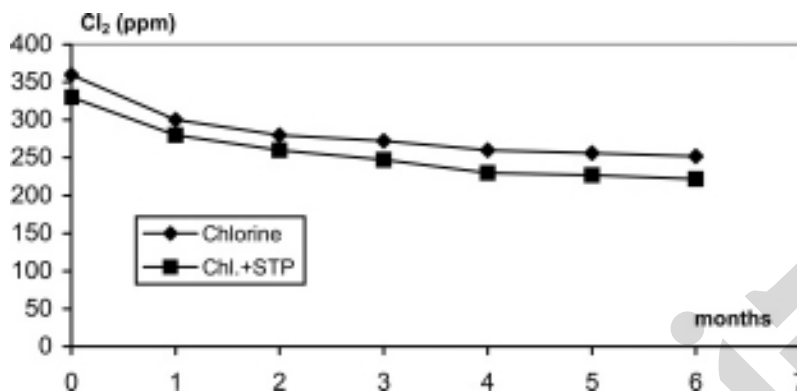


Figure 3.8 Chlorine loss at 25 °C as a function of time. **Chlorine blank:** Na hypochlorite + 5% KOH and soft water. **Chl. + STP:** Na hypochlorite + 5% KOH + 10% STP (Fe impurity ≤ 10 ppm).

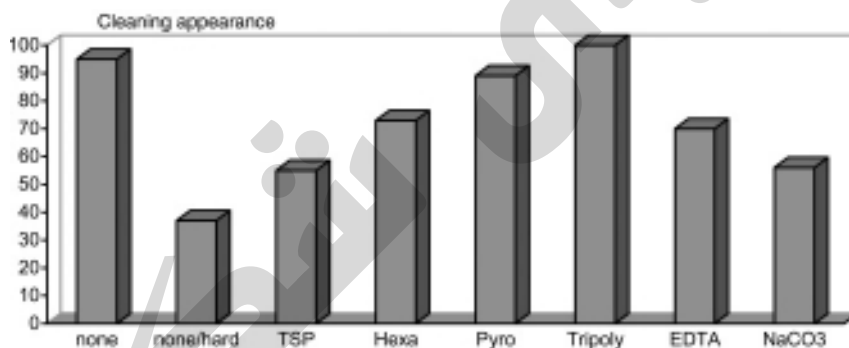


Figure 3.9 Effect of some chemicals on the cleaning capacity of a nonionic detergent in hard water. None = blank in soft water. None/hard = blank in hard water. Hardness 200 ppm CaCO_3 , builder concentration 0.2%. Courtesy of Porter [28].

A further property of STP is its flexibility. STP is used for every aspect of sequestration. It performs as a threshold sequesterant, a dispersant, and a suspension and anti-redeposition agent. It performs satisfactorily at low concentrations (<100 ppm), retarding precipitation and adhesion even in the presence of an excess of precipitants. When polyphosphate is used as a builder (concentration > 300 ppm), it performs not simply as a hardness controller, but also shows behavior peculiar to cleaners. Figure 3.9, adapted from Porter's investigation [28], shows the effect of some chemicals on the cleaning capacity of a nonionic detergent in hard water. In terms of detergency, orthophosphate (TSP) behaves as poorly as carbonate (precipitant), showing almost the same result as the blank, that is no additive to the hard water.

Some authors [29] ascribe the cleaning property to peptization, defining peptization as the action of bringing into colloidal solution. Peptization is considered the opposite to agglomeration and flocculation [30]. A colloid is dispersed in the shape of a sol and is transformed by physical effects (pressure, temperature) and chemical agents into a gel, which flocculates and precipitates because of its instability. Some chemicals are capable of peptization, which is simply the transformation of a gel into a sol [31] by decreasing the attraction between particles. Unlike emulsification, peptization occurs even in the absence of stirring and involves the most polarized or charged organic matter, such as proteins. Phosphoric acid has this property, and is widely employed to clean deposits of protein and fat off molds for shaping cheese and meat. As phosphoric is the best acid for this, peptization is the mechanism put forward to explain this effect, and as polyphosphates show detergency properties superior to simple sequestration, peptizing capacity has been attributed to the entire polyphosphate group.

Polyphosphates are claimed to possess surface active properties. Being adsorbed both onto the surface and the oily globule, they assist detergents in desorbing oil and fats [32–34].

Phosphates are also components of pH buffers used in detergents and solutions used in the analytical laboratory. Buffering power is provided mainly by mono-, di- and trisodium phosphates. Boron derivatives (e.g., tetraborate) are often added, with a synergistic action.

The inorganic phosphates can inhibit corrosion in aqueous solutions whether they are added alone or together with zinc [35]. Rastrick's theoretical mechanism [36] assumes cathodic protection through deposition of carbonate, which links phosphate. Hatch [35] confirmed the theory and proved that phosphate is more effective than carbonate in cathodic protection.

Further aspects concern consumer safety and environmental acceptability. (Poly)phosphates provide consumers with complete safety, and can even be used as food additives (cheese, meat, and soft drinks). Here, the question of acceptability involves different considerations from those relevant to environmental acceptability. The suspected correlation between phosphorus and eutrophication has influenced legislative decisions to limit their use in several categories of detergents and to determine the amount of phosphorus delivered to the environment.

Currently, food detergency essentially exploits two compounds: tripolyphosphate and phosphoric acid. The state of the art is based both on advanced investigation and applied experience aimed at selecting the best performing molecules and developing of new categories of sequestrants to replace other phosphorus-based compounds.

The chemicals shown in Figures 3.10 and 3.11 belong to the phosphoric acid group

3.4.1.1 Hexametaphosphate (HEMP)

Although some authors claim a linear chain, $(\text{NaPO}_3)_n$, for anhydrous sodium hexametaphosphate $[\text{Na}_6(\text{PO}_3)_6]$ [37], the most probable structure is cyclic [7].

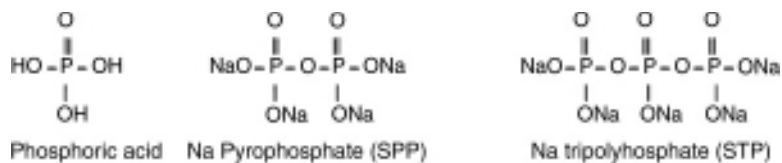


Figure 3.10 Structure of (poly)-phosphates.

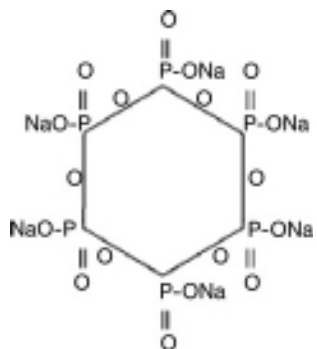


Figure 3.11 Sodium hexametaphosphate ring structure.

Viscosity limits its solubility. The utmost limit allowing for easy handling of the stock solution is ~40%. Since the efficacy of HEMP as a builder is undoubtedly lower than that of STP, the former is suitable for mild treatments such as raw water softening in glassy crystal form, corrosion inhibition on aluminum molds, and as a buffering component in enzymatic detergents. It has rarely been used in alkaline cleaning. The advent of phosphonates has made HEMP obsolete in food detergency. Currently, it still remains as a co-buffering agent for enzymatic treatments and a corrosion inhibitor in solutions of phosphoric acid to prevent darkening of the aluminium.

3.4.1.2 Pyrophosphate

Pyrophosphate has historically been reputed to be the most efficient sequestrant to clean hard surfaces. However, every time it is compared with tripolyphosphate, the latter consistently shows better performance, as Cutler and Davis [29] describe in various tables (see Table 3.5).

Experience in the field confirms STP to be better performing than SPP. STP has therefore replaced SPP in almost all its applications. SPP is no longer applied in food detergency even though the hydrolysis rate is significantly lower than that of STP. Albright and Wilson's investigation [25] reports the following result for 10mM solutions of the chemicals after 5 h at 100 °C and neutral pH:

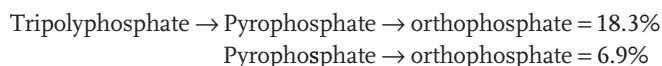


Table 3.5 Properties of SPP and STP.

	Stability constant ^{a)}	Detergency (%) ^{a)}	Sequestration ^{b)}				
			g Ca ²⁺ /100g sequestrant at pH				
			8	9	10	11	12
SPP	5.9	24	0.4	2.4	3.7	4.0	3.6
STP	6.3	27	3.9	7.1	7.5	7.4	7.0

a) Sequestrants 0.0045 mole/liter, Ca 225 ppm, pH 10, anionic surfactants (ABS) 0.075%.

b) Sequesterant 0.1%, Na oxalate 0.1%, 25°C, Ca 0.1 M as titrant.

3.4.1.3 Monomeric Phosphates

As well as phosphoric acid, this group includes salts with three degrees of neutralization: *mono-, di-, and trisodium phosphate*. These can buffer pH, the degree of stabilization of which is a function of the ratio of the three chemicals. Monosodium phosphate solution gives acidic pH, disodium weakly alkaline and trisodium near causticity (pH $\approx$ 12). Thus, the pH is adjusted and stabilized to the desired value simply by varying the relative concentrations.

Monomers have no effect on detergency. The alkalinity of TSP and its capacity to convert hardness into an amorphous sludge led it to be selected for boiler treatments at a time when the knowledge on calcium and magnesium sequestration was rudimentary. Many small boilers are still treated with TSP in spite of the current availability of additives including sophisticated combinations of sequestrants and suspending and dispersing agents, chemicals to give alkaline conditions, and oxygen scavengers.

3.4.1.4 Tripolyphosphate

The behavior of STP has already been described. It gives the best benefits among the phosphate group in sequestration, anti-redeposition, deflocculation, suspension, dispersion, peptization, and detergency. For this reason, tripolyphosphate remains the only sequesterant able to satisfy every cleaning requirement in alkaline systems. Where provisions of the law limit its use, combinations of several different sequestrants are required to enable detergents to perform like STP.

Anhydrous sodium tripolyphosphate is slowly hydrated to the hexahydrate form ($\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$) in an exothermic reaction. The hexahydrate STP, known as phase-one, proves to have higher solubility, enough to exceed the solubility of the anhydrous STP, even when the hexahydrate concentration is low. Different ratios of STP hydrates are manufactured in order to satisfy the need for soluble slurries. Slurry is a physical form where STP is simultaneously present in dissolved and dispersed form, and can be defined as a 'liquid

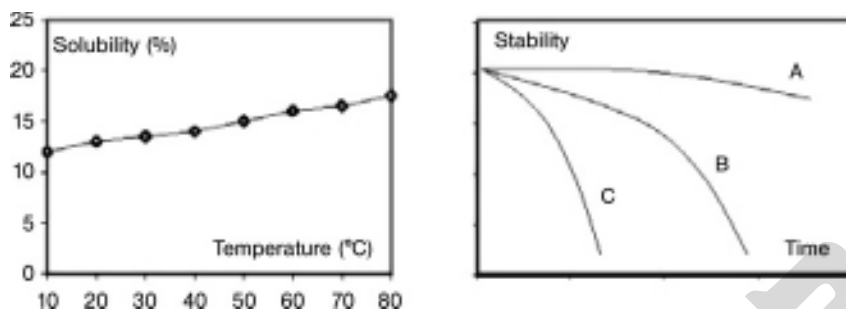


Figure 3.12 STP solubility as a function of temperature (adapted from Ref. [38]) and stability of a liquid detergent [A = 30% Na hypochlorite (12%), B = A + STP, C = B + silicate].

powder'. It provides a tool to manage a high concentration of STP powder as a liquid.

The solubility of STP is low anyway, and slowly increases with temperature. It is difficult to keep detergents clear and stable at room temperature with a concentration of STP above 15%. Detergents are even more unstable when tripolyphosphate is blended with caustic salts, silicate, and hypochlorite (see Figure 3.12).

Despite stability tests carried out in the laboratory, precipitation often occurs unexpectedly both at low and high temperature in the course of warehousing. Only a drastic reduction in the total salinity sometimes solves the instability problem. Even the purity of the plastic forming the containers is crucial to guaranteeing stability. Nonregenerated plastic is mandatory for containers for detergents containing high concentrations of STP and chlorine.

STP performs far better at caustic pH in preventing incrustations, as already mentioned (Section 1.1.4.2) and confirmed in Table 3.6.

As its effectiveness fails at a transitional pH (11–12), STP is used either in concentrated form or along with caustic detergents. Thus, when stability is not a problem and the provisions of the law are complied with, alkaline detergents based on STP and synergized with phosphonate (e.g., ATMP, PBTC) provide food detergency with excellent results.

3.4.2

Phosphonates

The organo-phosphorus compounds (phosphonates) currently constitute the leading group of chemicals supplying positive answers to the demand for the control of polyvalent metals in every sector. The history of phosphonates is relatively recent. It can be roughly dated back to 1938 with Woodstock's patent [39], which describes the production and use of sequestering structures involving O–P–N bonds. Their extensive application is even more recent. The establishment of the category of phosphonates was practically concluded in the seventies

Table 3.6 Caustic pH improves the STP performance.

	pH 10				pH 11				pH 12				pH 12.5				1% NaOH			
	100	200	300	400	100	200	300	400	100	200	300	400	100	200	300	400	100	200	300	400
	Ppm				ppm				ppm				ppm				ppm			
STP	—	—	+	++	—	—	—	++	—	—	—	—	—	—	—	++	+++	+++	+++	+++

Rating: – insufficient + sufficient ++ good +++ excellent hardness control.

Condition: 40 dF, 60°C, 20 h of static soak, glass slides.

(1970–1980) when their properties with respect to scale and corrosion inhibition were sufficiently disclosed [40–44] and their availability was guaranteed.

Phosphonate is the generic name to describe phosphorus-containing compounds having both phosphorus-oxygen (P–O) and phosphorus-carbon (P–C) bonds. It differs from (poly)phosphate (only P–O bonds) and phosphate compounds where oxygen also bonds between P and C (P–O–C). Considering their efficacy and also cost-in-use, 6 compounds among the synthesized molecules have actually proved to give real benefits in food detergency:

- ATMP = aminotrimethylenephosphonic acid
- HEDP = hydroxyethylidenediphosphonic acid
- EDTMP = ethylenediaminetetramethylenephosphonic acid
- HDTMP = hexamethylenediaminetetramethylenephosphonic acid
- DTPMP = diethylenetriaminopentamethylenephosphonic acid
- PBTC = phosphonobutanetricarboxylic acid.

and their salts. In practice, only three of these are widely involved in detergents as effective builders: ATMP, PBTC, and HEDP. The peculiar properties that make phosphonates extremely flexible are summarized below:

- **Efficacy at very low concentration:** A few ppm are sufficient to exploit threshold ability in raw water and a small percentage to improve the builder capacity in detergents.
- **Solubility:** They are soluble in every medium and can be used quite freely in concentrated form in acidic, neutral, and alkaline products.
- **Temperature stability:** The direct phosphorus-carbon bond (P–C) imparts great stability at extremes of temperature under all conditions of pH [7].
- **Stability constant:** This is high enough to compete with the commonest precipitants, except for long-chain soaps and orthophosphate.
- **Corrosion inhibition:** Phosphonates, alone and in combination with zinc, nitrogen derivatives, and molybdate inhibit the corrosion of copper and its alloys, aluminium, and steel [7].
- **Phosphorus content:** Their relatively low phosphorus content (<20% in raw materials as supplied), low concentration in use, and negligible contribution to eutrophication mean that phosphonates generally comply with the provisions of the law on environmental safety.
- **Stability to chlorine:** The development of phosphonates (e.g., PBTC) stable to chlorine has further contributed to this fundamental sector of cleaning.
- **Stabilizer of peroxides:** The addition of phosphonates to peroxide formulations prevents degradation by the catalytic action of heavy-metal impurities.
- **Environmental safety:** Phosphonates show low toxicity to aquatic life. They are removed from the environment through moderate biodegradation and abiotic mechanisms such as photodegradation [45].

The outlined benefits are so satisfactory that the majority of current detergents include phosphonates. The structural formulae of the phosphonates most used in food cleaning are given in Figures 3.13 and 3.14.

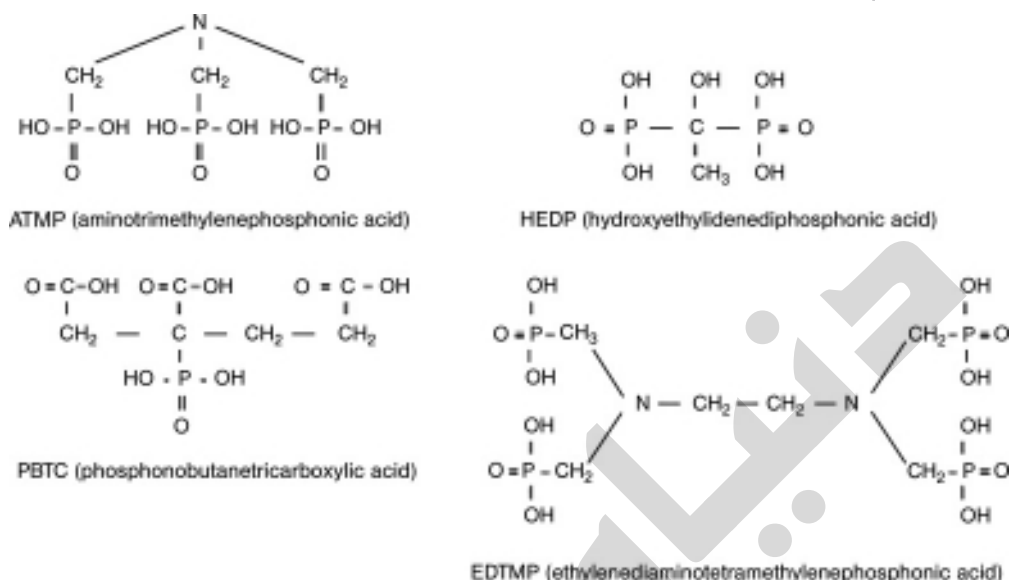


Figure 3.13 Structure of phosphonates.

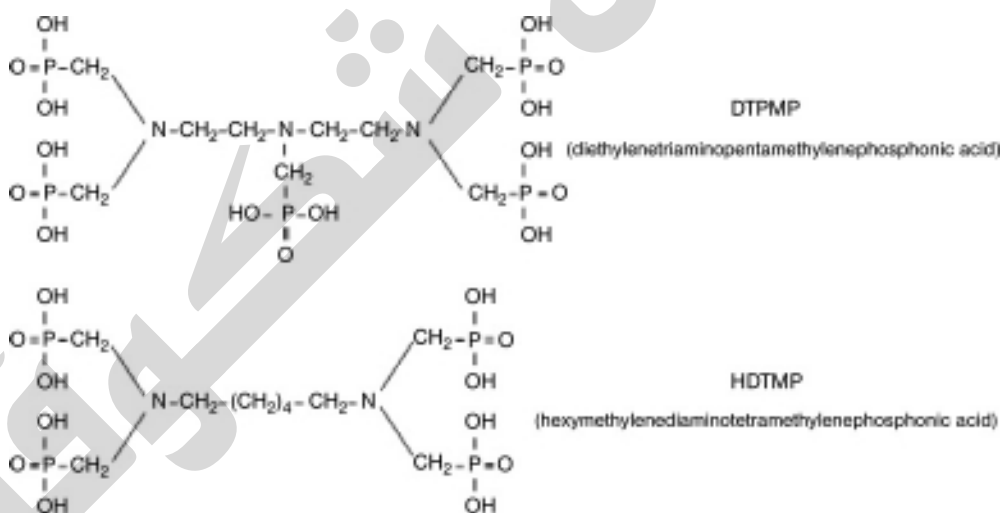


Figure 3.14 Structure of phosphonates.

3.4.2.1 Phosphonates and pH

The activity of phosphonates depends on pH because

- They remain sensitive to the critical pH (ca. 11–12), though less so than other groups of sequestrants.
- Some perform better at a low pH, others at a high one.

This behavior is remarkable. It distinguishes between two of the most important phosphonates for food detergency: ATMP (caustic pH) and HEDP (neutrality). The ATMP efficiency in caustic conditions was discovered at the same time as the investigations on sodium gluconate [46]. Their efficacy is compared to the other phosphonates in Table 3.7.

ATMP and DTPMP work at their best in caustic solutions. HEDP excels in neutral conditions. PBTC activity is evenly distributed across the pH range. An interesting conclusion can be drawn from comparing the table to the theoretical values of sequestration of Figure 3.15, namely that it is practically impossible to deduce the overall behavior from the sequestering power only (oxalate test).

Table 3.7 Relative efficacy of phosphonates.

	pH 10				pH 12				1% NaOH			
	ppm				ppm				ppm			
	100	200	300	400	100	200	300	400	100	200	300	400
ATMP	–	+	+++	+++	–	++	+++	+++	+++	+++	+++	+++
HEDP	–	+++	+++	+++	–	–	–	–	–	+	++	++
PBTC	–	++	+++	+++	–	++	++	+++	+++	+++	+++	+++
EDTMP	–	++	+++	+++	–	++	+++	+++	++	+++	+++	+++
DTPMP	–	+	++	++	–	++	+++	+++	+++	+++	+++	+++

Rating: –, insufficient; + sufficient; ++ good; +++ excellent hardness control. Conditions: 40 dF, 60 °C, 20h static soak, glass slides, sequestrants adjusted at 40% active matter.

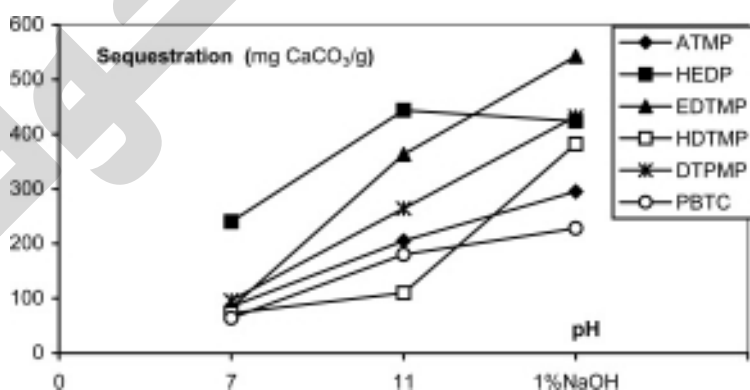


Figure 3.15 Activities of various sequestrants plotted against pH. Conditions: sequestrant 1 g L⁻¹, 20 ml Na oxalate 0.2%, Ca added as CaCl₂ 0.2 M, 20 °C. Sequestrants reported to 40% active matter.

The more the alkalinity increases, the more ATMP prevents deposits and proves to be more active than HEDP even though HEDP exhibits higher values of pure sequestration (oxalate test). This is a typical example of scale prevention performed in different ways. Complexes of sequestration can initially form but do not last in competition with the ionic strength of strong ligands such as hydroxyl and carbonic ions. Thus, dispersion and anti-adhesion of salts become more important than the formation of soluble complexes (sequestration). Phosphorus reveals these properties. The more phosphorus there is in the molecular structure, the more the dispersion, suspension, and anti-adhesion properties are enhanced.

PBTC is efficient in every application, but its excellent stability to chlorine makes it preferred to all others in chlorinated alkaline detergents.

EDTMP and DTPMP are considered to be specialties for food detergency because of the low ratio of their active matter to cost-in-use compared to ATMP, HEDP, and PBTC. For this reason, their use is associated to particular treatments rather than being general builders for cleaning.

Its ability to prevent scale means that ATMP is widely used in the bottlwasher rinse. This application is consistent with the alkalinity of the first rinse, where a pH in the range 12–10 is customary. Actually, the rinse consists of three or more stages. The pH changes from alkaline to neutral potable water as one stage is succeeded by another. When the first rinse runs at low pH (≤ 10), the rinse behaves like a neutral system. Then, in this case ATMP loses part of its activity and, in order to prevent scale, is replaced by or blended with HEDP and PBTC.

Theoretical sequestering capacity, dispersion, anti-deposition, and the relationship between laboratory tests and field applications enable the most pertinent choice to be made in terms of dependence on pH, cleaning systems, and cost-in-use adapted to each sector of food detergency.

3.4.2.2 Stability of Phosphonates

The stability of phosphonates to temperature, alkalinity, and acidity is one of their most widely claimed and confirmed properties. Figure 3.16 shows their stability compared to that of polyphosphates.

ATMP is reported [9] to be 2^{13} times more stable than sodium pyrophosphate and 2^{16} than sodium tripolyphosphate at pH 10.

While PBTC is stable to chlorine and chlorine dioxide, chlorine dioxide makes the activity of ATMP and DTPMP decrease to 50% within 24 h [3]. Ozone affects all the phosphonates within a few minutes. However, PBTC still remains the most compatible [3]. Conversely, the stability of phosphonates in peroxide formulations (peracetic acid and hydrogen peroxide) is so high that it is sometimes added just to preserve them from the catalytic degradation caused by traces of heavy metals.

Sodium hypochlorite has been traditionally formulated with tripolyphosphate even though the clarity and stability of products based on STP are often unpredictable. Phosphonates (PBTC alone and together with 4500MW polyacrylates) replace sodium tripolyphosphate to enhance the stability of the product and keep the majority of the applications working with the same effectiveness.

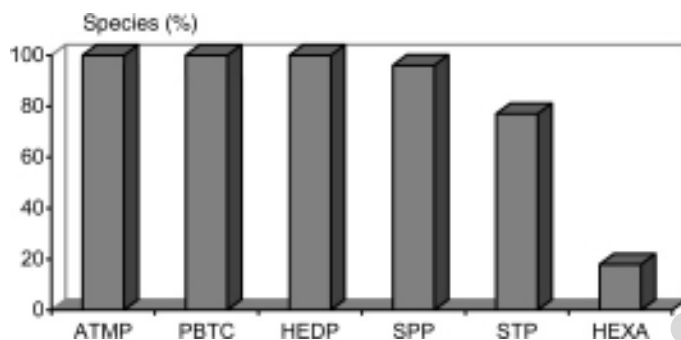


Figure 3.16 Comparative stability of phosphonates. Conditions: 70 °C, 125 h, pH 9. ATMP and HEDP adapted from Ref. [19]. SPP, STP and HEMP adapted from Ref. [25] and PBTC from Ref. [3].

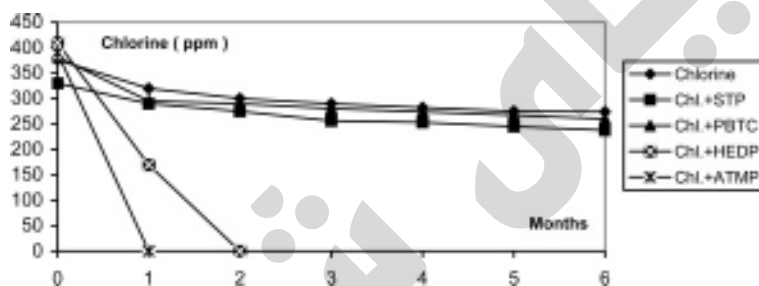


Figure 3.17 Stability of sodium hypochlorite (Na hypochlorite + KOH 5% and soft water) to which sequestrants are individually added.

As only the nitrogen-free phosphonates prove to be stable to chlorine, HEDP should theoretically be stable also. Nevertheless, HEDP leads to chlorine loss and precipitation of crystals with time. The reason is ascribed to impurities not removable from the raw material using current refining processes. Figure 3.17 shows the chlorine loss at room temperature with different sequestrants in the same formula.

The stability to chlorine at room temperature is acceptable if over 50% of the starting concentration still remains after 6 months. ATMP degrades chlorine to zero within 2 weeks, HEDP halves the chlorine concentration in a month.

3.4.2.3 Phosphonates and Corrosion Inhibition

Phosphonates combine sequestration with corrosion inhibition on metals. PBTC is claimed to be effective on carbon and stainless steel [3], and EDTMP and AMTP even on aluminium in acidic medium. Generally speaking, phosphates and phosphonates behave as cathodic inhibitors. According to Bayer AG [3] and the PBTC inhibition mechanism proposed by Ashcraft *et al.* [47, 48], the cathodic inhibition is due to a film covering the metal surface. This prevents contact between bare

metal and aqueous solution. Sequestrants become incorporated in this film through a chemical reaction with surface iron, calcium, and complexed heavy metals (e.g., zinc). The presence of insoluble Fe^{3+} makes the film effective. This insoluble iron is produced at the moment of primary corrosion, which soon occurs at the interface in the presence of oxygen. FeOOH (hydrated iron oxides) has to remain included inside the film to make the inhibition effective. This is possible in alkaline solutions and even in neutral condition when sequestrants stabilize calcium carbonate. Although the oxidation rate is considerably faster at high pH, ions of stabilized carbonate still produce a mildly alkaline solution sufficient to insolubilize Fe^{3+} inside the protective film. Ashcraft *et al.* provide documentation of the process in two NACE Papers [47, 48]. They give the chemical composition of the protective film with PBTC as the corrosion inhibitor (Figure 3.18).

Inhibition does not cause the corrosion process to stop but rather the rate to reduce. Hence, the mechanism of the process involves a kinetic rather than a thermodynamic interaction.

The decrease in the corrosion rate is evident on aluminium soaked in phosphoric acid solution. ATMP and HEMP prevent blackening, as demonstrated in Figure 3.19.

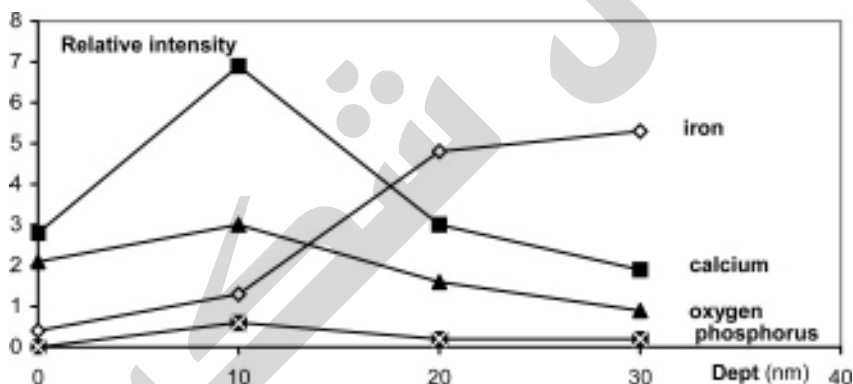


Figure 3.18 Profile of surface after 24 h (courtesy of Ashcraft [47, 48]).



Figure 3.19 Prevention of blackening by ATMP and HEMP. Conditions: 50°C and 72 h soak. Phosphoric acid 2%, + 2 g L⁻¹ HEMP (20 h), + 2 g L⁻¹ HEMP (72 h), + 2 g L⁻¹ ATMP.

When aluminium is soaked in acidic solutions of phosphoric acid, corrosion starts uniformly on all the samples. The hydrogen release stops after a few minutes in solutions containing HEMP and ATMP. Corrosion is made evident by the darkening of the aluminium (iron and manganese oxides impurities in Al-alloy). HEMP and ATMP keep the aluminium surface protected and clean. However, the efficacy of hexametaphosphate ceases after ~40 h of soak. The loss in inhibiting effect depends on the rapid hydrolysis of the polyphosphate in acidic conditions (Section 1.2.5). HEMP proves to be an effective inhibitor only in polymeric form and is not able to protect aluminium when it is hydrolyzed to monomer. ATMP is less effective than HEMP, but its stability is a useful aid to the acid cleaning.

ATMP has a further interesting property. It promotes the scavenging of oxygen by sulfite (synergistic effect). When the ATMP structure (Figure 3.20) is compared with well-known oxygen scavengers (e.g., hydroxylamine and diethylhydroxylamine) the reason for this ability becomes clear, as explained below.

Boiler treatment benefits from this synergism. In the presence of ATMP, sulfite lasts longer than expected from its stoichiometric reaction with oxygen. Thus, a reserve of sulfite is regularly assured to the process, and ATMP has priority of reaction.

As already mentioned, sequestration is only a part of the detergency process. Good sequestration does not always mean good cleaning. ATMP and HEDP exemplify the concept. ATMP enhances scale prevention at a caustic pH better than HEDP. However, HEDP sometimes performs cleaning better than ATMP. This difference in behavior is evident with casein and starch, for example.

Figure 3.21 shows that ATMP cleans casein off more rapidly, whereas HEDP is more effective with starch. If the soil is derived from milk, the cleaning result

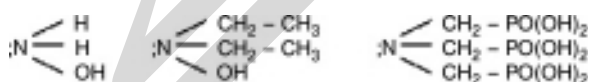


Figure 3.20 Hydroxylamine, diethylhydroxylamine, and ATMP.

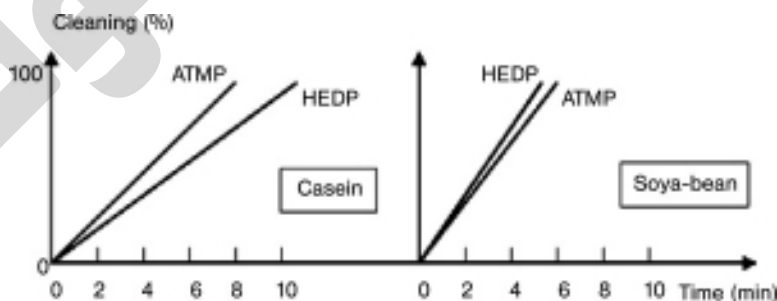


Figure 3.21 Properties of ATMP and HEDP. Conditions: soil on glass slide: 5 mL of 20% pure casein or starch dispersed in hard water (25 dF). Dry for 15 min at 105 °C; cleaner: 1% solution of [30% NaOH + 5% sequestrant + soft water], 40 °C, 25 dF, 300 rpm.

Table 3.8 Time required for label removal as a function of the type of glue.

Chemicals	LRV (min)	
	Glue	
	Casein/soy-bean starch	Soy-bean starch
ATMP	9.2	6.4
EDTMP	9.5	6.7
DTPMP	10.4	6.9
HEDP	10.9	5.9

is the same as with casein, except that more time is needed because of the presence of fat.

The same result is observed in the process of detaching labels in bottlewashing. When the glue is based on (or includes) casein, nitrogenous chemicals give more rapid removal, whereas the removal time due to nitrogen-free molecules differs only as a function of their steric hindrance. As far as phosphonates are concerned, the times of label removal (LRV) from glass bottles are reported in the Table 3.8 (laboratory tests).

N-phosphonates detach casein-glued labels more rapidly than HEDP, although HEDP is molecularly smaller. Among N-phosphonates, steric hindrance establishes the priority, reducing the DTPMP efficiency in comparison with that of EDTMP, although several nitrogen groups are available in DTPMP. Steric hindrance is the only relevant parameter on starch (N-free substance). Thus, HEDP (the smallest phosphonate) is by far the best. This result also supports the empirical rule which states that a chemical loves similar chemicals. Thus, proteins (peptide bond) preferably interact with N-phosphonates whereas N-free hydroxy compounds (starches) love the small N-free HEDP.

3.4.3

Hydroxy Acids

Sequestering compounds structured with C, O, and H in hydroxyl and carboxylic groups are generically defined as sequestering carbohydrates. The group is also known as sequestering agents based on hydroxy acids as well as sequestering sugars and acidic sugars. The following chemicals are of considerable importance in food cleaning:

- Gluconate group
 - gluconate (gluconolactone)
 - heptonate and glucoheptonate
 - borogluconate
 - boroheptonate

- Sorbitol and dextrose (COOH-free chemicals included in this family)
- Tartrate
- Citrate
- Hydroxyacetic acid.

Complexation of metal ions is a reaction that forms a part of several industrial activities such as rinse improvement, label detaching, increasing the shine of a surface, demulcents for skin, derusters, and salinity dispersants.

Hydroxy acids behave as bi-functional chemicals, depending on the pH. They are relatively inefficient and stoichiometric sequestrants below pH 11. The more the causticity increases (>pH 11), the more they become effective, changing into threshold sequestrants [49]. This is illustrated graphically in Figure 3.22, although it should be noted that the high sequestering power of citric acid indicated on the graph has no practical importance in food cleaning as this acid loses its effectiveness at high temperatures

The stability of the complexes of the hydroxy acids and their efficiency in dispersing heavy metals (aluminium, copper, iron) in caustic media are explained by the involvement of hydroxyl groups in the coordination bonds. Causticity opens up the hydroxyl groups and leads to enolates for complexing (...-CHO⁻-CHO⁻...). The enolate ligand explains the negligible activity close to neutrality and the pronounced threshold effect on heavy metals in caustic solutions [49, 50]. The meaning of 'threshold' has to be related to dispersion and suspension rather than threshold sequestration.

The moles of gluconate and citrate per mole of sequestered Ca²⁺ clearly reveal the bi-functionality (oxalate test at room temperature). Figure 3.23 from Chaberek and Martell [49] shows the sharp change in profile which separates the inefficient stoichiometric behavior from threshold/dispersing behavior.

The hydroxy acids are moderately effective on calcium but excellent on heavy metals. The stability constants are reported for gluconate in Table 3.9 [51].

Calculation of the number of atoms sequestered per molecule proves the ability of the hydroxy acids to complex heavy metals. The data for sodium heptonate are reported in Table 3.10 [52].

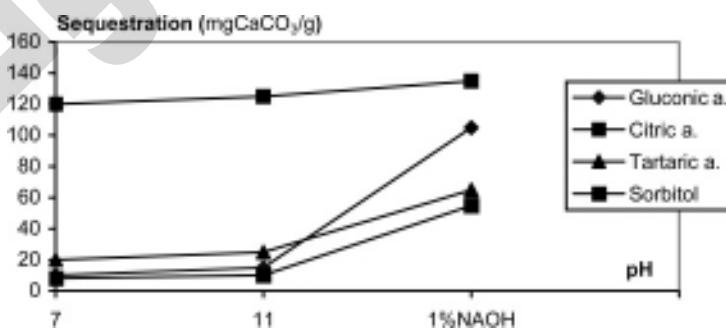


Figure 3.22 Sequestering power of hydroxyacids. Conditions: sequestrant 1 g L⁻¹, 20 mL of 0.2% solution of Na oxalate, titrant CaCl₂ 0.2 M, 20°C.

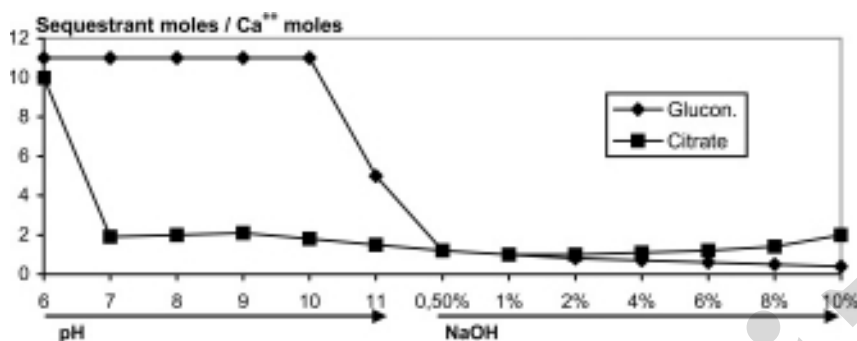


Figure 3.23 Change in efficacy as a function of alkalinity.

Table 3.9 Courtesy of Akzo-Nobel [51].

Metal ion	pH	Stability constant
Ca and Mg	>1.5% NaOH	1.21–2.16
Cu	>8.3	38.9
Fe ²⁺	>8.3	1.0
Fe ³⁺	>8.3	37.2
Zn	>8.3	1.8
Ni	5	25.2

Table 3.10 Courtesy of Bowmans Chemicals [52].

Metal ion	pH 7	pH 10	1% NaOH	5% NaOH
Al	1.5	1.5	Soluble	Soluble
Ca	0.015	0.02	0.02	1.1
Mg	—	0.6	1.5	0.6
Mn	—	0.3	1.0	—
Fe ²⁺	1.0	1.0	3.7	—
Fe ³⁺	3.0	3.0	14.5	15.0
Cu	1.2	2.0	6.0	6.0
Zn	0.2	0.2	Soluble	Soluble

Gluconate is often added to chlorinated products just to control unwanted traces of heavy metals (usually iron) and prevent a rapid loss of chlorine. As decrease in alkalinity leads to rapid loss in sequestering capacity of hydroxy acids, these cannot be profitably applied in neutral systems (<pH 11). For instance, caustic solutions from a bottlewasher contain gluconate, which passes to the rinse by carry-over. The mild alkalinity in the rinse weakens the strength of the gluconate,

which releases metals (e.g., Al) from the complexed state, free again to deposit as scale. Thus, it is always recommended to boost gluconate with threshold sequestrants.

Polyhydroxycarboxylic acids are included in acidic detergents and descalers claimed to be eco-friendly. The real meaning of this term comes down to detergents low in or free of nitrogen and phosphorus. Hydroxy acids only just comply with this concept of eco-compatibility.

The mildness of these chemicals is more noticeable even than that of phosphoric acid, which is considered the eco-friendliest mineral acid. In Table 3.11, corrosion rates on iron exposed to organic and phosphoric acids are compared [53].

The molecular structures in Figure 3.24 are assigned to the gluconate group.

Borogluconate consists of two molecules of gluconate connected through boron. Boroheptonate is a mixture of heptonate and organo-compound bound up with boron. In terms of detergency, the equilibrium existing between gluconate and gluconolactone in aqueous solution leads one to consider them as a same molecule.

Gluconate and heptonate are quite comparable in their sequestering capacity per molecule. However, the sequestering capacity per gram differs because of their different molecular weights and calcium complex stabilities. The heptonate complex stability quickly decreases with time. Heptonate releases calcium and

Table 3.11 Conditions: 24.19 cm² of metal surface, 1 h, 25 °C.

Acid (0.5%)	Loss (mg)
Phosphoric	281.7
Tartaric	117.6
Citric	89.0
Gluconic	13.8

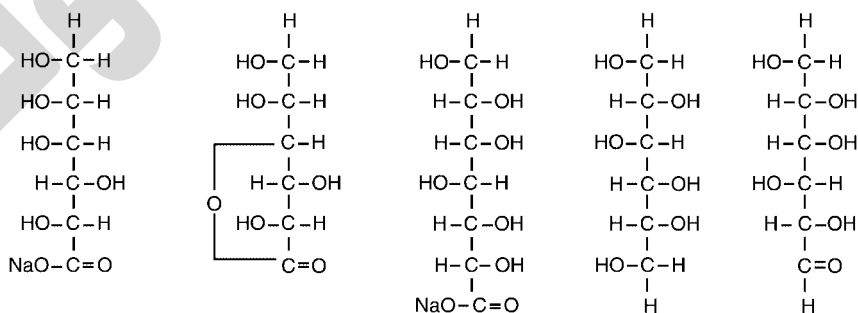


Figure 3.24 Structures of sodium gluconate, gluconone δ-lactone, heptonate (α-isomer), sorbitol, and dextrose [D(+)-glucose].

deposits scale. Amounts of calcium (mg) kept soluble in 1% alkalinity by various amounts of sequestrant are reported in Table 3.12 [54].

Boron reacts with organic matter and forms stable organo-boron [55] compounds. Borogluconate and boroheptonate improve sequestration at lower alkalinity than gluconate and heptonate. However, sequestration deteriorates at high alkalinity, as illustrated in Figure 3.25 [51].

Since the hydroxy acids are used in caustic cleaning, boron compounds are of less interest in the usual conditions of the food detergency. Moreover, sequestration by boroheptonate decreases with time while that by gluconate is unchanged. Serial dilutions in hard water (460 ppm) indicate that boroheptonate is not as effective as gluconate in preventing scale, as demonstrated in Table 3.13.

Table 3.12 Courtesy of Noury & Van der Lande [54].

Time	Gluconate	Heptonate
Just titrated	249	231
3 h after	201	111
3 days after	64	15
7 days after	64	13

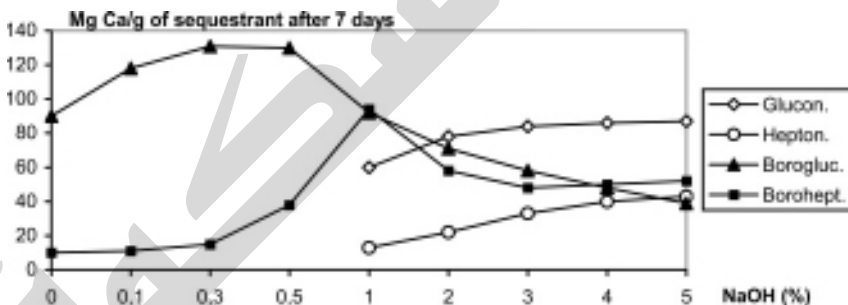


Figure 3.25 Influence of alkalinity on metals control.

Table 3.13 High effectiveness of gluconate in preventing scale.

	Concentration (%)			
	0.5	1.0	2.5	5.0
Bottlewashing formula with gluconate	Scale	Scale	No scale	No scale
Bottlewashing formula with boroheptonate	Scale	Scale	Scale	Scale

Bearing in mind the fact that organo-boron compounds are also more expensive, detergency technologists decided to use gluconate as the predominant hydroxy acid in food cleaning.

Gluconate is stable to alkalinity and temperature (Figure 3.26). Alkalinity up to 50% and 70 °C does not affect its stability [53].

Gluconate increases the rate of dissolution of aluminium foil, prevents or delays the aluminium conversion to hydroxide, and disperses any hydroxide as it is formed [56, 57]. The bottlewashing process shows its effectiveness in detaching paper labels from glass bottles. It is known that the cleaning of the bottle mostly depends on the rapidity of the label detachment. Gluconate and its group considerably reduce the detachment time. For this reason, gluconate is considered the fourth parameter for the proper management of a bottlewasher besides temperature, alkalinity, and time of contact. A comparative test (Figure 3.27) shows the shortening of the removal time.

A test carried out at 50 °C demonstrates a condition in which small positive differences in detaching speeds mean great benefits at the steady conditions in

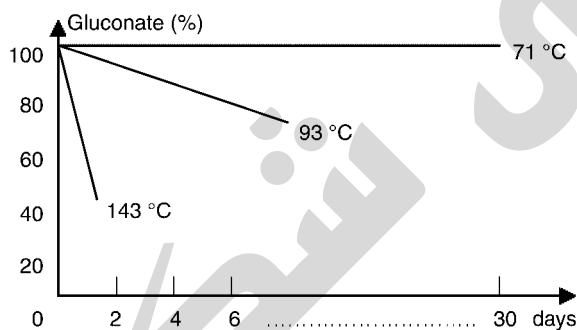


Figure 3.26 Stability of gluconate.

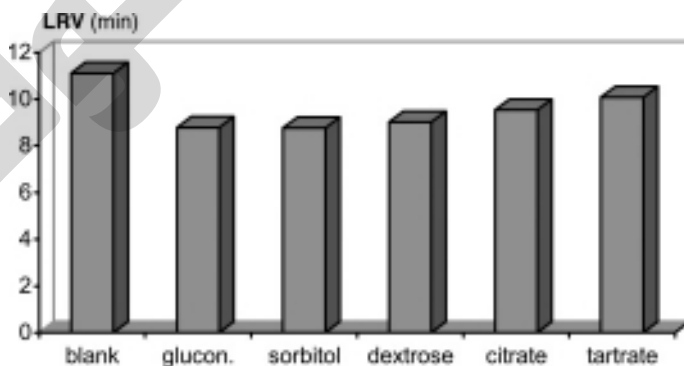


Figure 3.27 Comparative LRV values. Conditions: 50 °C, casein-soybean starch glue, 1% alkalinity, sequestrant 1 g L⁻¹, defoamer 0.3 g L⁻¹. Blank = STP 1 g L⁻¹ and defoamer 0.3 g L⁻¹.

the field. Temperature is the main parameter to attain rapid removal. It has been demonstrated that satisfactory removal of labels and thorough dissolution of glue are impossible below 60°C within the available time (usually <9 min). The efficiency in removing labels at low temperatures depends on the number of washing cycles. Gluconate, for instance, is reduced in effectiveness after roughly 6 cycles at low temperature (below 50°C). By plotting LRV against the number of treatment cycles of the bottles, the trend is shown (Figure 3.28).

Thus, cleaning glass bottles at low temperature (<60°C) is not recommended because of chemical and even microbiological problems (Section 6.2).

The ability of gluconate to emulsify grease is a further interesting property [58]. Unlike cleaning in solvents, degreasing in aqueous system generates repulsion between grease and water because grease is apolar and water polar. The polarity of sodium gluconate allows the grease to stand in between. The carbon chain to which hydrogen and hydroxy groups are linked behaves as an apolar site while the carboxylic group behaves as a polar one. Gluconate is able to neutralize the mutual repulsion like a wetting agent and brings fat and water together. It follows that a solution free of gluconate can have a floating oil layer, while the same solution with gluconate changes the oily layer into an emulsion easy to disperse. Besides this, the affinity to metals interposes gluconate between surface and grease, enhances degreasing, and prevents redeposition of the oily soil [58].

Alkaline foam and gel cleaners utilize gluconate to keep the surface wet longer. Wettability is a basic parameter of cleaning technology in open plants (Chapter 11). The longer the surface stays wet, the more effective is the cleaning.

Summing up, gluconate is one of the most exploited chemicals in food detergency. Bottlewashing, in particular, profits from sequestration, aluminate dispersion, detaching of molds and labels, removal of tartrates, derusting of bottle necks, and prevention of iron hydroxide precipitation.

Sorbitol and Dextrose lack the carboxylic group and cannot be defined as hydroxy acids. Nevertheless, they are discussed here because of their excellent

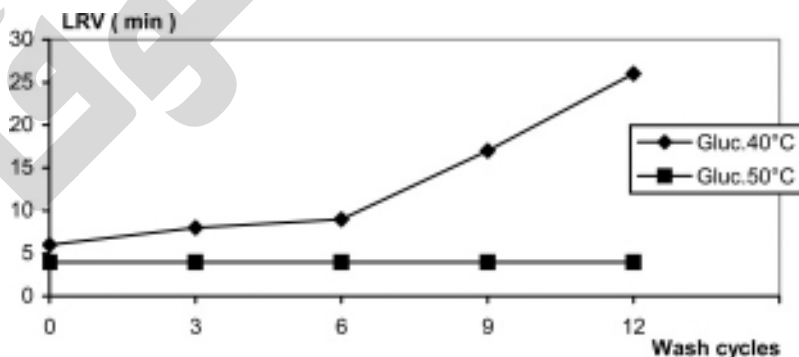


Figure 3.28 LRV values after various numbers of wash cycles. Conditions: alkalinity 1%, gluconate 1 g L⁻¹, defoamer 0.3 g L⁻¹.

label-removing capabilities in bottlewashing. The absence of the carboxylic function actually decreases the strength of the stability constant and lessens the efficacy of the sequestering polyhydroxy structure, primarily its dispersion properties. Sorbitol and dextrose are less effective than gluconate, and are therefore never used as builders in food cleaning. Conversely, their compatibility with skin enables them to be used on farms as sequestrants and emollients (e.g., antimastitis treatment of cow udders).

Citric and Tartaric Acids are discussed together as they behave in similar ways and manifest theoretically comparable applications in food detergency. Their molecular structures are represented in Figure 3.29.

Tartaric acid is at a disadvantage because of its lower sequestering capacity and its high cost. Citric acid was officially proposed as a substitute for STP when restrictions on the use of phosphorus were decided, and it was thoroughly investigated for domestic cleaning. Tartaric and citric acids provide glass surfaces with a brilliant finish, which means improvement in the draining effect, hiding salinity, which changes from a white powder to a dispersed and fairly invisible deposit, and masking typical stains from hard water. This produces shining surfaces in spite of using hard rinse water in sectors such as bottlewashing and tunnel pasteurization of glass bottles, painted jars, and tins.

Apart from the properties described, citrate performs worse than the usual sequestrants (e.g., STP and phosphonates). Its sequestering activity is negatively influenced by temperature. In Table 3.14 [59] and Figure 3.30, citrate and STP are compared.

Although the calcium sequestration seems good at room temperature (20°C), citrate quickly loses its efficacy when the temperature increases [14, 59] (see also Table 3.1). Moreover, it does not improve the label removal, shows negligible dispersing capacity, and has more difficulty in chelating bivalent than trivalent

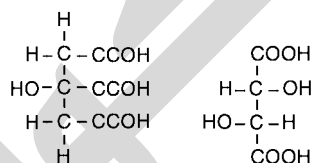


Figure 3.29 Structures of citric acid and tartaric acid.

Table 3.14 Courtesy of Houston [59].

Property	Sodium citrate	STP
Solubility	Good	Fair
Sequestration	Fair	Good
Peptization	Poor	Good
Buffer	Fair	Good
Detergency	Fair	Good
Lime soap dispersion	Fair	Good

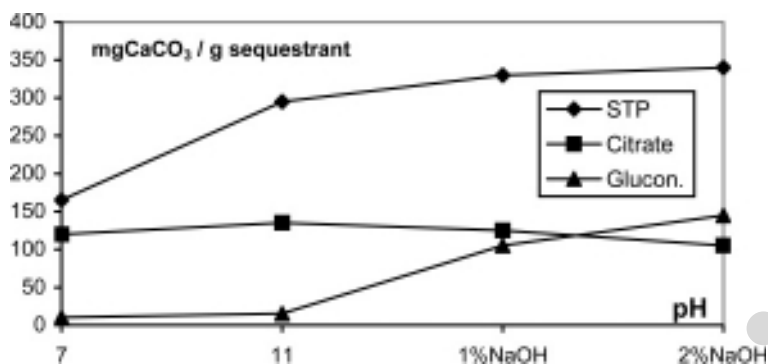


Figure 3.30 Sequestering power. Conditions: sequestrant 1 g L⁻¹, 20 mL L⁻¹ of 0.2% Na oxalate Ca added as CaCl₂ 0.2 M, 20°C.

ions [60]. As the bivalent alkaline-earth cations are very important in food detergency, citric acid is targeted toward marginal applications such as pH buffering, as an inhibitor of aluminium darkening in acid soaking technology (phosphoric acid), and to improve draining and shiny surfaces.

Hydroxyacetic Acid is the first member of the alpha-hydroxy carboxylic acids series, and is also known as glycolic acid: HOCH₂-COOH.

Glycolic acid is widely used

- combined with mineral acids (e.g., phosphoric) to enhance cleaning of organic soil
- combined with organic acids (e.g., citric and oxalic) to descale (i.e. remove iron oxide) without corroding [61]
- combined with citric, lactic and sulfamic acid to form eco-friendly acidic detergents and descalers (N and P free acid).

Hydroxyacetic acid is claimed to be one of the best acids for removing proteins (casein in particular) [7], being second only to phosphoric acid. Its ability to clean off the ring of beer soil in fermenting tanks is an example. However, its effectiveness as a sequestrant is considered to be as good. Glycolic acid involves both the hydroxy and carboxylic groups and forms five-membered ring complexes with polyvalent metals. Its complexing capacity is useful to prevent metal hydroxides from insolubilizing in acidic solutions and metal ions from redepositing during the rinse [61]. When an acidic solution containing metal ions (e.g., iron and copper) is titrated with sodium hydroxide, the hydroxide formation shifts to a higher pH in the presence of hydroxyacetic acid. This shift suggests a sequestering activity even in acidic conditions, as Table 3.15 indicates [62].

The solubility (sequestration) of calcium and magnesium glycolate increases with temperature. For instance, as the temperature changes from 18 to 60°C the solubility of calcium glycolate changes from 1.2% to 3.9%, and that of magnesium glycolate from 7.9% to 12.1% [61]. The improved cleaning capacity of glycolic acid compared to other organic acids is ascribed to the hydroxy group inside a small

Table 3.15 Condition: 10 moles acid / mole of salt, room temperature. Courtesy of Dupont Co. [62].

Salt solution	pH range of metal hydroxide precipitation	
	Without hydroxyacetic acid	In the presence of hydroxyacetic acid
CuCl ₂	5–5.5	7–9
FeSO ₄	4–6	7–8
FeCl ₃	3	10–11
MnSO ₄	5–6	9–11
CaCl ₂	7–8	9–9.5
MgCl ₂	9–10	10–11
AlCl ₃	6–7	9–10

molecule (low steric hindrance). Carboxylic and hydroxy groups in a small structure develop sequestering ability (keeping soluble what is already in solution) and carrier function (loosening soils by stripping out metals).

Besides being a sequestrant, glycolic acid provides biocidal activity. Sectors where glycolic acid is approved in the European Biocide Products Directive (BPD) are

- **PT2:** private and public health area disinfectants
- **PT3:** veterinary hygiene biocidal products
- **PT4:** food and feed area disinfectants.

The DuPont company has reviewed the anti-microbial activity of glycolic acid, comparing some commonly used acids in Table 3.16 [63].

Use of the term ‘disinfectant’ requires a minimum of 99.99% kill. The concentration differs according to the strain resistance.

Glycolic acid undergoes typical reactions of oxidation and reduction [61]:

- Sulfuric acid and zinc reduce glycolic acid to acetic acid.
- Hydrogen peroxide and ferrous ions convert glycolic to glyoxylic acid.
- Hydrogen peroxide and ferric ions convert glycolic to oxalic acid.

As hydrogen peroxide is frequently used to enhance the cleaning strength of a detergent, particular care should be taken if glycolic acid is present in sanitizing redox solutions (see preceding paragraph).

3.4.4

Poly(co-poly)acrylates

Poly(co-poly)acrylates constitute a very complex group of sequestrants. They derive from a huge number of molecules based on a nominal polymer not corresponding to a single molecule but rather to a mixture following the Poisson distribution. The peak is assigned to the molecular weight which distinguishes

Table 3.16 Anti-microbial activity of some acids.

Organism	Glycolic		Citric		Phosphoric		Lactic		Gluconic		Salicylic	
	%	% kill	%	% kill	%	% kill	%	% kill	%	% kill	%	% kill
<i>E. coli</i>	1.0	>99.9999	5.0	Neglig.	5.0	99.999	1.0	>99.9999	5.0	40	0.2	99.9999
<i>E. coli</i> 0157:H7	5.0	99.999	5.0	Neglig.	5.0	Negligible	5.0	99.99	5.0	40	0.2	99.999
<i>Staphylococcus aureus</i>	5.0	99.99	5.0	80	5.0	99.999	5.0	99	5.0	90	0.2	>99.9999
<i>Salmonella typhimurium</i>	5.0	>99.9999	5.0	80	5.0	>99.9999	5.0	>99.999	5.0	40	0.2	99.999
<i>Listeria weishimeri</i>	5.0	>99.9999	5.0	50	5.0	99.9	5.0	>99.9999	5.0	25	0.1	>99.9999
<i>Pseudomonas aeruginosa</i>	1.0	>99.9999	5.0	99.99	1.0	>99.9999	2.0	>99.9999	5.0	99.6	0.1	>99.9999
	pH = 1.8–2.7		pH = 1.8–2.2		pH = 1.2–2.1		pH = 2.0–2.9				pH = 2.3–3.3	

the chemical. Thus, variations in the synthesis mean that a consistent composition is unlikely to be obtained from one manufacturer to another or even from different batches of the same manufacturer. The number of compounds depends on hundreds of homo- and co-polymers steadily rising in molecular weight. Homopolymers repeats the basic structural unit while copolymers combine acrylic with monomers such as vinyl, maleic, and allyl. Examples of the impressive potential of this group are listed in Figure 3.31.

Looking at the sequestering power (see Sections 3.1 and 3.3 and Figure 3.32), no significant differences stand out with regard to the efficacy in binding calcium as a function of the molar mass. However, the molar mass of the polymer influences the way deposition is prevented. There is an optimum molar mass for every application although these molar masses apparently give the same values of calcium-binding efficiency. The explanation seems to lie in the tertiary structure of polymers and their folding [17]. It is, therefore, quite difficult to draw any conclu-

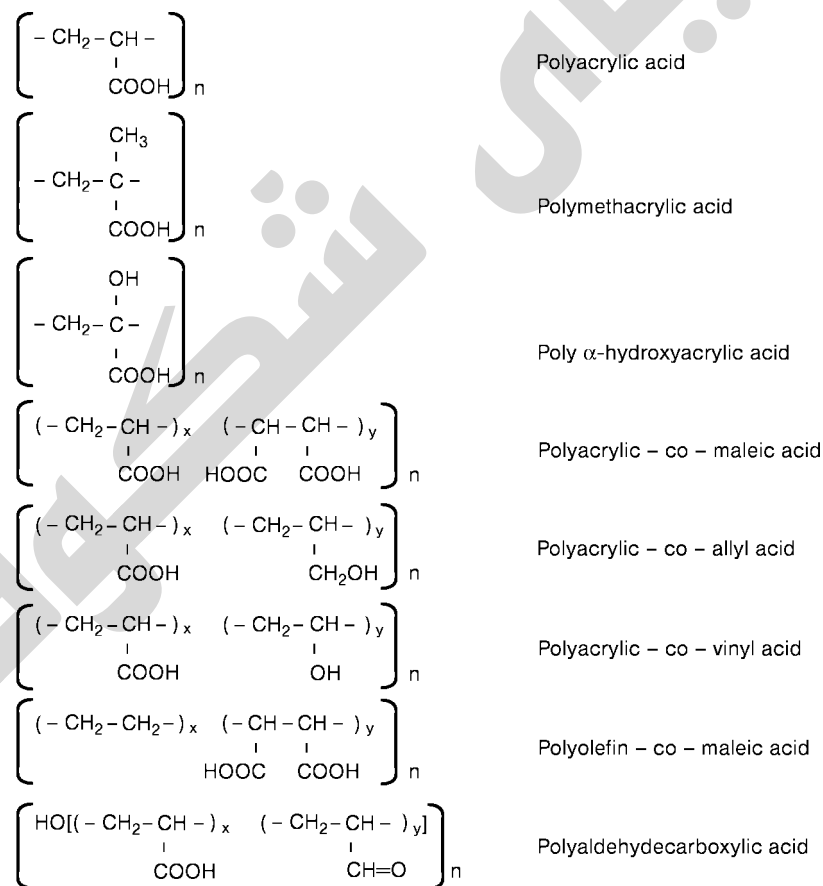


Figure 3.31 Possible combinations in the (co)polyacrylates group.

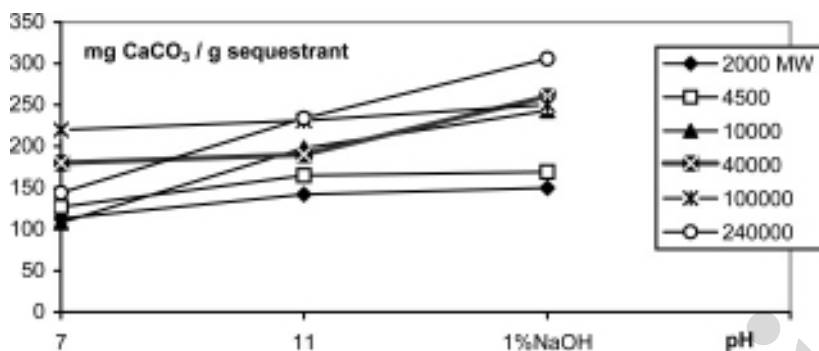


Figure 3.32 Sequestering power and molecular mass. Conditions: homopolyacrylates 1 g L⁻¹, 20 mL L⁻¹ of 0.2% Na oxalate, Ca added as CaCl₂ 0.2 M, 20 °C, homopolymers reported to 45% of active matter.

sion starting from the only theoretical measure of sequestration, namely the oxalate test. Many factors affect processes and applications: hardness, dispersion of contamination, the use of recovered or virgin cleaning solutions, as well as synergisms from blending polymers having different molecular weights. The best applications come from laboratory tests and field trials capable of identifying those properties suited to the particular purpose.

Water treatment (neutrality) and detergents application (causticity) produce remarkable differences in efficiency among the molar masses of polymers. The low-molecular weights exhibit higher sequestering power, while dispersion and suspension are associated with higher molecular weights. Thus, the former group suits neutrality and mild alkalinity, the latter the caustic solutions (detergents) where dispersion and suspension become more crucial in preventing deposition than simple sequestration.

Figure 3.32 does not reveal significant differences among the polymers. This relatively flat result is expected from the turbidimetric test (oxalate), which measures the immediate sequestration without supplying information on dispersion and suspension. However, detergency aims at attaining surfaces free of deposits rather than keeping calcium soluble. When they undergo the suspension test (Figure 3.33), polymers reveal differences in behavior.

With rising pH, the differences become more noticeable. Polyacrylates adsorb onto negatively charged surfaces unless charges are so large that the electrostatic repulsion dominates the weaker molecular force [17]. Hydroxyl ions (causticity) develop stronger bonds, are preferentially adsorbed, displace the polymer, and cause loss in suspension. However, the calcium suspension is enhanced as a function of the increase in molar mass. This tendency becomes increasingly indistinct above a molecular weight of 4500. It follows that the suspending effect enhances the information on the behavior of the polyacrylates, but still remains insufficient to determine an effective ability to prevent deposition. The prevention of the adhesion of scale basically depends on the dispersing capacity of the

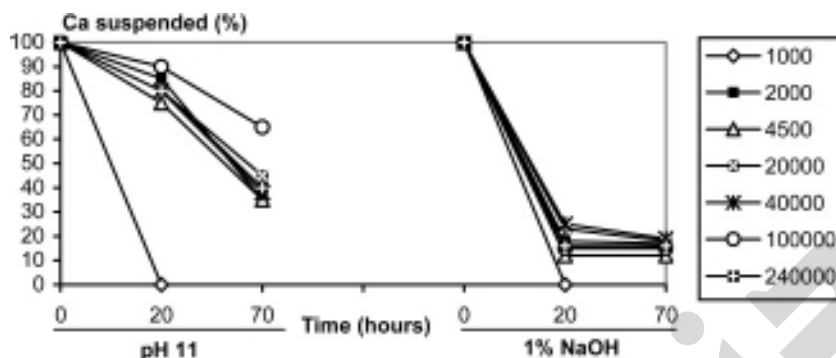


Figure 3.33 Suspension properties of various polymers. Conditions: homopolyacrylates 1 g L⁻¹, 160 mL L⁻¹ of 2% Na oxalate, 20°C, CaCl₂ 100 mL in overstoichiometry (Figure 3.32). Ca titrated with EDTA methodology.

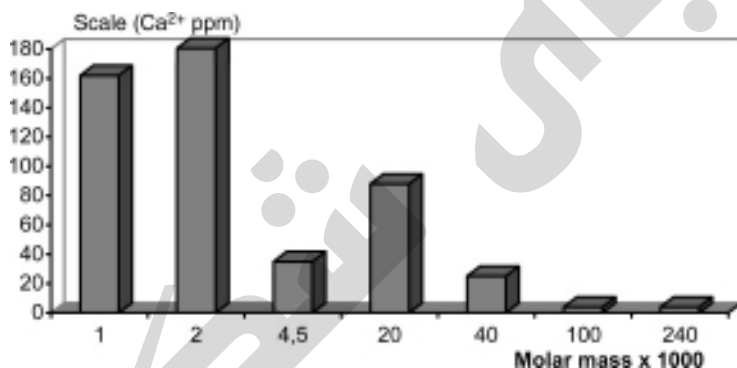


Figure 3.34 Dispersing power of various polymers. Conditions: homopolyacrylates 1 g L⁻¹, 2% sodium oxalate 160 mL L⁻¹, 20°C, 100 mL of CaCl₂ in overstoichiometry, 1% NaOH, 70 h of rest. After rinsing scale is dissolved in HCl 0.1 M and Ca detected with EDTA.

polymer. The investigation of the dispersion gives the result shown in Figure 3.34.

The tendency to prevent deposition continuously increases as a function of the molar mass. It is, however, interesting to point out the significance of the molecular weight of 4500. The investigation results are reported in Table 3.17.

Besides confirming the existence of a critical pH between 11 and 12 (Section 1.1.4), Table 3.17 indicates 4000–5000 as the optimum molar mass. Most of the cleaning processes do not last so long as to need the dispersing power of higher molecular weights. Therefore, it is more useful to identify a few polymers able to give all the efficiency benefits in sequestering, suspending, and dispersing even though these functions are not performed to maximum effect individually. Being also aware that a polymer suitable for every application cannot exist, the conclu-

Table 3.17 Tendency to prevent deposition.

	pH 10				pH 12				1% NaOH			
	ppm				ppm				ppm			
	100	200	300	400	100	200	300	400	100	200	300	400
1000*	—	—	—	—	—	—	—	—	—	—	—	—
2000*	—	—	++	+++	—	—	—	—	—	++	+++	+++
4500*	—	+	+++	+++	—	—	—	—	+++	+++	+++	+++
40000*	—	—	+++	+++	—	—	—	—	—	++	+++	+++
70000*	—	—	+	+++	—	—	—	—	—	+	+++	+++
240000*	—	—	—	—	—	—	—	—	—	—	+++	+++
4000**	—	—	+	+++	—	—	—	—	++	+++	+++	+++
70000***	—	—	—	—	—	—	—	—	—	—	++	+++

Rating: — insufficient; + sufficient; ++ good; +++ excellent hardness control.

Conditions: 40 dF, 60°C, 20 h static soak, glass slides, sequestrants adjusted to 40% active matter.

Sequestrant: *polyacrylate; **modified polyacrylate; ***acrylic-maleic copolymer [4500* is Acusol 445 (Rohm and Haas trademark), 4000** is Sokalan CP10 (BASF trademark)].

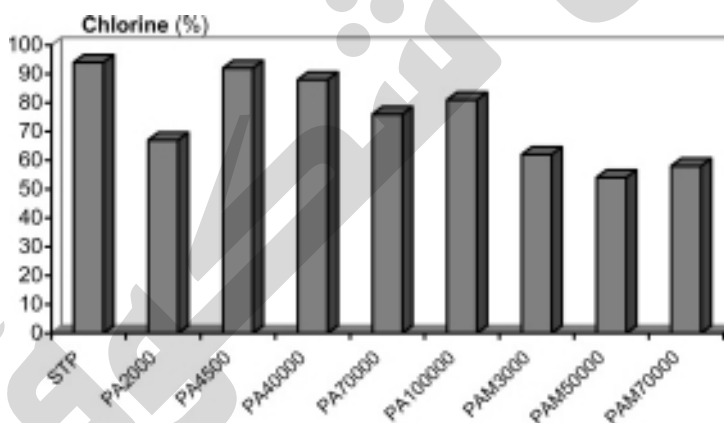


Figure 3.35 Stability to chlorine. Conditions: 10% NaOH + 3% chlorine + 2% sequestrant + soft water, 30°C, 1 month. PA = acrylic homopolymer. PAM = acrylic-maleic copolymer.

sion from Table 3.17 is preferably used for alkaline cleaning in the food sector. Thus, the polymers of MW 4500° fulfil most requirements and answer the purpose. Adding the fact that the homopolymer of MW 4500° provides chlorine with excellent stability (Figure 3.35), this acrylic homopolymer currently is the reference standard in food detergency.

The loss in chlorine depends on the unreacted material rather than the molecular structure of homopolymers. Conversely, the maleic structure is directly responsible for the loss. Thus, generally speaking and according to the whole investigation, homopolymers are preferred, although they partially lose efficiency in inhibiting scale compared to acrylic-maleic polymers [5]. Figure 3.36 shows the measurement of turbidity, which is directly proportional to scale formation.

The restrictions of phosphorus and the stability of chlorinated detergents have prompted a search for an alternative technology as effective as tripolyphosphate. Blends of homopolyacrylates (4500MW) and phosphonate (PBTC) match the performance of STP, cover most STP-chlorine cleaning requirements, and prove to be a good replacement stable in every circumstance.

Sequestering additives for bottlewashers need a low phosphorus content to ensure that they are being thoroughly rinsed off in the case of very hard water. The high concentration requested to control high hardness sometimes causes traces of phosphorus (phosphonate) to be detected in bottles. Low-phosphorus and phosphorus-free chemicals contribute to solving the problem. Polyacrylate (PA), modified polyacrylate (mPA), polymaleate (PM), phosphono-polyacrylate (PPA), and phosphono-polymaleate (PPAM) are polymers potentially suitable to replace phosphonates. However, acrylic and maleic compounds alone do not provide a satisfactorily cost-effectiveness treatment. They still need a small amount of phosphonate to give adequate hardness control and reasonable cost-in-use. As this small amount of phosphonic group is already present in phosphonopolyacrylates and phosphonopolymaleates (PPA and PPAM), such chemicals do not need to be supplemented by anything else. Blends of acrylic polymers, phosphonates, and phosphono acrylates are compared in Tables 3.18–3.21.

PBTC gives the best result but is also the most expensive in application. ATMP combinations with polymers give adequate cost-effectiveness. The differences in

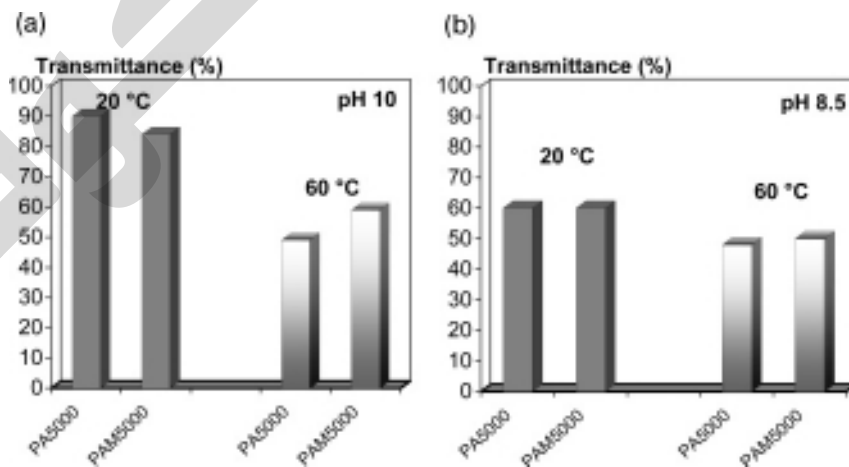


Figure 3.36 (a) and (b) Different values of turbidity mean different tendencies to scaling.

Table 3.18 PBTC and PA4500.

Ratio	Sequestrant (ppm)						
	100	200	300	400	500	600	700
0:100	—	—	—	—	—	—	—
10:90	—	—	—	—	+	++	++
30:70	—	—	—	++	+++	+++	+++
50:50	—	—	+	+++	+++	+++	+++
70:30	—	—	++	+++	+++	+++	+++
90:10	—	—	+++	+++	+++	+++	+++
100:0	—	—	+++	+++	+++	+++	+++

Table 3.19 ATMP and PA4500.

Ratio	Sequestrant (ppm)			
	400	500	600	700
0:100	—	—	—	—
10:90	—	—	+	+
30:70	—	—	++	+++
50:50	—	++	+++	+++
70:30	—	+++	+++	+++
90:10	++	+++	+++	+++
100:0	+++	+++	+++	+++

Table 3.20 ATMP and mPA4000.

Ratio	Sequestrant (ppm)			
	400	500	600	700
0:100	—	—	—	—
10:90	—	—	—	—
30:70	—	—	++	+++
50:50	—	++	+++	+++
70:30	—	+++	+++	+++
90:10	++	+++	+++	+++
100:0	+++	+++	+++	+++

Table 3.21 ATMP and PM < 1000.

Ratio	Sequestrant (ppm)			
	400	500	600	700
ATMP: PM < 1000				
0:100	–	+	++	++
10:90	–	+	+++	+++
30:70	+++	+++	+++	+++
50:50	+++	+++	+++	+++
70:30	+++	+++	+++	+++
90:10	+++	+++	+++	+++
100:0	+++	+++	+++	+++

Tables assessment:

Rating: – insufficient; + sufficient; ++ good; +++ excellent hardness control.

Conditions: hardness 40dF, pH 12, 70°C, 16 h of soak, glass slides.

Ratio: reported to 40% of active matter.

Table 3.22 Phosphonates and polymers at pH 8.

pH 8	Sequestrant (ppm)						
	100	150	200	250	300	350	400
Chemicals (40% active)							
PBTC	–	+	+++	+++	+++	+++	+++
HEDP	+	++	++	+++	+++	+++	+++
ATMP	–	–	–	–	–	–	–
PPA	–	–	–	–	+	+	++
PPAM	–	–	+	+	++	++	++
PA 4500 MW	–	–	–	–	–	–	–
PM	–	–	–	–	–	–	–

performance are even clearer when the chemicals are individually investigated (Tables 3.22–3.24).

From the above results, the polymers have been placed in order of activity for alkaline applications in the food industry:

PBTC-polymers > ATMP-polymers > PPA ≈ PPAM > PM > PA ≥ mPA

When two effective technologies are established, choice is decided by the cost-in-use. Phosphonopolymers (PPA and PPAM) are equivalent to the ATMP-polymers in use. Moreover, they notably improve the control of scaling and even the stability to chlorine compared to their equivalent homopolymers. PPA can therefore replace PBTC in chlorinated detergents.

Figure 3.37 shows sequestration and suspending power for PA, PM, PPA and PPAM.

Table 3.23 Phosphonates and polymers at pH 12.

pH 12	Sequestrant (ppm)						
	100	200	300	400	500	600	700
Chemicals (40% active)							
PBTC	—	—	++	+++	+++	+++	+++
HEDP	—	—	—	—	++	+++	+++
ATMP	—	—	++	+++	+++	+++	+++
PPA	—	—	—	+	+++	+++	+++
PPAM	—	—	—	+	+++	+++	+++
PA 4500	—	—	—	—	—	+	+
PM	—	—	—	—	+	++	++

Table 3.24 Phosphonates and polymers at 1% NaOH.

1% NaOH	Sequestrant (ppm)						
	100	200	300	400	500	600	700
Chemicals (40% active)							
PBTC	+++	+++	+++	+++	+++	+++	+++
HEDP	—	++	++	++	++	++	++
ATMP	+++	+++	+++	+++	+++	+++	+++
PPA	—	++	+++	+++	+++	+++	+++
PPAM	—	++	+++	+++	+++	+++	+++
PA 4500	—	+	++	+++	+++	++	+
PM	—	++	++	++	+++	+++	+++

PA 4500 = Acusol 445 (Rohm and Haas Co.) 4500 molecular weight
 mPA 4000 = Sokalan CP10 (BASF Co.) 4000 molecular weight
 PPA = Acusol 420 (Rohm and Haas Co.) 2000 molecular weight
 PM < 1000 = Belclene 200 (Ciba-Geigy Co.) <1000 molecular weight
 ATMP = Dequest 2000 (Monsanto Co.)
 PBTC = Bayhibit (Bayer Co.)
 PPAM = Acusol 425 (Rohm and Haas Co.) 2000 molecular weight

As previously observed, it is quite difficult to detect significant differences in preventing deposition purely from sequestration and suspension. Dispersion tests supply the real differences in activity among chemicals. Integrating the graph of the dispersing efficacy of homopolymers (Figure 3.34) with PPA and PPAM, the comparison is shown in Figure 3.38.

Phosphonoacrylates confirm the improvement in scale prevention in comparison with the low-molecular-weight acrylic homopolymers (PA) and copolymers (mPA).

When the control of deposition is investigated with reference to the aluminum chemistry in the alkaline condition (e.g., aluminate precipitation in bottl

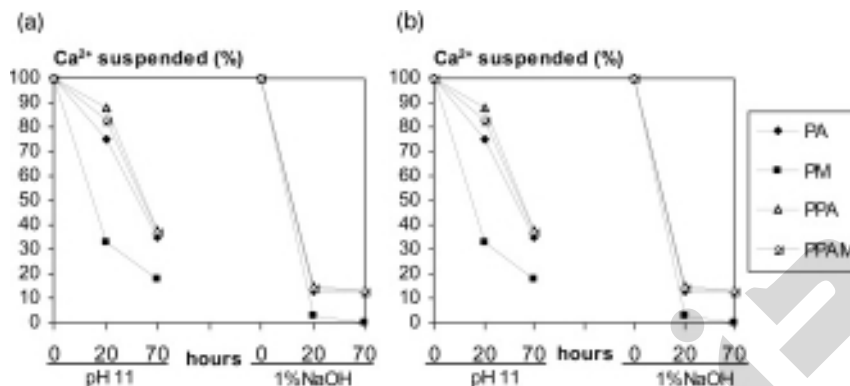


Figure 3.37 Sequestration and suspending power. (a) Conditions: polymer 1 g L^{-1} , 0.2% Na oxalate 20 mL L^{-1} , Ca added as CaCl_2 0.2 M , 20°C , polymers reported to 45% of

active matter. (b) Conditions: polymer 1 g L^{-1} , 2% sodium oxalate 160 mL L^{-1} , 0.2 M CaCl_2 100 mL of overstoichiometry, 20°C Ca titrated with EDTA.

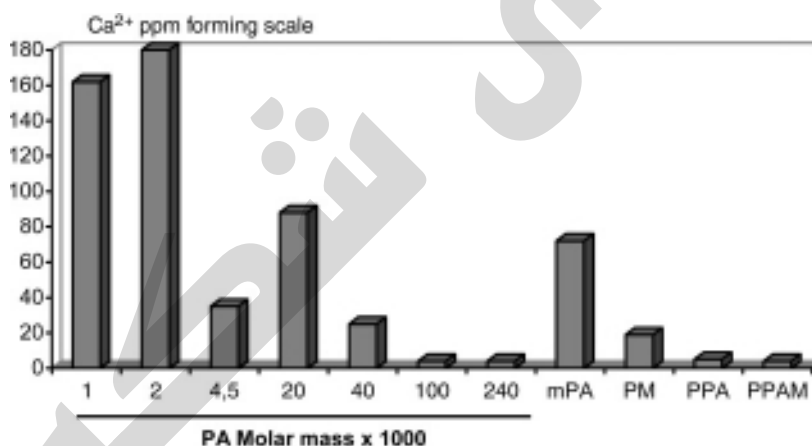


Figure 3.38 Dispersion tests with mPA, PM, PPA, and PPAM. Conditions: polymer 1 g L^{-1} , 160 mL L^{-1} of 2% Na oxalate, 20°C , 100 mL of CaCl_2 in over-stoichiometry, 1% NaOH, 70h of rest. Scale is dissolved in HCl 0.1 M , Ca detected with EDTA.

gluconate remains the only chemical able to stop the conversion of aluminate to a rock-like deposit. Although the pure sequestration power of polymers seems almost comparable to that of gluconate [Figure 3.39 (a)], polymers leave a stony deposit of alumina quantified in Figure 3.39 (b) and illustrated in Figure 3.40.

Thus, phosphono-polymers cannot replace gluconate in preventing aluminate precipitation in caustic solutions.

Phosphinopolycarboxylate (PPC) belongs to this group of chemicals. It is reported to behave both as phosphonate and polyacrylate. PPC has a low content

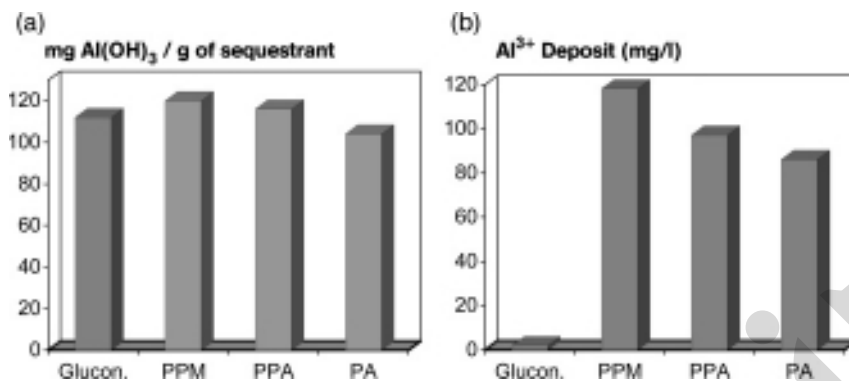


Figure 3.39 Deposition of alumina. Conditions: sequestrant 1 g L^{-1} , 20 mL L^{-1} of sodium oxalate 2%, 20°C , 1% NaOH, Al added as Al sulfate. Polymers reported to

45% of active matter 10% of Al sulfate in overstoichiometry, 70h of rest at 20°C . Deposit solubilized in concentrated HCl.



Figure 3.40 The absence of alumina deposit confirms the efficiency of gluconate.

of phosphorus equal to 0.86% as P [64]. Figure 3.41 compares its sequestering power to that of other chemicals.

PPC is claimed to be effective against calcium sulfate, barium sulfate, and calcium carbonate in water treatment. However, its stability to chlorine historically assigned it to the role of first builder in chlorinated detergents as an alternative to sodium tripolyphosphate. Currently, combinations of phosphonates and polyacrylates provide equivalent and cheap performance. Hence, PPC has become of less interest in food cleaning although its position in the results shown in Figure 3.42 is fairly satisfactory (deposit prevention).

Polyaspartic acid (PASP) is not an acrylic polymer, being a compound with a polypeptide structure, but is discussed here for convenience (Figure 3.43) [65].

It was synthesized as a biodegradable alternative to acrylic homo- and copolymers. Depending on the degree of polymerization, it is possible to synthesize

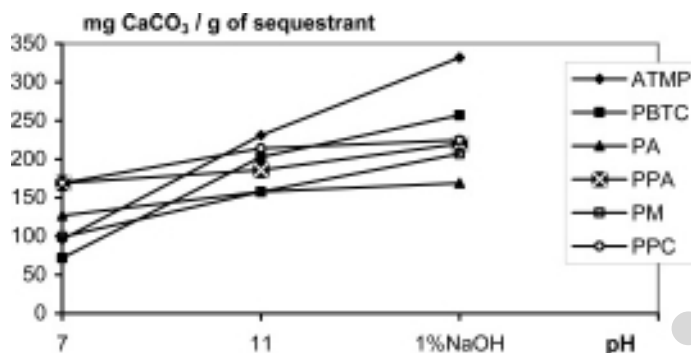


Figure 3.41 Sequestering power of phosphinopolycarboxylate (PPC). Conditions : polymer 1 g L⁻¹, 20 mL L⁻¹ of Na oxalate 0.2%, 20°C Ca added as CaCl₂ 0.2 M,

chemicals reported to 45% of active matter. PPC: phosphinopolycarboxylate [Belsperse® 164 is a Ciba-Geigy Co. trade mark].

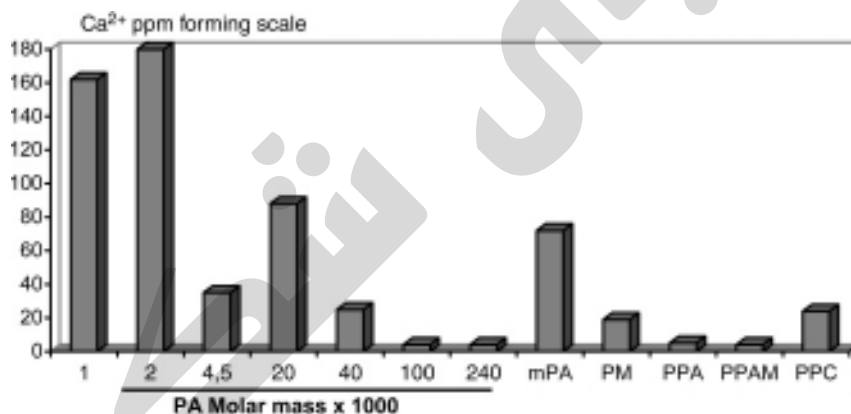


Figure 3.42 PPC efficacy in preventing scale.

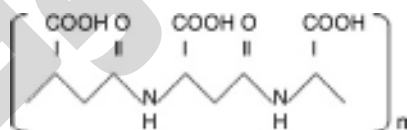


Figure 3.43 Polyaspartic acid (PASP).

polypeptide polymers up to a molecular weight of ~20000 behaving as dispersants, 100 000 as flocculants, and much in excess of this figure as thickeners. The optimum molecular weight to comply with food detergency (steady dispersion) is roughly 18–20000. However, the difficulty in synthesis makes it a critical raw material. The synthesis starting from maleic anhydride produces relatively short molecules (<5000). The reaction based on bio-synthesis gives rise to high manu-

facturing costs. Moreover, bearing in mind the application in the field, nitrogen is sensitive to chlorine, so that PASP becomes unfit for chlorinated detergents. Conversely, toxicological and eco-toxicological data as well as rapidity in biodegradation (above 60% from maleic [65] and even more from biosynthesis) contribute to a sustainable preservation of the environment compared to all the other acrylic (co)polymers. Therefore, environmental issues could change the priority and restore a strategic position to PASP in food detergency.

3.4.5

Aminopolycarboxylic Acids

Soon after the discovery of the chemistry of coordination bonds, roughly at the end of the nineteenth century [66], aminopolycarboxylates were synthesized. Manufacturing on an industrial scale started in the early 1930s in Germany [BASF]. The group immediately assumed world-wide importance.

Aminopolycarboxylates are the most investigated class of sequestrants. A huge literature has been produced on sequestering functionality [7, 29, 49, 67, 68] and toxicological and environmental issues [69–71]. EDTA is the most important of the aminopolycarboxylic sequestrants. It exactly illustrates the term ‘chelation’, proposed by Morgan and Drew [72] for the coordination structure, looking like a crab’s claw, as represented in Figures 3.44 and 3.45.

Aminopolycarboxylates and phosphonates have similar molecular structures in which carboxylic or phosphonic groups are embedded. Aminopolycarboxylates behave quite unlike phosphonates, being free of any threshold activity. However, they compensate for this by forming very strong bonds to metals. Thus, aminopolycarboxylates and phosphonates synergize with each other in food detergency.

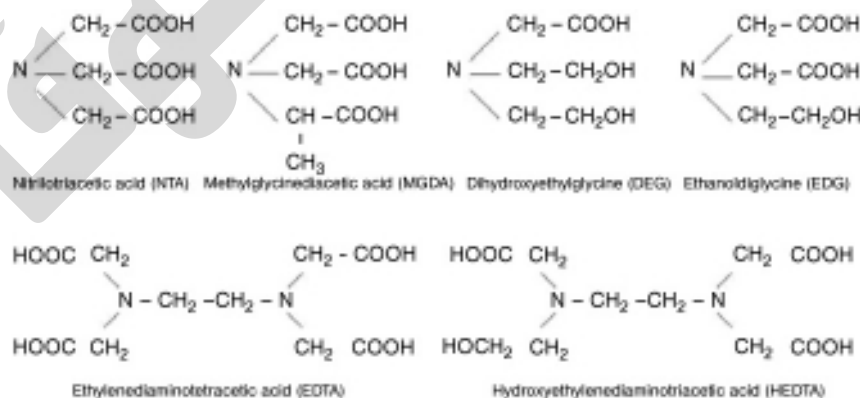


Figure 3.44 Aminopolycarboxylic sequestrants.

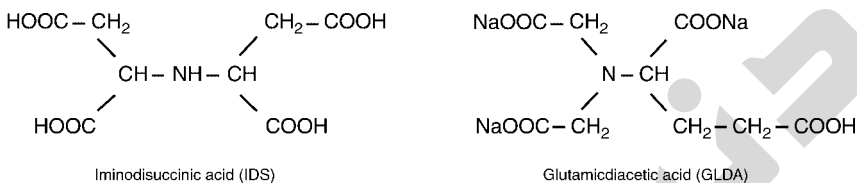
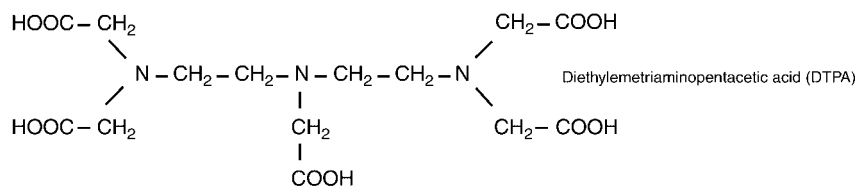


Figure 3.45 Aminopolycarboxylic sequestrants.

Table 3.25 The formation of enolate groups improves the control of the heavy metals.

Chemical	Number of enolate	Sequestration peak (pH)	References
NTA	0	4	[73]
EDG	1	9	[73]
DEG	2	12	[60]
TEA	3	>13	[74]
EDTA	0	5	[73]
HEDTA	1	9	[60]

MGDA, DEG, and EDG are considered to be variations of NTA, while HEDTA derives its structure from EDTA. HEDTA differs in having higher biodegradability and chelating with ferric ions. The addition of the hydroxyethyl group to EDTA orients the molecule for the iron chelation. Chelation to iron and heavy metals improves as a function of rise in pH and formation of enolate groups. The peak of sequestration shows the progression reported in Table 3.25.

The more hydroxyethyl groups the molecule contains, the more this increases the strength of the bond with heavy metals, as TEA confirms [29]. However, hydroxyethyl groups weaken the strength of complexes with the common ions calcium and magnesium. Thus, modifying the original structure means losing efficiency in food detergency. For these reasons, the derivatives are used in applications in sectors governed by restrictive provisions of the law, environmental issues, and less severe labeling. Thus, when doubts arise associated with environmental sustainability and toxicology, manufacturers recommend MGDA, HEDTA, IDS, EDG, and GLDA as acceptable alternatives to NTA and EDTA.

Comparison of the stability constants [73] offers the first assessment of activity (Table 3.26).

Table 3.26 Stability constants at 25°C.

Metal	NTA	EDTA	DTPA	HEDTA	MGDA ^{a)}	IDS ^{b)}
Mg ²⁺	5.5	8.8	9.3	7.0	5.8	6.0
Ca ²⁺	6.4	10.6	10.8	8.2	7.0	6.7
Al ³⁺	11.4	16.5	18.7	14.4		14.1
Pb ²⁺	11.3	17.9	18.7	15.5	12.1	11.0
Cu ²⁺	12.9	18.7	21.4	17.5	13.9	14.3
Zn ²⁺	10.7	16.4	18.3	14.6	10.9	13.0
Cd ²⁺	9.8	16.6	19.0	13.1	10.6	13.5
Hg ²⁺	14.6	21.5	26.4	20.1		7.6
Mn ²⁺	7.5	13.8	15.5	10.8	8.4	7.3
Fe ²⁺	8.3	14.3	16.4	12.2	8.1	8.2
F ³⁺	15.9	25.0	28.0	19.8	16.5	16.1
Co ²⁺	10.4	16.3	19.2	14.5	11.1	10.5
Ni ²⁺	11.5	18.5	20.2	17.1	12.0	12.2

a) Adapted from [75].

b) Adapted from [76, 77].

EDTA and DTPA appear to be the most powerful molecules. In practice, investigation and applied experience lead to the following conclusions:

- MGDA, GLDA and IDS have an effect comparable with that of NTA.
- HEDTA is far from comparable with EDTA. It has an efficiency similar to that of NTA.
- DTPA shows higher stability constants with heavy metals and values comparable with EDTA for calcium and magnesium. As DTPA is significantly more expensive than EDTA, it is only considered for special applications in food cleaning. One of these is its use to enhance the sequestering strength in single-step caustic detergents based on EDTA (cleaning without the acidic step). Here, if the concentration of sodium hydroxide is increased, that of EDTA must be decreased and vice versa, but if high contents of caustic soda and EDTA are required at the same time, DTPA can partially replace EDTA to provide higher sequestration and stability of the detergent.
- IDS (iminodisuccinic acid) is equivalent to NTA as far as the stability constants and field results are concerned. Thus, IDS appears in the Cutler and Davis list [29] of stability constants in an average position (Figure 3.51). It competes for carbonate, oxalate, sulfate, and short-chain fatty acids but does not for >C₁₂ fatty acids and orthophosphate, precipitants responsible for the main problems in the food detergency. The poor competition of IDS for strong precipitants means that it is not preferred for applications in those sectors where they are present (e.g., dairy and meat industries) unless restrictions do not permit the use of EDTA or NTA.

Higher stability constants with heavier metals is an advantage in applications such as stabilization of peroxides (e.g., hydrogen peroxide). IDS, primarily forming complexes with heavy metals, only controls the cations adversely affecting the stability of peroxide and leaves available those helping stability (e.g., magnesium).

Even though EDTA ensures better efficiency and constancy in cleaning, low toxicology and eco-toxicology as well as rapid processes of biodegradation point to IDS as the most environmentally friendly material compared to the other members of the group [77]. It is primarily recommended as a sequestrant suitable to replace NTA in those countries where NTA is not permitted or its use is limited. MGDA and GLDA perform alike. In order to reinforce cleaning in severe applications and approach the EDTA performance, these sequestrants need hydrogen peroxide as a booster.

Aminopolycarboxylates are the most typical example of stoichiometric sequestrants. Stoichiometry means effectiveness only when the covalent and dative bonds exceed the concentration of the multivalent metals in the system. Since the metals concentration is difficult to calculate (part of it comes from process contamination), the use of stoichiometric sequestrants alone might cause unexpected deposits and failure in cleaning. This is prevented by adding threshold sequestrants. Therefore, the use of aminopolycarboxylates should be always planned together with thresholds (phosphonates).

The stoichiometric value of the group is determined through the oxalate test. Figure 3.46 shows the result.

In the current state of the art, EDTA remains the only sequestrant able to compete with long-chain soaps ($>C_{12}$) and orthophosphate for calcium. Figure 3.47 gives further evidence of this. EDTA, HEDTA, and MGDA are in solutions of soap-based lubricant, which is diluted by hard water, after which the turbidity (calcium soap insolubilization) is checked by UV/Vis analyzer.

Absorption means turbidity and turbidity means fatty acids as winners for calcium. The hydrophobic calcium soap clogs pipelines and nozzles. Clogged spray nozzles make the plant lose productivity.

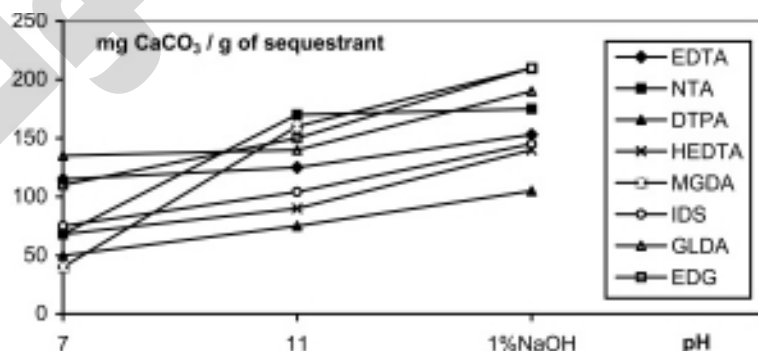


Figure 3.46 Chemicals reported to 40% active matter.

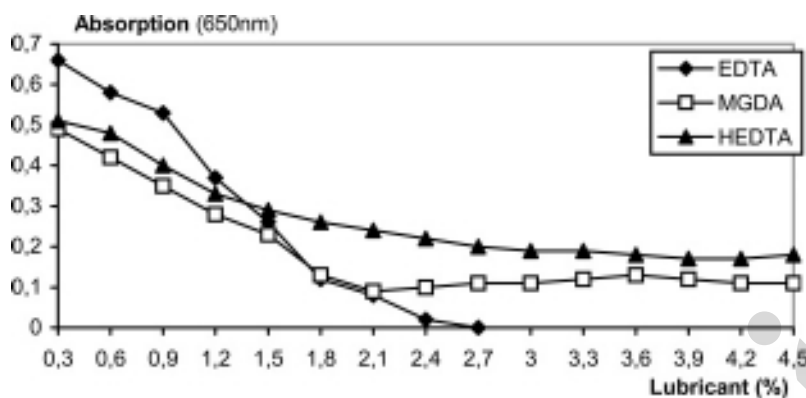


Figure 3.47 Competition by EDTA for calcium. Lubricant: 10% oleic-stearic (60:40) + 5% KOH + 3% sequestrant. + 10% isopropyl alcohol + soft water. Dilutions in hard water 27 dF.

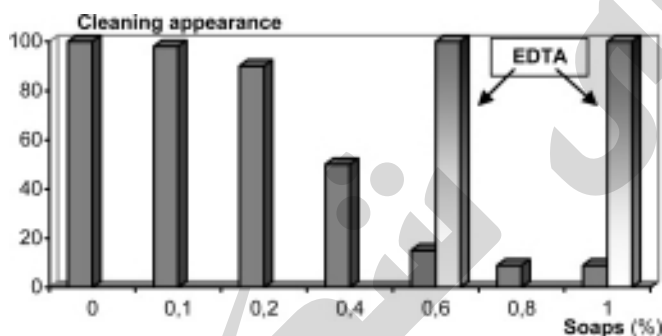


Figure 3.48 PPA+IDS versus EDTA. Cleaning conditions: 60°C, 300rpm. Rating after 20 min.

MGDA does not achieve a completely transparent solution and does not succeed in competing adequately with oleic-stearic fatty acids for calcium. Even though it is possible to reach transparency by still further increasing its concentration (ionic strength competition), the lubricant would nevertheless be rejected as expensive in comparison with the EDTA-based one.

The key to the success of EDTA in food detergency is simply its capacity to compete with strong precipitants. If EDTA is limited or not permitted, the synergism between PPA and IDS has been proposed as well as NTA, MGDA, and GLDA. However, the more the calcium soaps and calcium phosphate increase in the solution, the more the PPA+IDS combination fails, as Figure 3.48 proves.

The contamination used in the test represented in the graph is based on 4% casein dispersed in 40dF hard water to which various percentages of 60:40 oleic:stearic acids are added. The pH is adjusted to 8 with NaOH. The contamination (3 mL) is dried on glass slides for 1 h at 105°C, and 3 slides are then cleaned with 3% of the following detergents:

- a) 16% NaOH + 10% PPA + 5% IDS + defoamer + soft water
- b) 16% NaOH + 12% EDTA + 3% ATMP + defoamer + soft water.

Detergents based on PPA-IDS show loss in cleaning from 0.4% of fatty acids onwards. Detergents based on EDTA perform consistently. This suggests a different mechanism of detergency. EDTA acts directly on the fatty acids and takes calcium away, forming a soluble complex and maintaining an anti-redepositing effect. PPA-IDS does not attack calcium soap, which is only dragged out as insoluble matter inside the casein agglomerates. The latter mechanism evidently accomplishes cleaning only when the concentration of fat is below a critical limit.

Although MGDA does not compete well with soaps for calcium, it provides detergents with interesting properties, being able to disperse calcium fat, prevent its agglomeration and, at the same time, keep foam controlled. Figure 3.49 is a photographic record of this behavior.

Calcium soap agglomerates in the course of the washing process. MGDA disperses the calcium soap, which performs as a defoamer. Thus, the use of MGDA leads to cheaper detergents, non-foaming even at room temperature (detergents free of any antifoam system). However, the detergent based on MGDA cannot be used in a one-step cleaning operation. It needs a further acidic step.

Investigation on the cleaning of calcium phosphate shows a result quite similar to that for fatty acids. The re-solubilization of calcium orthophosphate is thoroughly accomplished by detergents based on EDTA, and cleaning is complete within 10 min, as shown in Figure 3.50.

Competing strength governs sequestrants and precipitants. As Cutler and Davis reported [29], the stability constant of any sequestering agent is such that it is able to dissolve all the precipitated salts that leave a higher concentration of free calcium in solution. IDS, MGDA, GLDA, HEDTA and orthophosphate are included in Cutler and Davis's results Figure 3.51 [29].

The inductive effect of the long hydrocarbon chain on the carboxylic group provides fatty acids with one of the strongest affinities to bivalent metals. The inductive effect is evident in the scale of solubility. The oleic double bond

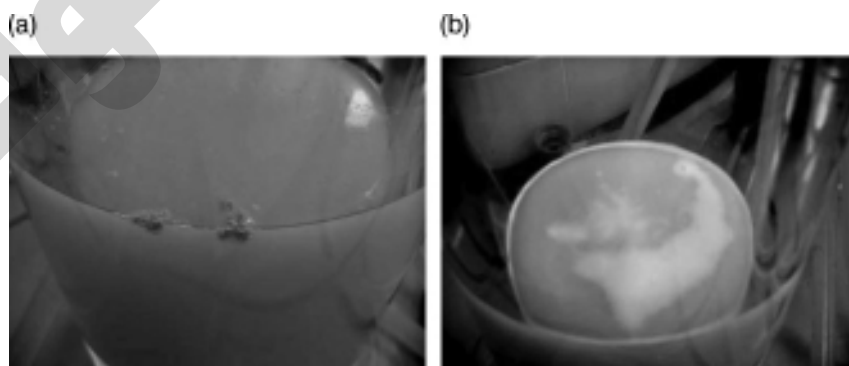


Figure 3.49 Detergent based on NaOH+PBTC (a) and NaOH+MGDA (b).

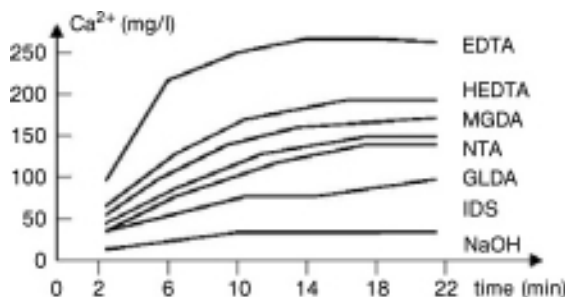


Figure 3.50 Resolubilization of calcium by EDTA. Conditions: calcium phosphate precipitated from trisodium phosphate with calcium chloride. Ca is re-dissolved with 10 g L^{-1} of sequestrant in 0.5% NaOH, 60°C .

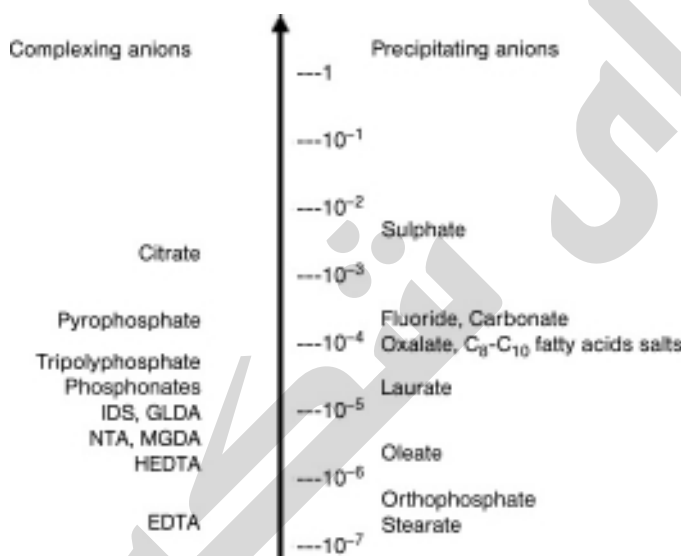


Figure 3.51 Comparative stabilities according to Cutler and Davis [29]. Moles of free calcium per liter are shown on the chart.

interrupts the inductive effect of the chain and positions oleic acid higher than saturated stearic acid (a stronger competitor). Hence, calcium removal from soaps $\geq \text{C}_{12}$ is extremely difficult and feasible only by sequestrants on the same level. EDTA still remains the best. However, to achieve a reduction in environmental contamination with EDTA, a wise choice of detergents can minimize its use. Detergents need EDTA only for specific applications such as soap-based lubrication, milk pasteurizers, the meat industry, sterilizers, and crossflow filtration. Other sequestrants are equally efficient where fatty acids and orthophosphate are negligible.

EDTA and NTA are progenitors of their group and the cheapest members. As has been proved, alteration in their structure gives weaker sequestrants. Tracing detergency back to its origins, it is easy to understand why the use of EDTA and NTA has been ever-increasing. Regional laws are now decisive for their application. However, a very bizarre approach to the environmental impact is evident. In those countries where NTA is permitted, EDTA is usually not, but the opposite can also occur citing the same reasons. In actual fact, NTA proves to have a higher negative impact on health, leading to its re-classification in Europe as a carcinogenic, mutagenic, and reproductive toxicant (CMR). As a consequence, '*limited evidence of a carcinogenic effect*' (R40 risk phrase) is included in safety data sheet when its concentration exceeds 1%. Owing to these restrictions, the search for useful alternatives is still continuing. Although GLDA and MGDA cannot compete with EDTA for preventing calcium deposition in stressed conditions, they are comparable with NTA. Typical applications include de-staining, removal of clay and ambient contamination, and cleaning of floors in processed food plants are operations where GLDA, MGDA, HEDTA, IDS, and sometimes EDG perform satisfactorily. In the current state of the art, only EDTA has no effective alternative in well-defined sectors of food detergency where orthophosphate and long-chain fatty acids occur. Further different tests (Figures 3.52 and 3.53) confirm this conclusion.

Caustic soda precipitates calcium carbonate from hard water and calcium phosphate from milk processes. The acidic step follows the caustic one to remove the deposit left behind. One stage added to the procedure means two more stages of rinse. Milkstone is a typical self-protected contamination. It is so resistant as to need traditionally high concentration of caustic soda (3%), nitric acid (3%), temperature (80°C) and long running time (>30 min). Nitric acid is mandatory, being able to re-solubilize deposits of calcium phosphate. The overall cost of the treatment is high. Therefore, one single alkaline step was investigated. The one-step

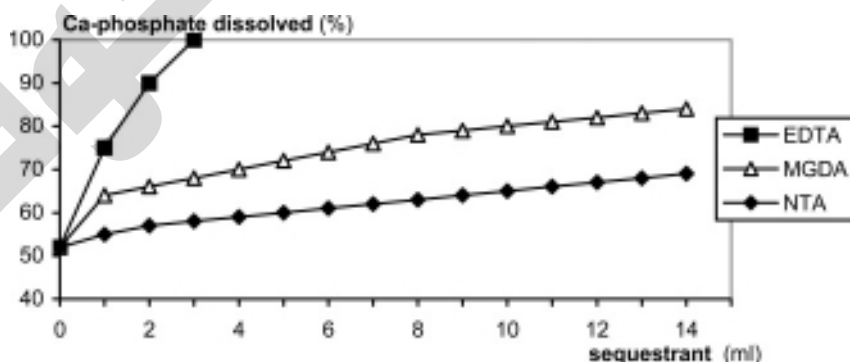


Figure 3.52 Competition for calcium in calcium phosphate by EDTA. Calcium phosphate 0.0005 M, sequestrant 0.05 mol L⁻¹, 60°C, 0.5 mL added every 5 min, evaluation by transmittance (figure adapted from [78]).

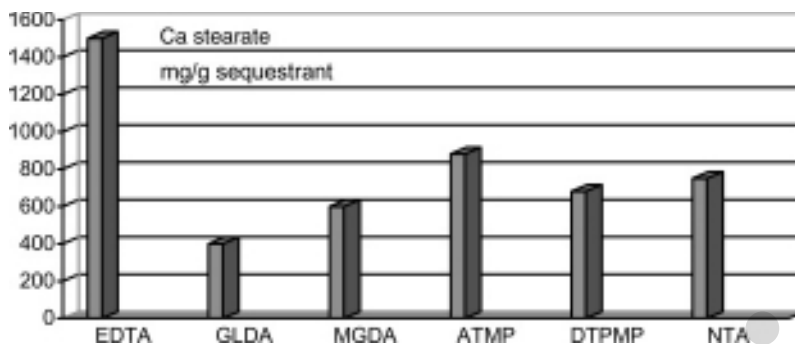


Figure 3.53 Chelation of calcium in calcium stearate by various sequestrants.

(monophase) technology bases its success on the EDTA carrier efficacy in capturing metals from the inside, pulling them out, and enabling an easier attack on the loosened deposit. The technology involves a lower concentration of caustic soda (0.5 instead of 3%) as well as no acidic step. The one-step technology was discovered in the early 1960s [79, 80] but it took more than 20 years to be widely exploited. The increase in productivity and savings in energy and water forced industry to consider alternatives to the crude use of raw materials (nitric and caustic soda). The monophase technology fulfils the promise.

An additional benefit of the one-step technology concerns monitoring the cleaning ability of the equipment without dismantling it. In particular, when free EDTA is still detectable in the exhausted solution at the end of the cleaning, the user is sure that plant is thoroughly clean. Otherwise, the washing needs to be repeated and the procedure revised.

The effect of EDTA on metals points to its potential corrosivity. EDTA and even MGDA, NTA, and stoichiometric sequestrants may cause a specific, non-dangerous type of corrosion in alkaline media at high temperatures called oxide conversion.

The first effect of EDTA is the removal of metal oxides (rust). EDTA, when included in alkaline and neutral derusting products, helps to solubilize spots, rings, and rusted surfaces.

A second corrosive event occurs on weakened stainless steel. Rather than corrosion, it is considered to be a type of preservation different from the natural barrier of chromium oxide. Such preservation stands out as a brown-violet-black layer. The pasteurizer plates in the Figure 3.54 show an example of such surface conversion.

The black layer seems to be so firmly bonded to the surface as to be removable only by hydrofluoric acid or a permanganate redox procedure (permanganate in a caustic step followed by an acidic one). This layer resistant to chemicals resembles the oxides produced by thermal welding. Thermal oxides (e.g., magnetite $[\text{Fe}_3\text{O}_4]$, hematite $[\text{Fe}_2\text{O}_3]$, and wustite $[\text{FeO}]$) are formed at high temperatures in an oxidizing atmosphere together with precipitation of metal carbides at the edge

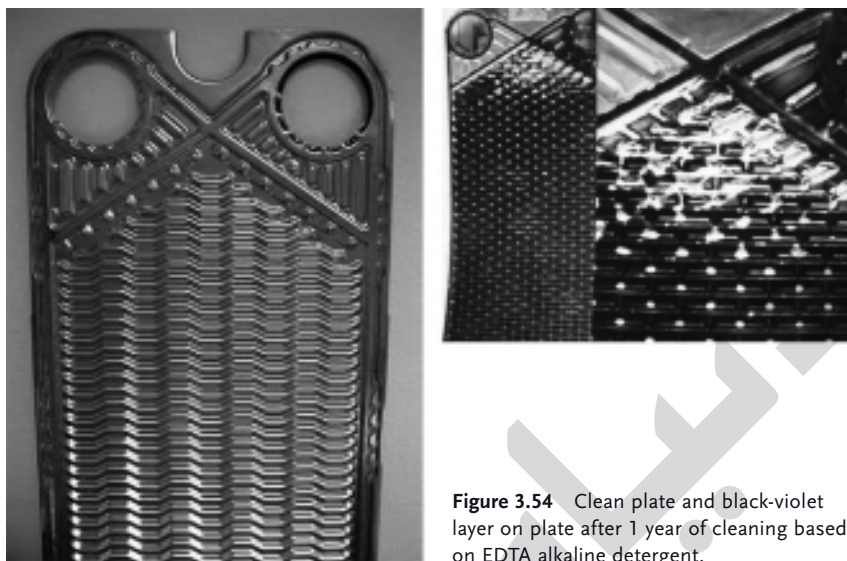


Figure 3.54 Clean plate and black-violet layer on plate after 1 year of cleaning based on EDTA alkaline detergent.

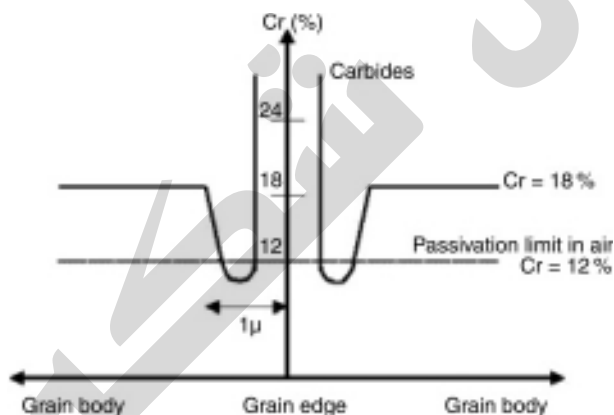


Figure 3.55 12% is the ultimate limit to a consistent passivation in air condition.

of the alloy grains [78, 81]. Precipitation causes chromium to be depleted round the edge and generates a localized de-passivation of stainless steel. The difficulty in remaining passivated makes stainless steel more susceptible to chemical corrosion. Easy corrosion occurs below 12% of chromium, which is the ultimate limit providing consistent passivation in air conditioning, as is clearly visible in Figure 3.55 [82].

The carbon content is recognized as the main factor responsible for carbide precipitation. The presence of carbon in amounts higher than its limit of solubility in the austenitic matrix (accepted limits $C \leq 0.03\%$) causes steel sensitization

[78]. Below 0.03%, for instance, the precipitation of chromium carbide takes more than 100 h at 600°C, while one hour is sufficient in the presence of 0.06%. Investigation of the blackening due to EDTA in an alkaline medium leads to the following conclusions:

- The black-violet layer on stainless steel only increases in the presence of EDTA and aminocarboxylic sequestrants, long contact with caustic solutions, and high temperature (60–90°C). Then, such sequestrants act as promoters of the precipitation of oxides, which starts as a yellow-brownish layer and rises in intensity up to a black-violet shade with time.
- AISI 304 is the most utilized stainless steel for food industrial plants, and therefore the blackening is usually observed on it. Springs made of AISI 302 are frequently affected as well. However, blackening does not always occur when AISI 304 comes into contact with caustic/EDTA. A few cases of blackening are observed, but the occurrence is increasingly correlated to the installation of new plants.

Thus, a specific reason exists and explains the occurrence. X-ray fluorescence analysis and energy dispersion microanalysis (EDX) of the modified surface confirms this scenario. The exposure of the black-violet deposit to X-ray fluorescence and diffraction reveals alloying elements and absence of hot-formed crystal oxides. Magnetite, hematite, and wustite are detected, as shown in Figure 3.56.

The EDX analysis of surfaces with different amounts of darkening shows an increase in carbon and ions such as those of Cl, K, Ca, and Na deriving only from the lightly soiled surface. The typical alloying elements do not change, as shown in the overlapping parts of Figure 3.57.

It is known that cations (M^{n+}), such as iron, precipitate their oxides at high pH. It is also known that the presence of complexing agents acting on M^{n+} can modify the corrosion potential (E). Thus, two metals or compounds may even reverse the

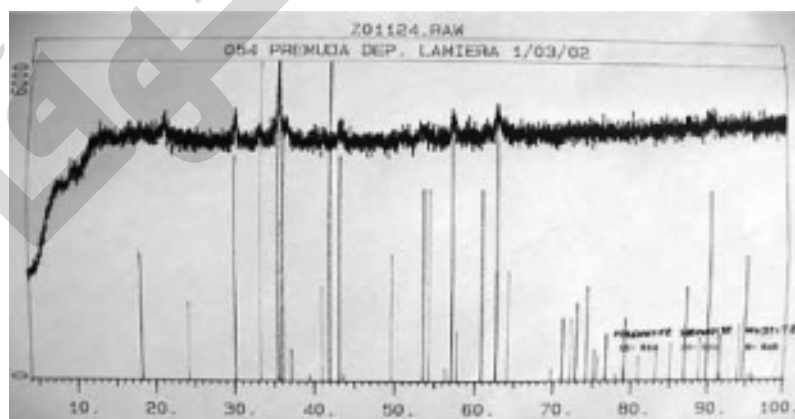


Figure 3.56 X-ray fluorescence.

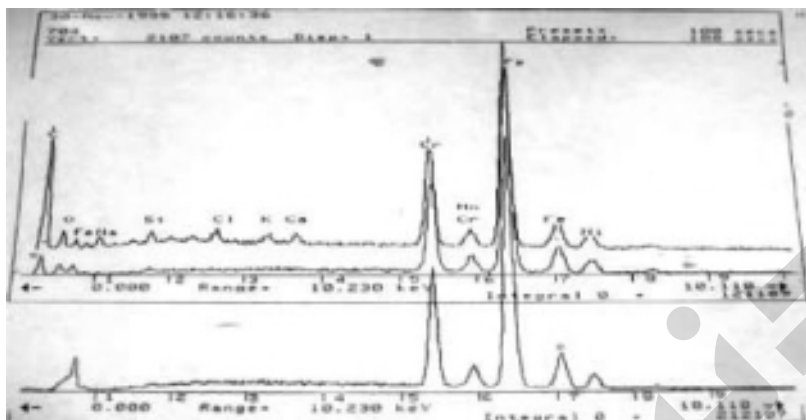
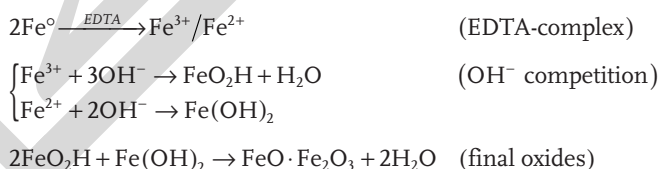


Figure 3.57 Virgin AISI 304 (lower), initial yellow-brownish layer (intermediate) and intense black-violet layer (upper graph).

polarity of dissolution (E_M' and E_M'') as a function of colloidal or crystal deposits, the stability constant of M^{n+} salts, and the stability constant of complexes [78]. Iron is subject to this heterogeneous field of competitions. In hot solution and at $\text{pH} > 11$, EDTA initially dissolves iron as a complexed cation. Subsequently, competition from the hydroxyl ion (OH^-) displaces metal from the complex, and the process ends with the iron precipitated as oxide (e.g., magnetite, hematite, and wustite). Thus, iron oxides are mainly responsible for blackening. The deposit of iron oxides replaces the natural chromium oxide and protects the surface from further corrosion. The reaction is known as surface or oxide conversion:



$\text{FeO} \cdot \text{Fe}_2\text{O}_3$ is the essence of the dark polymeric structure which coats and protects the metal surface. As the event usually occurs on mild steel (high carbon content) and only occasionally on stainless steel in contact with EDTA-alkaline solutions, the investigation attributes the blackening event to sensitization of the stainless steel (e.g., carbon content above the limit, alloy composition deviating from the specification, uncontrolled cooling process). Thus, only some kinds of poor-quality stainless steel undergo the oxidation process due to contact with EDTA and members of this group of sequestrants.

The violet-dark layer is hard, coherent with the surface, and inert to the chemicals commonly used in this field (e.g., nitric and phosphoric acids, alkalis, and sequestrants). It is not released and does not affect the processed food. It follows that there is no need to remove this dark layer. In those cases where improvement



Figure 3.58 Dots and streaks from non-rinsed chlorine.

of the appearance of the surface is desired (mainly for aesthetic reason), the most acceptable procedure is to apply the permanganate redox step in alkaline medium followed by the acidic step. The toxic and highly corrosive hydrofluoric acid is obviously not applicable in food cleaning.

Inadequate rinsing off of chlorine and chlorinated alkaline detergents may cause similar darkening, and the deposit has a dotted and streaky appearance (Figure 3.58). Every dot is a pit from which by-products of corrosion leak and generate dark streaks. Dark by-products differ from the oxide conversion because they can be removed, and the metal surface brilliance can be restored simply by treating the streaks with a strong acid.

3.4.6

Polysaccharides and Bentonites

Long-chain saccharides and aluminosilicates are here referred to as polysaccharides and bentonites. Carrageenans, alginates, xanthans, galactomannans, starches, and cellulose derivatives (e.g., carboxymethyl [ethyl] cellulose) form the polysaccharide group.

The bentonite group includes minerals with 60–80:10–20 ratios between SiO_2 and Al_2O_3 . It also contains traces of other minerals. Bentonite differs from zeolite in its property of swelling as a result of hydrothermal treatments. The lamellar strata able to form a gel in a water suspension [83] are claimed to constitute the structure responsible for absorption. Bentonite, also known as Mineralgel®, with an $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 74.4:12.8, is the main representative compound (Mineralgel® is a Winkelmann Mineraria trademark).

The group is characterized by the ability to keep surfaces clean through a sequestering reaction [84, 85], flocculation, dispersion, absorption, and anti-redeposition. All of these entrap dirt in an irreversible inertization. Dirt takes an active role inside the cleaning solution. It is balanced between surface and detergent [31] and can be expressed in a general equation:



It follows that



According to the general rule of chemical equilibria, a reaction moves toward the side where one of the components is removed. In order to obtain a clean surface it is crucial to remove the dirt as soon as it is separated from the metal surface. The dirt removal is accomplished both by making it inert (no longer able to re-deposit) and keeping it inert until the rinse is completed. The concept is derived from Reitemeier's theory [6] of the inactivation of calcium ions and is also applicable to the entire decontamination process. The simple dispersion and anti-redeposition action through polyphosphate, polyacrylate, and phosphonate is affected by changes in the concentration of the soil, which accumulates in recovered and re-used solutions. Re-use of solutions frequently occurs in the cleaning procedures of the food industry. The solution remains unchanged (partially restored) even for several months. Therefore, in order to attain effective and long-lasting anti-redeposition efficiency, contamination is absorbed inside structures that provide a sort of wrapping and convert it into a material that is inactive and dispersed in solution for an indefinite period of time. When the mechanism is effective, a longer-life solution, constancy of detergent power, cleaner equipment, and fewer disposals are to be expected. Bottlewashing, milk pasteurization, and metal degreasing benefit from this group of chemicals.

Besides remaining efficient in the presence of a considerable concentration of contamination, solutions containing polysaccharides and bentonite produce flocs and mud physically removable by centrifuges, settlers, and filters. The physical removal of inertized dirt makes the solution last for a theoretically infinite time. This way of controlling dirt leads to less maintenance and enhances productivity and environmental sustainability. Deciding when to renew a bottlewasher bath is an example. The replacement of the caustic solution can be carried out when the suspended solids exceed a fixed value pre-established from the history of the bottlewasher (e.g., suspended solid after 2 h in Imhoff cone). In spite of a high volume of mud, this group of conditioners keeps the amount of suspended solids lower than that achieved by traditional detergents, as shown in Figure 3.59.

The addition of high-molecular weight cationic polyacrylamides to the caustic solution gives faster agglomeration and settling of the suspended solids (clarification). Bentonite absorbs dirt and polyacrylamide collects it into heavy agglomerates more easily removable by physical systems such as centrifugation, filtration, and decanting. The cleaning solution, purified and restored, can thus be re-used without limit.

The problem in managing this group is to produce stable liquid products. Polysaccharides and aluminosilicate minerals remain insoluble in any condition and sediment out in traditional liquid systems. These can be handled either as powder detergents or slurries, a slurry being a physical form where liquid and solid coexist. Even though viscosity and thickening partially succeed in preventing

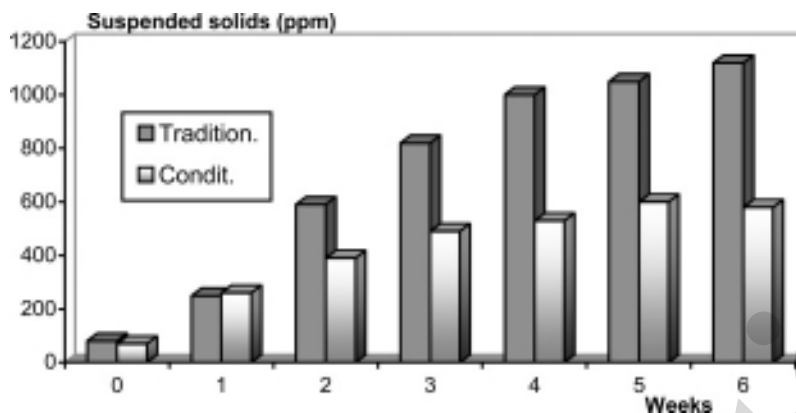


Figure 3.59 Traditional: additive to caustic soda based on gluconate and tripolyphosphate. Conditioned: additive to caustic soda based on gluconate, tripolyphosphate, bentonite (Mineralgel), and carboxymethylcellulose.

the sedimentation of solids, a slurry has only a few months of shelf life. This difficulty in handling therefore does not allow the described technology to be widely applied.

In the absence of an inertizing additive, the same contamination can sometime help the clarification process. Several foods and containers release a contamination structured like the chemicals belonging to this group. Starch and casein are often present in the contamination and can perform as useful conditioners of the system. Glue in bottling (paper labels), casein in dairy, starches and casein from sausages, carrageenans, alginates, and xanthans from thickened and gelled foods, and starches from flour-containing foods are well-known forms of contamination and also examples of synergism between contamination and detergency.

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Part Two

Characterization of Chemicals Used in the Sanitation Process

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4

Laboratory Tests

This chapter describes the main procedures used in the investigations from which most of the data included in this work are derived. Many qualitative and quantitative tests are described in the academic literature and in that supplied by the manufacturers of sequestrants. When investigations are aimed at deriving practical benefits rather than pure theoretical data, the tests must be able to reproduce what happens in the field or be as close as possible to it. The results of this work enable us to minimize risks and, at the same time, optimize the cost-effectiveness of cleaning. Some tests require a hardness standard in order to reproduce and homogeneously compare data. One of the synthetic waters was prepared according to Block [1], who takes the procedure from a Curl's publication (1956) in the US Federal Register.

Two stocks of solutions were prepared:

- **Solution A:** MgCl_2 (31.74 g) and CaCl_2 (73.99 g) dissolved in deionized water and adjusted to 1 L.
- **Solution B:** NaHCO_3 (56.03 g) dissolved in deionized water and adjusted to 1 L.

Each mL of solution A added to 1 L of deionized water, containing 4 mL of solution B, generates 100 ppm hardness calculated as CaCO_3 . However, if hardness is only obtained from the above mixture, the precipitate does not show good adhesion to the surface and the test reproducibility fails. Therefore, since a CaCO_3 concentration of 400 mg L^{-1} is believed to be suitable as a hardness standard, the hardness most suitable for laboratory tests will be achieved with a blend of 25 dF tap water and 15 dF of the synthetic water. Operationally, 4 mL of solution B and 1.5 mL of solution A are added to the tap water (reported to 25 dF with deionized water). The chemical composition of the tap water is given in Table 4.1.

4.1

Turbidimetric Tests

Sequestrants must keep metal ions in solution or re-solubilize them if precipitated. If this ability is suppressed by an excess of metal ions, metal complexes

Table 4.1 Chemical composition of tap water.

Conductivity at 18 °C	535 μS
Total hardness	27 dF
Total alkalinity	41 mL HCl 0.1N
Kübel test	0.9 mg L ⁻¹ O ₂
pH	7.8
NH ₄ ⁺	0.0
NO ₂ ⁻	0.0
NO ₃ ⁻	4.7 mg L ⁻¹
Cl ⁻	13.8 mg L ⁻¹
PO ₄ ³⁻	0.0
SO ₄ ²⁻	63.6 mg L ⁻¹
HCO ₃ ⁻	277 mg L ⁻¹
Fe ³⁺	0.0
Cr ⁶⁺	0.0
Mn ²⁺	0.0

become insolubilized, giving turbidity. The initiation of turbidity quantifies the sequestering power of a chemical.

Sequestrants compete with precipitants for metals. Thus, the test includes a competitor in order to reproduce practical field conditions. However, the competitor can be changed according to the target of the investigation. Several variants of the same test are possible. The most suitable procedures are described here in order of merit.

4.1.1

Sequestration Test (Oxalate)

The sequestration test based on oxalate as competitor is a well-known methodology. It is reported in the literature as a method specific for the determination of the sequestering power of EDTA [2, 3] and several other sequestrants, some stoichiometric and some not. A solution containing an amount of sequestrant and sodium oxalate is titrated with calcium to the first permanent turbidity and the result is expressed as calcium or calcium carbonate sequestered per quantity of sequestrant. The procedure, to be carried out at pH 11 (ammoniacal buffer), can be adapted to different pH values by adjusting with NaOH or HCl.

- 1 g of sequestrant is dissolved in 1 L of distilled water.
- 20 mL of 2% sodium oxalate solution are added.
- pH is adjusted with 1 N NaOH or 1 N HCl. A pH of 11 is reached with 30 mL of ammoniacal buffer.
- The temperature is set at the desired value.

- The solution is stirred and titrated with 0.2 M calcium chloride solution.
- The titrant solution is added in small aliquots (≤ 0.5 mL), stirring for 5 min after each addition.
- The end point is the first permanent slight turbidity.

The result is expressed as CaCO_3 sequestered per g of sequestrant as follows:

$$\text{mg CaCO}_3/\text{g sequestrant} = \text{mL}_{\text{CaCl}_2} \times M_{\text{CaCl}_2} \times 100$$

4.1.2

Nephelometric Titration

The visual assessment of turbidity cannot always be reproducible, but an instrumental measurement of light transmittance through the solution avoids this visual inaccuracy. The nephelometric titration [4] defines the end point as the intersection of the lines drawn through the point of transmittance at every addition. The graph in Figure 4.1 shows a typical slope.

Turbidity reduces the transmittance and indicates the end of the sequestering power. The procedure is carried out as described above in Section 4.1.1.

4.1.3

Sequestration Test (Hampshire)

When the competitor is sodium carbonate and calcium is added as its acetate, the method is identified as the Hampshire test. The presence of carbonate makes the test suitable for alkaline pH and is more sensitive to the method of adding calcium. Moreover, the longer time taken to show turbidity makes the assessment by photometer preferred. The procedure is as follows:

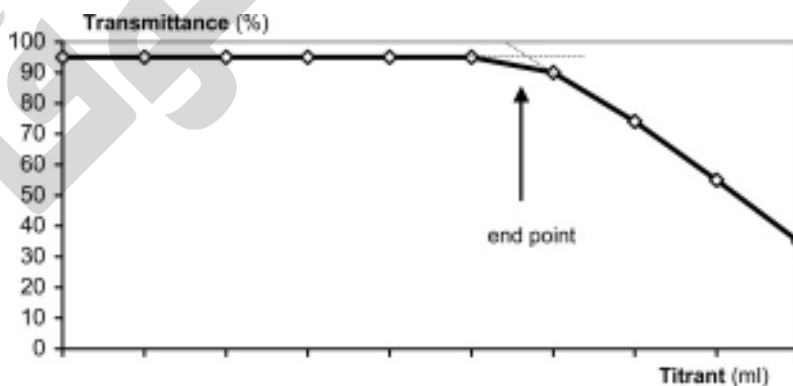


Figure 4.1 Nephelometric titration. The intersection of the lines determines the end point.

- 1 g of sequestrant is dissolved in 100 mL of distilled water.
- 10 mL of a 2% sodium carbonate solution are added.
- pH is adjusted with 1 N NaOH or 1 N HCl to a value >8, normally 11.
- The temperature is set at the desired value.
- The solution is stirred and titrated with a 0.1 M calcium acetate solution
- The titrant solution is added in small aliquots (≤ 0.5 mL), stirring for 5 min after each addition.
- The end point is the first permanent turbidity.

The following equation is used to calculate the sequestrant capacity:

$$\frac{\text{mL}_{\text{Ca-acetate}} \times M_{\text{Ca-acetate}}}{g_{\text{sequestrant}}} \times 100 = \text{mg CaCO}_3/\text{g sequestrant}$$

A narrow pH range and high sequestration capacity values reduce the direct usefulness of this methodology in food detergency. However, it gives approximate information about the threshold capacity of polymers.

4.2

Suspension Test

In order to measure the ability of a chemical to keep calcium suspended in a super-saturated solution, the following method has been developed:

- 0.5 g of sequestrant are dissolved in 300 mL of deionized water.
- The pH is adjusted with 1 N NaOH, 1 N HCl or 20 mL of ammoniacal buffer (pH 11).
- 80 mL of 2% sodium oxalate solution are added.
- 50 mL of 0.2 M CaCl_2 solution are added (overdose) at the stoichiometric point. (stoichiometry derives from Section 4.1.1).
- The volume is adjusted to 500 mL with deionized water.
- The temperature is set at the desired value.

The concentration of calcium kept suspended is checked at regular intervals by the following procedure:

- 10 mL of solution sampled from the top are transferred to a conical flask.
- 30 mL of 0.01 N EDTA are added together with the ammoniacal buffer and EBT indicator (Eriochrome Black T).
- The excess of EDTA is titrated with 0.02 M CaCl_2 .
- the difference between the added EDTA and the titrated excess determines the available calcium.
- the percentage of suspended calcium is found from the ratio of the amount of calcium detected to the initial amount.

4.3

Dispersion Test

When insoluble matter is part of the system or is to be formed, the useful dispersing effect can be measured by the ability of a sequestrant to prevent deposition. Therefore, the absence of deposits when sequestration is sub-stoichiometric (excess of calcium) indicates the dispersing efficiency of the sequestrant. One of the simplest procedures is described below:

- 0.1–0.3 g of sequestrant are dissolved in 500 mL of hard water (40 dF).
- The pH is adjusted with 1 N NaOH or 1 N HCl to the desired value.
- The volume is adjusted to 1 L with the same hard water (40 dF).
- The container is covered (to avoid evaporation) and stood at 70 °C for one night.
- The following day (ca. 16 h later) the solution is slowly poured out and the container is gently rinsed with deionized water.
- The scale adhering to the surface is dissolved in 50 mL of 1 N HCl.
- The residual acidity is neutralized (methylorange) with 1 N NaOH.
- 25 mL of ammoniacal buffer and EBT indicator are added.
- The dissolved Ca^{2+} is titrated with 0.1 M EDTA (or a less concentrated solution).

The ability to prevent deposits is determined from the amount of calcium found. The smaller the amount of calcium found, the greater is the dispersing capacity.

4.4

Static Test of Scale Forming

This test simultaneously assesses the sequestering and dispersing capacity of a chemical. It detects the exact concentration of sequestrant needed to prevent scale under normal use conditions. Thus, investigation of the water used in the field will give a result that can be transferred to the operational process. Bottlewasher rinsing and tunnel pasteurization, for instance, can benefit from application of the following procedure:

- Increasing concentrations of sequestrant are dissolved in glass beakers containing 1 L of water. Increasing concentrations means
 - Start with 20 ppm of sequestrant (as active material) and increase up to 200 ppm (at least) in pH > 10 systems.
 - Start with 2 ppm of sequestrant (as active material) and rise up to 20 ppm (at least) in pH < 10 systems.
- Three clean glass microscope slides are leant against the wall of the container.
- Beakers, covered to avoid evaporation, are thermostatted at the desired temperature (usually 70 °C) for one night (16 h).
- After allowing them to stand, the microscope slides are rinsed with deionized water and dried in the oven.
- The slides are arranged for inspection and visually evaluated (calcium deposit can be quantified by titration as described in Section 4.3).

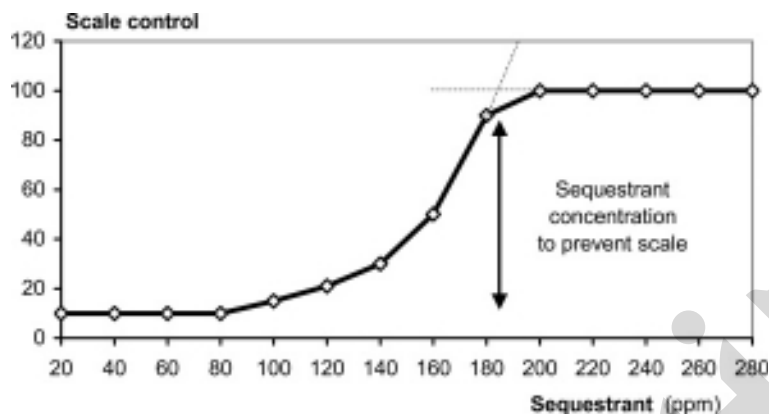


Figure 4.2 Control of scale by sequestrant. The intersection of the lines determines the end point.

A decrease in scale is observed up to a complete absence of scale as a function of the sequestrant concentration. The visual assessment or the intersection defines the exact concentration of sequestrant needed to prevent scale. A example of intersection lines is given in Figure 4.2.

4.5

Dynamic Test of Scale Formation

A moving solution (stirring and recycling) enhances the rate of deposition and makes scale prevention harder. Higher concentrations of sequestrant are generally required to prevent deposits in moving solutions than in static ones. The dynamic test can be used to confirm the results of previous sequestering tests.

An advantage of the dynamic test is that the efficiency of a detergent in cleaning a specific contamination can be assessed. While the static test is more useful when raw waters are being investigated, the dynamic test assesses the process of cleaning and anti-redeposition in the field. A procedure is described below.

- A suitable concentration of detergent (or sequestrant) is dissolved in a glass beaker containing 1 L of standard water (or a sample of field water).
- Three glass (or stainless steel) slides are suspended below the surface of the solution.
- The temperature is set at the desired value.
- The solution is stirred or recycled with a pump.
- After 20 min, the slides are rinsed with deionized water and dried in an oven.
- The slides are visually evaluated.

4.6

Static Test of Scale/Soil Dissolution

Several deposits prove to be more resistant to removal when they become thick or dry out. Beer stone, milk stone from heat exchange treatments, vegetable stone and deposits in concentrators are typical examples of residues so hard to remove as to require extraordinary measures and long times of contact with chemicals. Cleaning and cleaning times are estimated in the laboratory investigating the industrial contamination using the following procedure:

- A suitable quantity of contamination (or virtual contamination prepared in the laboratory) is placed in a glass beaker containing 1 L of detergent solution.
- The temperature is set at the desired value.
- The time of solubilization or dispersion is checked at regular intervals.
- The chemical attack is repeated, changing the detergent, in order to identify the best performing one within the shortest time.

4.7

Dynamic Test of the Dissolution of Scale/Soil

The dynamic test is carried out similarly to the static one except that the solution is moved in specific equipment or in a beaker with a magnetic stirrer.

- A sample of field contamination (or soiled slides) is placed in the equipment or suspended in a beaker below the surface of the cleaning solution.
- The temperature is set to the desired value.
- The solution is moved with a magnetic stirrer and/or recycling pump.
- The time of solubilization or dispersion is checked at regular intervals.
- the chemical attack is repeated, changing the detergent, in order to identify the best performing one in the shortest time.

4.8

Chemical Stability Test

A sequestrant should be stable during the time between its manufacture and its use. Contact with concentrated caustics or acids should not affect its molecular stability or, consequently, its efficacy.

Stability is referred to a formula, seasonal conditions, and an average time in the warehouse. Tests are directly carried out on the neat detergent at 'summer' temperature (40°C), which is believed to be the most critical. Two classes of detergents are involved: caustic/acidic products and chlorinated ones. For the former, persistence of sequestering efficacy is determined, and for the latter the stability of the chlorine (loss of chlorine).

- **Alkaline detergents** are prepared with a 1% solution of the sequestant. The sequestration test (Section 4.1.1) is performed at time zero (detergent just made) and after planned periods of storage at 40°C. Differences in sequestration reveal loss of stability. Defoamers disturb turbidity, so that the detergents are are tested defoamer-free.
- **Acidic products** (defoamer-free) are prepared with a 1% solution of the sequestant, neutralized with 1N NaOH. The sequestration test (Section 4.1.1) is performed at time zero (just made) and after planned periods of storage at 40°C. Differences in sequestration reveal loss of stability and/or efficiency in inhibiting corrosion.
- **Chlorinated detergents** are prepared with the sequestant. The chlorine loss is checked at regular intervals of time. Differences from a blank (sequestant-free) reveal the instability.

4.9

Solution Stability

The next test is specific for soap-based lubricant solutions. Stoichiometry and stability constant govern the competition between EDTA and fatty acids for calcium. This means that the solution is clear when just made and can turn turbid with time. A 650-nm spectrophotometric analysis of the lubricant solution identifies the point of initial transparency. The same solution, after aging, can show turbidity. A suitable concentration in use is inferred from the average point at which zero absorption occurs (Figure 4.3).

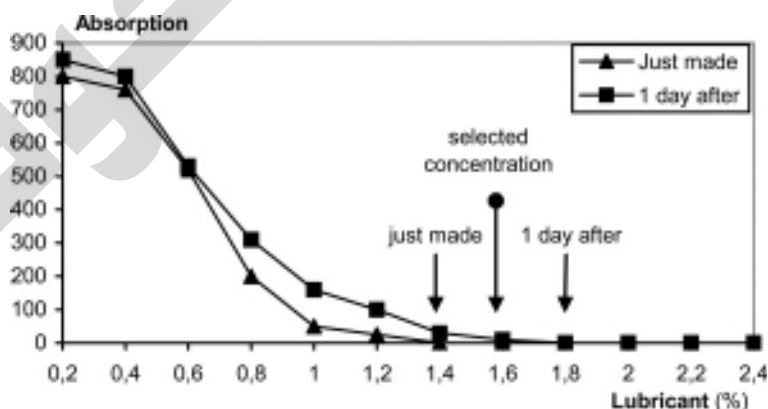


Figure 4.3 Stability of soap-based lubricant solutions. The suitable concentration for use is the average point between the newly made and the aged solution.

A suitable concentration needs traces of calcium soap as a defoamer. This occurs one day after the point of complete clarity, and the opalescence is negligible (selected concentration).

4.10

Sequestrant Stability

Phosphonates tend to precipitate in the form of calcium and magnesium salts depending on many factors such as pH, water hardness, type of salinity, turbulence, and type of colloids. These conditions cannot be exactly reproduced in the laboratory. Thus, the test is directly carried out on the field water in order to decide, firstly, which type of sequestrant is the most suitable and, secondly, what is its best concentration. The procedure can be as follows:

- 7 (or more) beakers are filled with 500 mL of water.
- Sequestrant (from 2 to 2000 ppm) is added to the water.
- The pH is buffered to 9 with NaOH.
- The beakers are allowed to stand for one week at room temperature.
- The appearance of the solutions are visually and spectrophotometrically (650 nm) assessed during this time (120 hours at least).

The pH and temperature can be set in accordance with the field circumstances.

4.11

EDTA and Calcium Titration

EDTA and calcium titration is a well known methodology widely used to determine standard concentrations of reagents and several analytical requirements in the field. These procedures are therefore included in this section.

4.11.1

Titration of EDTA

- Place 1 g (or more) of EDTA in a conical flask.
- Add 100 mL of deionized water.
- Add 10 mL of ammoniacal buffer and EBT indicator.
- Titrate with 0.2 M calcium chloride solution.
- The change from blue to pink-violet color establishes the end point.

$$\text{EDTA acid \%} = \frac{\text{mL CaCl}_2 \times \text{M CaCl}_2 \times 292}{1000 \times \text{g sample}} \times 100$$

4.11.2

Titration of Calcium Salts

- Place a calcium-containing sample (can be in various forms) in a conical flask.
- Add 50 mL of deionized water (if solid).
- Add 10 mL of ammoniacal buffer and EBT indicator.
- Titrate with 0.1 M EDTA2Na solution.
- The change from pink-violet to blue determines the end point.

$$\text{Calcium salt \%} = \frac{\text{mL}_{\text{EDTA2Na}} \times M_{\text{EDTA2Na}} \times \text{MW}_{\text{Ca-salt}}}{1000 \times g_{\text{sample}}} \times 100$$

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5

Surfactants, Caustics, and Acids

Cleaning products are typically formulated using a multiplicity of materials. The chapter on sequestrants contains several sections, since sequestrants prove to be the key factor in most of the cleaning successes in food detergency. Surfactants, caustics, and acids are briefly discussed in the present chapter to complete the account of the main chemicals involved in cleaning. Caustics and acids are components supplying the brute force, whereas sequestrants and surfactants refine, manage, and channel that force to achieve a rapid and thorough result.

5.1

Surfactants

The action of surfactants as cleaners in the food detergency is less fundamental than the caustic/acidic strength and the control of metals (sequestrants). As well as manual neutral-pH applications, surfactants cover areas where a complementary activity is required. Being in food detergency, the ancillary action of surfactants is for their defoaming, wetting, and emulsifying properties, and for foam gel generation. The value of their presence is considerable, as their effectiveness in wetting allows the other components of the formula to reach contamination sited in critical points such as the unevenness and porosity of a surface, as schematically represented in Figure 5.1.

The following overview does not aim at discussing their chemical characterization and theoretical properties. Numerous authoritative dissertations can be found in the literature for each category of surfactant, and there provide basic background information about their synthesis, chemical and physical peculiarities, and generic use [1–10].

The application of surfactants in the food detergency benefits from five properties:

- foam control (defoamers)
- wettability (wetting agents)
- detergency (cleaning agents)

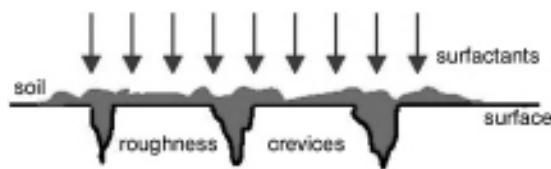


Figure 5.1 Contamination in a porous surface.

Table 5.1 HLB and solution appearance.

HLB range	HLB by dispersibility
1–4	No dispersibility in water
3–6	Poor dispersion
6–8	Milky dispersion
8–10	Stable milky dispersion
10–13	Translucent to clear dispersion
13–20	Clear solution

- disinfection (disinfectants)
- foam and gel builder (structural boosters).

5.1.1

HLB

The hydrophilic-lipophile balance (HLB) is a crucial parameter in the attainment of a good solubilization or emulsification of fats. The HLB is a number which expresses the hydrophilic (water-loving) and lipophilic (oil-loving) proportion of single or blended surfactants. The contamination itself has an HLB, so when a surfactant (or a blend) matches the HLB of the contamination, cleaning is faster and steadily attainable. In practice, a scale up to 20 is adopted. 20 HLB means 100% hydrophilic substance so that 12 HLB will be 60% hydrophilic substance, 8 HLB 40%. The ratio between the molecular weight of the hydrophilic portion and that of the whole molecule multiplied by 20 roughly gives the HLB of the substance, i.e. $HLB = (MW_{\text{hydrophilic}}/MW_{\text{molecule}}) \times 20$.

Surfactants are classified according to a general correlation reported by the ICI Co. in Tables 5.1 and 5.2 [11].

The most efficient system consists of blends of two or more surfactants of different HLB. The most suitable detergent should have an HLB very close to that of the contamination. The correct HLB can be determined by the Atlas method [11].

Table 5.2 HLB and surfactant activity.

HLB range	Use
4–6	Water/oil emulsifiers
7–9	Wetting agents
8–18	Oil/water emulsifiers
13–15	Detergents
10–18	Solubilizers

- Place 1 g of soil, 4 drops of surfactants, and 10 mL of (heated) distilled water in a test tube. Shake for one minute.

The test is performed with different surfactants of known HLB. The one giving the most stable suspension is noted. Since a blend of surfactants is preferable, an easy way to calculate how much of any emulsifier (A) has to be blend with any other emulsifier (B) to reach an HLB of X is from the following [11]:

$$\%A = \frac{100(X - \text{HLB}_{(B)})}{\text{HLB}_{(A)} - \text{HLB}_{(B)}} \quad \%B = 100 - \%A$$

The rule of the cross is another empirical but useful help for a rapid calculation. For instance, if HLB 12 is required from a mixture of 16 HLB and 6 HLB emulsifiers, the HLB is inferred from the ratio:

$$\begin{array}{ccc} 16 & \diagdown & 6 \\ & 12 & / \\ 6 & \diagup & 4 \end{array} \quad 16 \text{ HLB } 6\% + 6 \text{ HLB } 4\% \rightarrow 12 \text{ HLB}$$

The best performing surfactant (or blend) is said to have the HLB of the contamination. Thus, a good detergent with a matching HLB will perform best.

The efficacy in dispersing and solubilizing depends on the formation of surfactant micelles inside the solution [12]. When a surfactant is added to water, its molecules migrate to the surface and lower the surface tension. Further addition of surfactant goes on concentrating and lowering the surface tension until the surface is completely covered. After this, no further reduction in surface tension is observed. The borderline concentration is known as critical micellar concentration (CMC). The excess of molecules is forced to remain in the liquid mass and form aggregates called micelles shaped as shown in Figure 5.2.

Unreactive fatty matter, added to a solution where the surfactant is below its CMC, remains insoluble. It dissolves or emulsifies when the CMC is attained [14]. Thus, micelles are the reserve of surfactant to form and maintain the interfacial layer so as to give solubilization, in other words, to clean off fatty material.

HLB is a macro-parameter of cleaning. The position of the lipophilic and hydrophilic fraction in the molecular structure has a remarkable effect on the surface-active properties. Linear or branched chain, small or large branched structure,

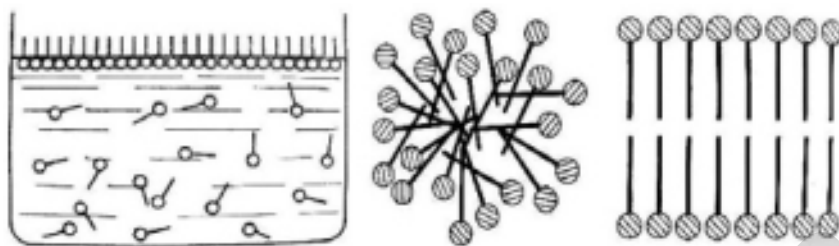


Figure 5.2 Schematic representation of surfactant molecules at the top and aggregates in the liquid mass. Courtesy of Gantz [13].



Figure 5.3 Basic structure of surface active agents.

and the way the hydrophilic-lipophilic fractions are arranged inside the chain influence washing efficiency, wetting ability, and anti-redeposition capacity.

5.1.2

Grouping of Surfactants

One of the primary problems of detergency involves the cleaning of fat and hydrophobic matter incompatible with water. The water is the only factor capable of carrying the contamination away. Then, every contamination must be held or carried away in water. Sodium and potassium soaps, the historical surface-active chemicals, can cause failure in practice because of their sensitivity to polyvalent metals (calcium) and their fixed molecular structure (HLB) which does not match the HLB of every fatty substance. It was crucial to find new molecules interacting with fats (lipophilic portion) but at the same time soluble in hard water (insensitive hydrophilic portion). The synthetic surfactants have the same basic structure as that of soap (Figure 5.3) in molecules where lipophilic and hydrophilic fractions can be multi-located and adjusted to meet every need of water/fat compatibility, as exemplified in the Figures 5.3 and 5.4.

The lipophilic part surrounds oil, and the hydrophilic part surrounds water. Both prevent contact between droplets and keep them emulsified. It follows that cleaning of fat is accomplished through

- adsorption of surfactants on the fatty material
- breaking up the fatty material
- enhancing the mutual repulsion between droplets
- keeping the droplets dispersed
- diminishing their tendency to redeposit.

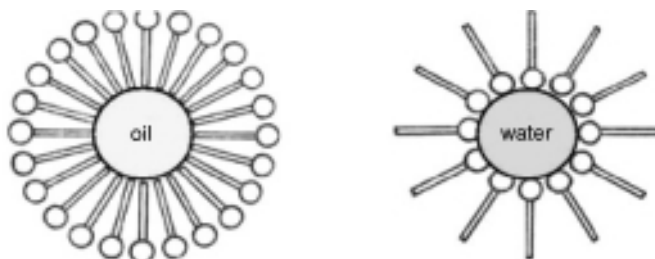


Figure 5.4 Oil in water and water in oil.

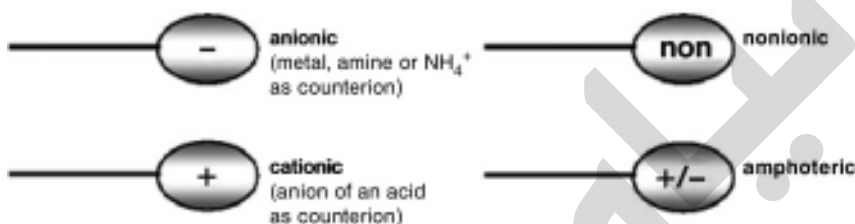


Figure 5.5 Classes of surfactants.

The investigation led to neutral molecules and molecules bearing anionic and cationic charges or both (amphoteric or amphiphilic molecule). Four types are available to solve problems of primary and ancillary detergency: anionic, non-ionic, cationic, and amphoteric surfactants, usually represented as shown in Figure 5.5.

The following sections briefly describe surfactants and their functionality in food detergency.

5.1.2.1 Anionic Surfactants

The negative charge defines surfactants as anionic. Soaps belong to this group. Being natural substances, soaps are no longer listed as polluting surfactants. A soap consists of a long lipophilic hydrocarbon chain ($>C_8$) and a carboxylic group as the hydrophilic tail. It is soluble in water if it contains monovalent cations (Na^+ , K^+) or alkanolamines, insoluble with multivalent metals (e.g., Ca^{2+} , Mg^{2+} , Fe^{3+} , Ba^{2+}). In synthetic surfactants the carboxylic groups are replaced with other hydrophilic groups such as sulfate, sulfonate and phosphate in natural, synthetic, linear, and branched lipophilic chains. Compared to soaps, cleaning is enhanced and sensitiveness to the water hardness suppressed.

ABS (alkylbenzene sulfonates) and LAS (linear alkylbenzene sulfonates) are typical examples. In particular, dodecylbenzenesulfonic acid is taken as the reference standard of the anionic category. Lauryl sulfate ($C_{12}-OSO_3^-$), lauryl ether sulfate [$C_{12}(EO)_3SO_4^-$], alkanesulfonates [$C_n-SO_3^-$ (SAS)], α -olefinsulfonates [$C_m=C_n-SO_3^-$ (AOS)], alkylethercarboxylate [$C_n(EO)_mCOO^-$] and alkylarylether sulfonates ($C_n-\phi-O-\phi-SO_3^-$) constitute the primary frameworks of the group.

Anionic surfactants are usually foam makers and the main components of foaming cleaners. As they have good skin compatibility (low irritant effect), anionics are ideal components of manual detergents, cosmetics and hand cleaners. The anionic charge makes them incompatible with cationics (positive charge) and responds to the MBAS analytical procedure (methylene blue active substance).

5.1.2.2 Nonionic Surfactants

Nonionic indicates surfactants free of any charge. Nonionic surfactants remain undissociated in aqueous solution and are compatible with anionics and cationics. The structure links neutral (nonionic) hydrophilic groups to hydrophobic fragments of the molecule through a controlled polymerization of ethylene oxide. It follows that the hydrophilic portion can be gradually extended by increasing the number of ethylene oxide groups (EO). As it is theoretically possible to condense from 2 to an unlimited number of EOs, a large number of molecules have been synthesized. When, as well as the basic lipophilic chain (e.g., C_n -alcohol, fatty amines and amides, alkylaryl groups), propylene and butylene oxides co-polymerize together, the combinations of different lipophilic and hydrophilic portions become endless. Thus, the applications of this group are also endless, exemplified by nonionics

- generating foam and complementing the detergent activity of the anionics
- providing less foam by suppressing and dissolving it (antifoam)
- emulsifying and/or solubilizing fats (matching HLB)
- enhancing wettability in order to enable the detergent to reach the interstices of rough surfaces
- aiding rinsing (rapid draining and consequent brilliance)
- stabilizing formulations, making components compatible (hydrotropes)
- being able to adsorb and keep disinfectants stable up to their final destination, such as iodine in iodophor disinfectants.

Nonionics cover every application of detergency. Fatty alcohols condensed with different amounts of ethylene and propylene oxides are well-known members of the group of nonionic surfactants. Generic and simplified definitions are assigned to nonionics and general prefixes are often reported in technical and safety data sheets of detergents:

- ethoxy (EO), when only ethylene oxide is polymerized
- ethopropoxy (EO/PO), when ethylene and propylene oxides are co-polymerized
- ethopropobutoxy (EO/PO/BO), when butylene oxide is added as well, normally at the end of the molecule.
- All the above definitions are also known as alkoxy and condensed surfactants.
- polymerization can involve different lipophilic molecules such as linear and branched, natural and synthetic fatty alcohols, acids, amines, amides, alkyl mono- and polyaromatic structures, glucoside and silicone derivatives. Hence,

the identification of nonionics incorporates names such as alcohol, aryl, alkylaryl, alkylamine, alkylamide, fatty ester and silicone.

- Examples: ethoxy alcohol 3EO, ethopropoxy fatty acid 9EO5PO, alkoxy amine 15EO and also C₁₂–C₁₈ fatty acids 7EO, C₄ diamine EOPO, and so on.

The nonionics group responds to the BiAS analytical procedure (Bismuth Active Substance). Picrate and Tetrakis methodologies are still used.

5.1.2.3 Cationic Surfactants

Cationics contain a positive charge in a molecule the hydrophilic site of which is the nitrogen atom linked to four organic radicals through single bonds (R₄N⁺). The nitrogen is quaternary and its derivatives are known as quaternary ammonium compounds (QACs). According to the type of molecule, QACs differentiate into emulsifying compounds, fabric softeners, antistatic agents, and corrosion inhibitors. Lacking cleaning action, disinfection is the most interesting property of the group in food sanitation. The C₁₂ chain and individual structures (e.g., imidazole and betaine compounds) prove to have the best disinfecting activity. Above C₁₂ they shift into softeners and corrosion inhibitors; below they take on hydrotrope ability. The more the chain moves away from C₁₂, the more the disinfecting efficacy is lost. A molecule can have one or several nitrogen groups, so that monomeric and polymeric compounds are available. Monomers are usually foaming and aggressive on painted and printed surfaces (fading). Polymerization lowers foaming and aggressiveness. Manual and foam applications, environmental atomization, and nebulization are used to disinfect equipment, tools, and environments.

Alkyldimethylbenzylammonium chloride (benzalconium or benzetonium chloride), dodecyldimethyl ammonium chloride, cetylpyridinium, chlorexidine digluconate, guanide and polybiguanide are well-known approved disinfectants for industrial applications. QACs in an acidic medium (phosphoric acid) are specifically recognized to be effective against *Listeria monocytogenes* [15].

5.1.2.4 Amphoteric Surfactants

Molecules containing both positive and negative charges are referred to as amphoters, and are also known as amphiprotic and zwitterionic surfactants. They have both acidic and basic characteristics and usually perform as cationics in acidic solutions and anionics in alkaline ones. For this reason, they are also known as ampholytic compounds and are compatible with cationic, anionic, and nonionic surfactants. When the positive charge is predominant, some of them behave as biocides and are often used to synergize with the disinfecting activity of cationics. Conversely, the negative charge provides them with wetting and cleaning capacity. Three characteristics are typical of amphoteric surfactants: foam generation, negligible skin irritation, and poor detergency. The way they behave makes them essential components of personal care products (shampoos and cosmetics), household detergents, disinfectants, and wetting and antistatic agents. Alkylbetaines, alkylsulfobetaines, imidazolinic compounds, and alkylpolyamineglycine belong to the group.

5.1.3

Defoamers

A comprehensive review of the various approaches to foaming and antifoaming mechanisms can be found in Garrett [16], who exhaustively describes theoretical and practical aspects.

Three agents are indispensable to produce foam: liquid, gas, and surfactant. The liquid is water, the gas is air, and the surfactants are derived from soil (e.g., proteins and soaps) and detergents. The foam formation is accompanied by an increase in interfacial surface and free energy. Systems usually tend to reduce their free energy. Thus, foam is thermodynamically unstable without adding energy [16]. Mechanical agitation and high-pressure spraying supply the energy necessary to make the air enter the liquid and keep it there. The presence of surface-active agents establishes a gradient of surface tension so as to stabilize the air inside and generate foam. Problems associated with excessive foam affect the majority of processes. Foam increases the volume of the stock, wastes the cleaning solution, reduces the effective capacity of pumps and tanks, carries over higher concentration of chemicals to rinse, decreases the cleaning efficacy, and increases the time and cost of a process. Figure 5.6 shows the stabilization of foam by absorption of surfactants.

Several classes of defoamers claim to suppress foam, such as calcium soaps, organic silicon compounds, phosphoric esters, and hydrocarbons. However, anti-foams need to be man- and eco-friendly. Friendliness is usually associated with specific nonionic surfactants having an intrinsic low surface tension and counteracting the stability of the foam.

Factors influencing the stability of the foam:

- surface elasticity (Gibbs Marangoni effect)
- surface viscosity (lower rate of draining of lamellae)
- electrostatic repulsion (repulsion forces stop the lamellae thinning any further)
- gas diffusion (new bubbles of different size cause the lamella to be unstable)

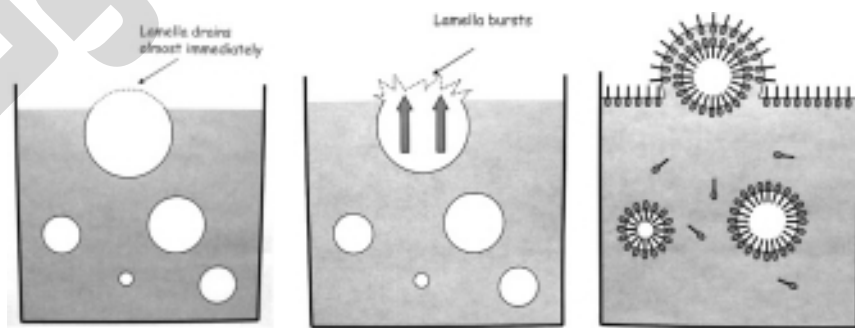


Figure 5.6 Schematic process of foam stabilization by surfactant absorption (Courtesy of JohnsonDiversey).

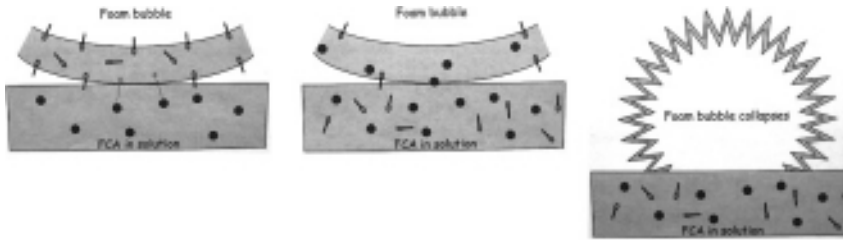


Figure 5.7 Schematic process of foam destabilization by defoamer (●) absorption (FCA = foam control agent). (Courtesy of JohnsonDiversey).

- temperature and pH (indirect effect on stability)
- concentration of foam-active substances (CMC).

Defoamers can reduce the surface elasticity, increase the speed of draining, and displace the foam-active substances from the interface [17]. In order to be effective, defoamers enter the liquid as undissolved particles or droplets having an optimum size, as the defoaming efficacy decreases if the droplet size is either too large or too small [16]. Figure 5.7 shows the process of foam destabilization.

Foam control is sometime described as defoaming or antifoaming capacity. Defoamer and antifoam really express the same activity observed from two different starting points. Defoamers are used to destroy the existing foam, antifoams to prevent its formation. In practice, there is no difference in the mechanism, and the same chemicals are used for both.

A cloud point typifies the majority of nonionic low-foam and defoaming surfactants. Defoamers are soluble in cold water and insoluble in hot (droplet formation). The temperature of the solubility change is known as the cloud point (solution turns turbid). Below, defoamers behave as conventional surfactants (fully solubilized and foaming substance). Above, the phase separation (insolubilization) makes them be foam-suppressing agents. Thus, the efficacy in suppressing foam depends on two different phases in the same system. Insoluble oil-like surfactants displace the foaming agents from lamellae and cause the foam to collapse. The usual cloud point of effective defoamers dissolved in water is between 20 and 50°C. This is the reason why CIP (clean in place) and spray cleaning need temperatures above 50°C at least to gain a good control of foam.

Different tests are available to assess defoamers. The Ross Miles methodology, originally proposed to investigate the foam quality of a surfactant [18], can be reversed to identify their ability in suppressing it. An example of a laboratory test is illustrated in Figure 5.8 (reverse Ross Miles).

5.1.4

Wetting Agents

The wettability concept relates a liquid to the surface hydrophobia described as the receding contact angle (φ) at the air-liquid surface measured on the liquid phase [19], as represented in Figure 5.9.

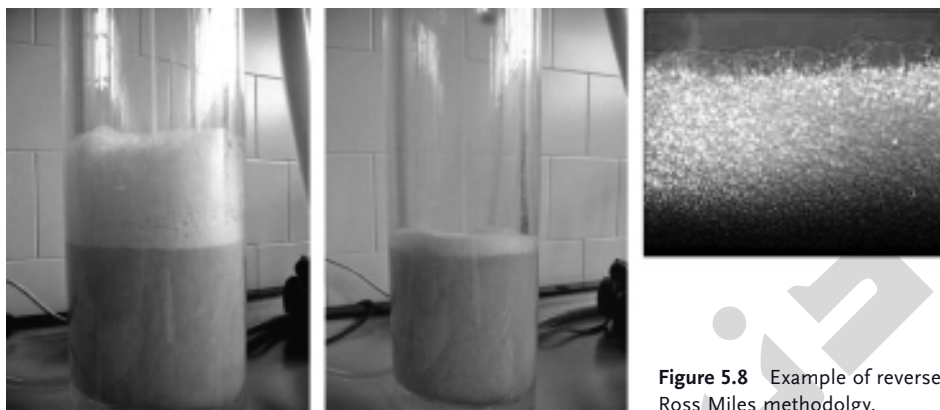


Figure 5.8 Example of reverse Ross Miles methodology.

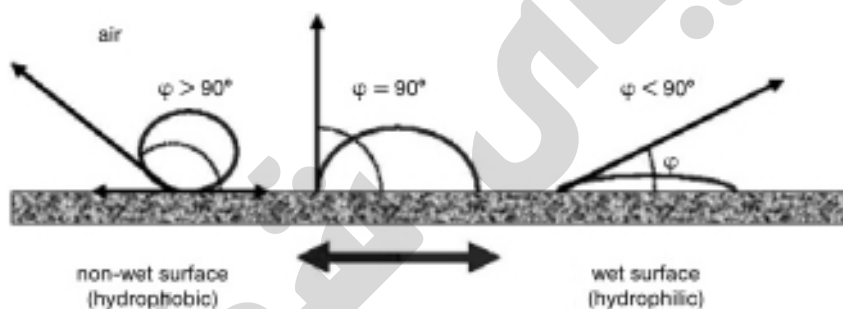


Figure 5.9 Representation of the contact angle.

Contact angles greater than $\pi/2$ (90°) indicate a non-wetted hydrophobic surface. Surface wettability is of the utmost importance on roughness, asperity, and porosity rather than on a smooth surface, since it enables the liquid to penetrate inside, displace air, and carry the cleaning agents into the interstices. Therefore, being an efficient wetting agent consists in reducing the solid-water interfacial tension by diffusing fast from the bulk solution to the interface and forming an oriented interfacial film [19]. The amphiphilic nature of surfactants distributes them both at solid-water and water-air interfaces and promotes the orientation of the hydrocarbon tail to speed up the adsorption onto the solid and decrease the surface tension of the water in contact with it. $\cos \varphi = 1$ ($\varphi = 0$) defines the critical surface tension of a solid in contact with a liquid. The limit of surface tension is a property specific to each solid, differs from one solid to another, and influences several applications in the food industry. Cold aseptic filling, for instance, requires the PET bottles to be disinfected rapidly. The hydrophobic behavior of the PET plastic is reduced by treatment with a wetting surfactant added to peracetic acid. Figure 5.10 shows the behavior of a hydrophobic surface with $\varphi \approx 180^\circ$.

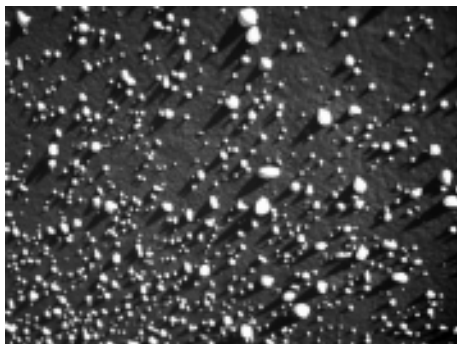


Figure 5.10 Water droplets under light grazing along a hydrophobic surface ($\phi \approx 180^\circ$).

Table 5.3 Surface tensions for common solids.

	PTFE	PP	PE	PVC	PC	PET	PS	Nylon 6,6
Surface tension ($\text{mN}\cdot\text{m}^{-1}$)	18	29	31	39	42	43	43	46

Examples of critical surface tensions for common solids are given in Table 5.3 [19, 20].

The greater the surface tension, the better is the surface coverage. Surfaces with high surface energy are wetted more readily than low-energy surfaces. Converting the theoretical dissertation into practice, cleaning is achieved when the wetting ability of the detergent reduces the contact angles of the liquid below $\pi/2$. A surface tension of $30 \text{ mN}\cdot\text{m}^{-1}$ for a solution is considered to give effective wettability [19]. Many surfactants reduce the water/solid surface tension to this value.

The type of surfactant and especially its concentration influence the surface wettability. A wetting surfactant is only asked to give a CMC suitable to penetrate the whole surface inclusive of soil. Thus, the concept of wettability differs from the concept of cleaning. Most of the cleaning mechanisms in food detergency exploit the brute force of caustics, acids, and sequestrants. Cleaning surfactants emulsify and even solubilize the fatty contamination. Wetting agents only assist the detergent to spread and quickly penetrate the micro-crevices in depth. Thus, the best wetting agents are not necessarily the best cleaning agents. As a consequence, the type of surfactant and its concentration change according to its purpose. The concentration of wetting agents fluctuates within the range 0.1–0.5% in the neat detergent. Fluorinated surfactants, for instance, are claimed to be excellent wetting agents even below the 0.1% level in the neat detergent but do not provide any cleaning properties. Anionic surfactants, such as branched short chain sulfates (2-ethylhexyl sulfate) and alkylarylether sulfonates, are preferred. Special nonionics give excellent wetting ability (e.g., alkylpolyglucosides and short-chain EO-PO condensed alcohols).

5.1.5

Cleaning Agents

In terms of detergency, contaminations are generically divided into

- solids: inorganic salts, metal oxides, wax, fat, proteins, starch, coagulated colloids, carbon black, and dust
- liquids: animal, vegetable, and mineral oil.

Although temperature can change a proportion of solids (fat and wax) into liquid, most contamination normally consists of solids and liquids together. The theory of soil removal (the process of washing) implies at least three processes:

- **Chemical removal:** soil solubilization by means of caustics (peptization of proteins, hydrolysis of starch and triglycerides) and acids [solubilization of limestone and metal oxides, peptization of proteins (phosphoric acid), solubilization of calcium phosphate (nitric acid)].
- **Physical removal:** solid-solid, solid-liquid, liquid-liquid and air-liquid interface adsorption of surfactants and sequestrants by Van der Waals attractions, Coulomb-Born repulsions, and potential energy of the system (Z-potential). The physical mechanism of enveloping by adsorption and removal by repulsion is the same process whether it is applied to solids (particles removal) or liquids (roll-up theory).
- **Carrier mechanism typical of sequestrants:** Sequestrants penetrate the contamination and extract (pull out) multivalent metals in the form of complexes. Soil is loosened and washing efficacy improves.

The removed contamination must be stabilized in solution. The mechanism is known as dispersion and anti-redeposition. The liquid soil is emulsified and the solid dispersed and suspended by the steric inhibition of stable soil-soil and soil-surface contacts. Adsorption, surface tension modification, repulsion, anti-redeposition, solubilization, and emulsification describe the sequence of mechanisms characteristic of surfactants and their efficacy in performing detergency.

5.1.6

Disinfectants

The cationic surfactants have relatively little effect on cleaning. On the other hand, these amino-compounds are fundamental as disinfecting agents in industry, hospital care, veterinary science, and personal and household treatments. Quaternary ammonium compounds (QACs) are the most well-known antimicrobial surfactants. Publications date back to the early twentieth century, but their real development in chemical and biological knowledge was only accomplished at the middle of that century [21]. Together with amphoteric surfactants and alkyl polyamines, QACs received attention and recommendation because of their bio-

cidal activity free of significant toxicity, corrosivity, and unpleasant odors. These characteristics differentiate them from halogens, phenol and cresol compounds, aldehydes, heavy metals, and peroxides.

The microbial activity is quite complex. There is no antimicrobial agent so complete and universal as to be able to combine all the properties asked of a biocide, which should be

- efficient at low concentration even in the presence of contamination
- friendly to handle
- safe on every surface
- safe to personnel
- easily removable in sewage treatment
- environmentally compatible.

Nitrogenous disinfecting surfactants meet the above demands. They allow safe use in every sector, both domestic and industrial. The presence of nitrogen makes them more strongly adsorbed. Residual absorption guarantees prolonged protection against re-infection. Thus, the nitrogen derivatives (QACs, fatty polyamines, fatty polyamines, glycine, and polybiguanide) take their rightful place among the most applied chemicals in industrial disinfection:

- open plant sanitation (foam and gel disinfectants)
- reduction of the environmental microbial charge (nebulization or atomization)
- CIP terminal disinfection (polymeric non-foaming QACs, alkylpolyamines, and polybiguanide)
- control of the microbial charge in heat exchange plants, cooling towers, tunnel pasteurizers, and swimming pools
- main agents of mold control and prevention
- synergism with ethyl and isopropyl alcohols for dry disinfection on open surfaces
- soak disinfection of utensils and dismantled parts of equipment
- general disinfectants in the poultry, breeding, and veterinary fields
- used in many pharmaceutical, cosmetic, and toiletry formulations
- used in manual and soak cleaning and disinfection in combination with nonionics.

Cationic surfactants show rather low killing activity against viruses, spores, specific (e.g., *Pseudomonas*, *Listeria*, *Salmonella*, *Brettanomyces*) or uncommon (e.g., tuberculosis agents) micro-organisms in industry. This low activity has to be related either to their slower rate of killing or the higher concentration required to reach the level of microbial reduction that defines it as a disinfectant.

It is reported [4] that the first industrial application was in the dairy industry on a pasteurization plant [22]. The activity of a compound free of taste and odor, having no corrosivity toward metals and rubbers, safety in handling, and low toxicity was greatly appreciated.

5.1.7

Structural Boosters

The volume of foam is not always a measure of the efficacy of a detergent. Foam and gel cleaners are an example. Rather than cleaning, surfactants primarily aim at building a foam framework which allows detergents to remain on vertical and angled surfaces longer. Open plants reach such complexity as to require much time and manpower to accomplish overall cleaning in depth without the use of foam technology, as illustrated in Figure 5.11.

The detergent, in foam and gel form, reaches every part and remains adhering for enough time for the the contamination to be attacked and then removed by the high-pressure rinse. Foam and gel cleaners are discussed in Chapter 11.

5.1.8

Biodegradability and Toxicity

The quality of the water in and the water out should be the same, but this is seldom achieved because some traces of the process pollution are always immovable. For this reason, and in order to prevent arbitrary decisions about disposal, there are laws and agreements governing limiting levels of chemical contamination in the water disposed of. As far as surfactants are concerned, molecular destruction (biodegradability) and death of plankton, fish, and trees (toxicity) are two basic eco-parameters directly involving surfactants and their by-products of degradation. Surfactants are considered biodegradable if they pass the biological screening test. If any doubt remains, they must pass the confirmatory test (OECD Screening Test and OECD Confirmatory Test [23, 24]). The degree of branching normally affects biodegradability, and the presence of straight-chain and condensed ethylene oxide facilitates it [25]. The percentage of acceptable biodegradation depends on agreements that establish the amount of degradation desired within a fixed time (ca. one month). A significant decrease in ecological problems (foaming rivers and bio-environmental death) has resulted from the application



Figure 5.11 Complexity of equipment in poultry slaughterhouse.

Table 5.4 Types of degradation.

Primary biodegradation	Loss of surface active properties measured by coloring reagents
Ultimate biodegradation	Total conversion to carbon dioxide, water, and minerals measured by carbon dioxide evolution and oxygen consumption

of the rules concerning permitted levels of chemicals released to the environment (a few ppm) and require levels of biodegradability.

Studies have often shown that biodegradability is in inverse relation to toxicity [26]. However, several traditional nonionic defoamers, even though they do not reach the biodegradation limits, have negligible aquatic toxicity compared to the by-products of the biodegradable ones. This leads an open debate on which should be recognized as having priority, biodegradability or ecotoxicity, with regard to the environmental impact. Toxicity is a property of the chemical and is independent of time, whereas time affects its biodegradability. The question is: will it be more favorable to the environment to admit a non-ecotoxic surfactant 60% biodegradable within 30 days or rather a 90% biodegradable surfactant which passes the ecotoxicity test just above the minimum limit? A fully biodegradable and non-ecotoxic surfactant is a utopian target. Therefore, biodegradability and ecotoxicity have been balanced in a sequence of actual effects on the environment and merged in the final decision.

The assessment of primary and ultimate biodegradation Table 5.4 makes the practical impact of degradation residues more evident. Various organic molecules could remain after the primary degradation, while the ultimate degradation (to $\text{CO}_2 + \text{H}_2\text{O}$) will be accompanied by a complete conversion into minerals.

On the other hand, a wise evaluation should be able to balance the environmental consequences from toxicity and biodegradability. Low toxicity should counterbalance a biodegradability lower than the theoretical defined limit. Hence, the classification of substances and preparations according to matrixes expressing the combined biodegradability and toxicity is given as a basic philosophy of grouping and labeling surfactants and detergents. Figure 5.12 exemplifies this inter-relationship [27].

The table integrates biodegradability and ecotoxicity by merging substances readily biodegradable above 60% with those having a toxic impact as a function of their LC_{50} (lethal concentration for 50% of life). The result crosses the raw materials with their concentration in preparations. 25% identifies the critical concentration. The matrix of values defines eco-impact and consistent labeling.

5.1.9

BPD and REACH

The European Biocide Product Directive (BPD) and Registration, Evaluation, Authorization of Chemicals (REACH) look after processes aiming at regulating

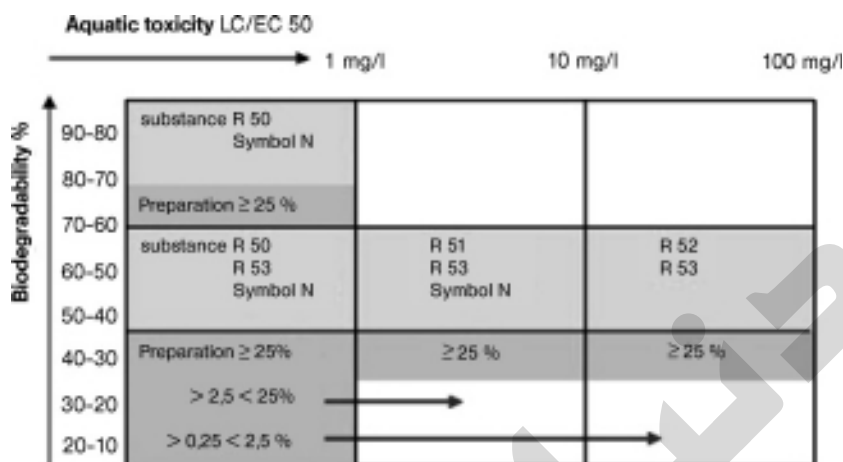


Figure 5.12 Different labeling of cleaning compounds. R 50: very toxic to aquatic organisms; R 51: toxic to aquatic organisms; R 52: harmful to aquatic organisms; R 53: may cause long term adverse effects in aqueous environment.

the number of biocidal and chemical molecules in terms of human and environmental safety into a globally harmonized system.

Health and environmental safety is the main guide to bringing chemicals onto the market. Thus, in order to be approved and authorized for sale, each chemical notified must be accompanied by comprehensive documentation about fields of activity, biodegradability, toxicity, mutagenicity, carcinogenicity, and assessment of general risks to health and environment by means of the best available technologies.

Only notified chemicals of proved reliability (should) receive authorization to enter the market.

5.2 Caustics

Alkaline builders are a group of materials having a pH > 7 diluted in water. They actually exhibit a cleaning effect above the phenolphthalein end point (>8.3), that is, when free hydroxyl ions are available in solution. In terms of detergency, alkalinity is divided into four zones:

- **pH from 7 to 8.3:** field of raw water and neutral detergents/disinfectants
- **pH from 8.3 to 10:** mild alkalinity, where calcium salts show the greatest adherent behavior. Detergents in this pH range are speciality (e.g., enzymatic) products, and normally maintain a constant pH in use by means of an inner buffer.

- **pH from 10 to 12:** medium alkalinity, where sequestrants have the greatest difficulty in controlling precipitation. A higher concentration is needed (critical pH). Medium-alkaline detergents have specific objects such as detergency with anticorrosion property (e.g., silicate on aluminium), cleaning and disinfecting activity (non-chlorinated sanitizers) and cleaning of crossflow filtration membranes.
- **pH above 12:** caustic zone, where floc-shaped hydroxo-agglomerates precipitate. Less adhesion to the surface and higher difficulty in rinsing occur. Detergents are referred to as caustic and perform most of the cleaning on food plants.

Caustics are multifunctional and aid in breaking, solubilizing and saponifying organic soils, especially fats and proteins. Caustics hydrolyze triglycerides and react with their fatty acids giving soluble soaps. They solubilize proteins, moving them up to their isoelectric point (point of the protein stability). The organic soil is sensitive to alkalinity. The more the alkalinity increases, the better the organic contamination is removed. Surfactants reduce the hydrophobic properties of the fatty material and help caustics to be more effective at removing soils in depth.

Sodium hydroxide (caustic soda, NaOH) and potassium hydroxide (caustic potash, KOH) are the main sources of alkalinity used in cleaning products. There are many other compounds that alkalinize aqueous solutions, and these are listed in Table 5.5.

However, salts other than caustic soda and potash are usually included in a detergent not for their alkalinity but for distinctive properties that supplement the detergent action. Silicate, for instance, adds the inhibition of corrosion of aluminium; trisodium phosphate forms a buffer system in combination with di- and monosodium phosphate; polyphosphates are included as sequestrants, dispersants, and antiredeposition agents; carbonate, bicarbonate, and sulfate are considered to be fillers.

Although some of the alkalis exhibit many good detergent properties, none is a complete multifunctional cleaner. Cleaning properties and side effects depend

Table 5.5 Alkalinity.

Chemical	pH 1% solution
Caustic soda	13.1
Caustic potash	13.0
Sodium metasilicate	12.6
Trisodium phosphate	12.1
Sodium carbonate	11.3
Tetrasodium pyrophosphate	10.1
Sodium tripolyphosphate	8.9
Sodium bicarbonate	8.2
Sodium sulfate	7.3

on the cation (Na^+ and K^+) and the anion that form the salt. Potassium reacts and gives salts more soluble than sodium and melting at lower temperature. It is easier to clean liquid contaminations than solid ones. Thus, caustic potash should preferably be used where fats are predominant (e.g., slaughtering and processed meats). Caustic soda performs better on proteins (e.g., dairy), mainly on thermally modified contamination (e.g., pasteurization, sterilization) and cooking processes. Moreover, KOH enhances the stability of formulations, being more compatible with dissolved salts and a promoter of freezing point lowering. 44% NaOH alkalinity, for instance, freezes at $+4^\circ\text{C}$, NaOH 30% + KOH 14% alkalinity freezes at -2°C . As the stability of a formulation is guaranteed between 0 and $+40^\circ\text{C}$, the benefits of using KOH are evident. However, caustic potash is considerably more expensive than caustic soda. Blends of both or products carefully arranged in hydrotropes, sequestrants, and cleaning surfactants provide a correct balance in cost-effectiveness.

Caustic soda and potash are difficult to rinse. As a rule, every alkaline compound precipitates polyvalent metals (except sequestrants, of course) and leads to deposits on equipment if sequestrants are not included in formulations. Therefore, caustics carry out an excellent cleaning only when their brute force is controlled and managed by proper co-formulants.

Oxidants are distinctive co-formulants often added to improve cleaning and disinfection of a caustic solution. Chlorine and hydrogen peroxide enhance the cleaning performance on all types of organic soils. They do break up proteins and fats, make them more soluble and, developing gas from the inside, cause even the most resistant contaminations to be rapidly cleaned off.

Enzymes play a considerable role in cleaning delicate equipment (e.g., crossflow filtration membranes). Aside from some enzymes, such as cellulase, which break the cellulose fibers at mild acidity ($\sim\text{pH } 5$), they are included in neutral or buffered low-alkaline detergents. Phosphate buffers are prepared to stabilize proteolytic and lipolytic enzymes within the pH range 9–10.

Table 5.6 is useful to convert from one expression of alkalinity to another [28].

Table 5.6 Alkalinity conversion.

Alkalinity % conversion		From						
		Na_2O	NaOH	KOH	K_2O	CaCO_3	Na_2CO_3	NaHCO_3
To	Na_2O	1	0.775	0.552	0.687	0.620	0.585	0.369
	NaOH	1.290	1	0.713	0.887	0.800	0.775	0.476
	KOH	1.810	1.403	1	1.244	1.122	1.058	0.668
	K_2O	1.455	1.128	0.804	1	0.902	0.851	0.537
	CaCO_3	1.613	1.250	0.891	1.109	1	0.943	0.595
	Na_2CO_3	1.710	1.325	0.945	1.175	1.060	1	0.631
	NaHCO_3	2.710	2.100	1.497	1.863	1.680	1.585	1

The behavior of the main alkalizers reported in the table is also discussed in Sections 1.2 and 3.4.1.

An extreme pH is not compatible with life, so that caustics at a high enough concentration are bactericidal. Temperature and time of contact foster the bactericide action (see Section 6.2).

The pH can be used to control the concentration of a solution (electronic devices), but this must not be confused with the actual determination of the percentage of alkalinity. Alkalinity is determined by a chemical titration with a strong acid to the phenolphthalein or methylorange end point. The known percentage of alkalinity gives a pH which can be measured using a probe (pH meter), which, connected to an electronic device, can subsequently control and automatically restore the concentration of the solution.

All alkalis are severely corrosive to aluminium, except silicate which performs as a corrosion inhibitor. Even though less aggressive (low kinetics), caustics are also corrosive to galvanized and tinned surfaces.

Strong alkalis are aggressive to human tissue. They can irritate, burn, and destroy skin and mucous membranes. The result is the same through environmental contacts with aerosols, fumes, and dust from powders.

Products should not be mixed unless specific instructions are given. They must be stored in groups according to type. Alkaline, chlorinated, and enzymatic cleaners can be grouped together and separated from the acidic ones. Powders should be stored away from liquid products. Never mix chlorinated cleaners with acid as this generates deadly chlorine gas.

5.3 Acids

Acids constitute a group of materials having a $\text{pH} < 7$ diluted in water. Acidity converts the organic contamination into a hydrophobic material, and therefore the use of acids is not the best way to perform detergency. Surfactants are often added to counteract hydrophobicity, aiding penetration of the soil so as to allow acids to perform detergency. However, the strength of the detergency of acids remains weak and is only suitable for cleaning of unstressed contamination, mainly fresh contamination which has not been thermally modified.

Acids are necessary to remove inorganic deposits, whether they come from water or as residues of various types of contamination (e.g., inorganic residue of milkstone, beerstone, eggstone, and vegetablestone), and are used either before or after alkaline cleaners. Acids directly act on scale in which carbonate is predominant (descalers). Carbonate is thermodynamically unstable in acid and, dissolving with release of carbon dioxide gas, also breaks up the insoluble materials (silicate and sulfate) and allows the deposit to be completely removed.

Descaling and detergency entail different process of cleaning, and different types of acid are involved. Table 5.7 lists the most common acids.

Hydrofluoric acid does not show cleaning activity although it is in fact the most corrosive acid. Thus, it is used for exceptional purposes where the other acids are

Table 5.7 Order of activity of acids.

Acids in order of decreasing strength	Acids in order of decreasing cleaning	Acids in order of decreasing descaling
Hydrochloric acid (HCl)	Phosphoric acid	Hydrochloric acid (on scale)
Sulfuric acid (H ₂ SO ₄)	Nitric acid	Nitric acid (on 'stone')
Nitric acid (HNO ₃)	Glycolic acid	Phosphoric acid
Phosphoric acid (H ₃ PO ₄)	Sulfamic acid	Oxalic acid
Sulfamic acid (NH ₂ SO ₃ H)	Citric acid	Sulfamic acid
Oxalic acid (HOOC-COOH)	Tartaric acid	Citric acid
Tartaric acid (C ₄ H ₆ O ₆)	Sulfuric acid	Tartaric acid
Citric acid (C ₆ H ₈ O ₇)	Oxalic acid	Sulfuric acid
Formic acid (HCOOH)	Formic acid	Glycolic acid
Acetic acid (CH ₃ COOH)	Acetic acid	Acetic acid
Glycolic acid (HOCH ₂ COOH)	Hydrochloric acid	Formic acid

ineffective, such as periodic floor maintenance, removal of tenacious rust and silicate deposits, and in all cases demanding the solubilization of part of a metal, ceramic or glass substrate to achieve cleaning.

Nitric and phosphoric are the most exploited acids in food detergency either separately or together (when they form the so-called phospho-nitric detergents).

The organic acids are not as strong as the mineral ones. Glycolic acid is particularly effective on proteic contamination and comes just behind phosphoric acid in removing proteins. The organic acids combined with surfactants constitute the group of ecological detergents, where 'ecological' means detergents and descalers free of nitrogen and phosphorus. As organic compounds do not conduct electricity, the conductivity of their formulation is obtained by adding a mineral acid, usually sulfamic acid.

Acetic acid is strategically important in food sanitation since it is the starting chemical for the production of peracetic acid, which is currently the most important terminal disinfectant in every sector of the food manufacturing. When necessary, nitric acid provides peracetic acid with conductivity.

Acid content is determined by titration with caustic soda and corresponds to a pH which can be measured using an electronic probe (pH meter) which can automatically manage the acid solution.

Concentrated mineral acids are corrosive to human tissue and present a greater hazard than organic acids. Like alkalis, they can irritate, burn, and destroy skin and mucous membranes. Nitric and hydrofluoric acids are particularly dangerous and must be handled with great care. Their vapor and fumes are highly irritant and potentially toxic. Acidic products should never be mixed with other cleaning products, even with other acids. Never mix chlorine and acid as a deadly gas is created. Never mix chlorine-containing cleaners with acid as this generates deadly chlorine gas.

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Part Three

Application to the Food Industry

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6

Bottlewashing

In order to be re-used, bottles must be acceptable in appearance and at least microbiologically suitable for containing potable liquids. Cleaning is only a part of the process; the latter part concerns sanitation. Cleaning and disinfection perform four important parts of the process:

- detaching labels
- removing interior soil
- scale control in rinsing (calcium carbonate) and caustic (aluminate) baths
- producing microbiologically acceptable bottles.

The use of PET (polyethyleneterephthalate), PEN (polyethylenenaphthalate) and PC (polycarbonate) containers necessitates extra care in maintaining the integrity of the plastic material on which chemical stress cracking and haze have to be prevented.

While scale control and microbiology are considered fixed parameters of washing, labels and soil vary according to the type of recovered bottles. When containers are not reliably labeled, a percentage of them can come from different bottlings and contain different glue, labels, and soil. The steady condition of a bottlewasher often depends on using one's own containers. Arrivals of miscellaneous soil and labels frequently cause unpredictable cleaning problems.

Many factors influence the success of the washing process. Choice of the correct chemicals, correct application of the selected chemicals, and recognition of key signals on the outgoing bottles are basic requirements for competency to plan and manage a positive cleaning.

As far as the layout of bottlewashers is concerned, it is easier to look up the technical documentation from specialized manufacturers and their customized solutions to all sorts of requests. Generally speaking, a machine includes alkaline baths, spray, rinse, and sometimes an acid section. Synthetically, bottlewashers are divided into two classes:

- **Single ended:** the same side houses both the inlet and the outlet. This type of machine normally serves medium to small bottlings covering up to approximately 40 000 bottles per hour. Ignoring some variations, the main

caustic wash, the caustic spray section, and the rinse characterize the basic layout, schematically represented in Figure 6.1.

- **Double ended:** loading is at one side, discharge at the other. As units called modules are used to build these machines, they are also known as modular machines. Modules (Figure 6.2) are structurally identical but numerically variable as a function of the washing needs (productivity). The units provide dimensional versatility, which allows great efficiency in cleaning, output even exceeding 100 000 bottles per hour.

Calcium carbonate is insoluble in alkaline solution. When calcium carbonate crystals foul recovered bottles, the refilled bottles may contain either crystal deposits (CO_2 -free water) or modified salinity (crystals dissolved in carbonic acid). Then, a subsequent acidic module accomplishes the complete cleaning. Such crystals grow from hard water in partially emptied bottles kept for a long time. Figure 6.3 shows calcium carbonate crystals in a bottle of mineral water.

A modular machine with an acidic section is shown schematically in Figure 6.4.

Instead of adding a module, the acidic step can be coupled outside the alkaline washing with a single-end machine. The same path of water joins the machines from the acidic single-end to the modular alkaline one. This is schematically represented in Figure 6.5.

The temperature and alkalinity of a bottlewasher have two gradients:

- **The temperature gradient** (Figure 6.6) applies to the bottles from infeed to discharge in order to protect the glass from thermal shock which could occur on passing from ambient to hot zones and back again.

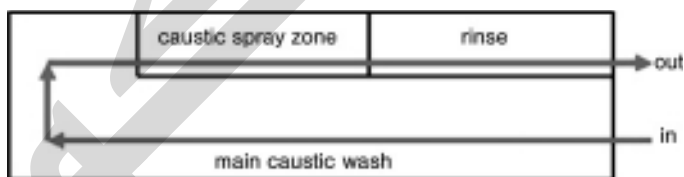


Figure 6.1 Bottle path in the single-end machine.

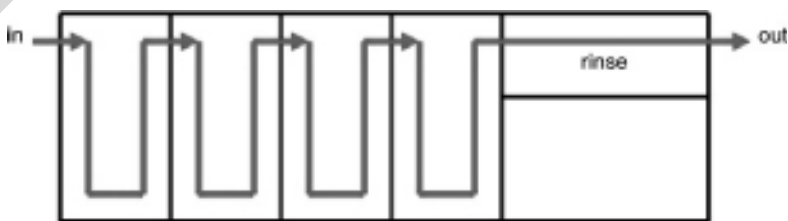


Figure 6.2 Four modules machine.



Figure 6.3 Deposit of calcium carbonate crystals from mineral water left in open bottle.

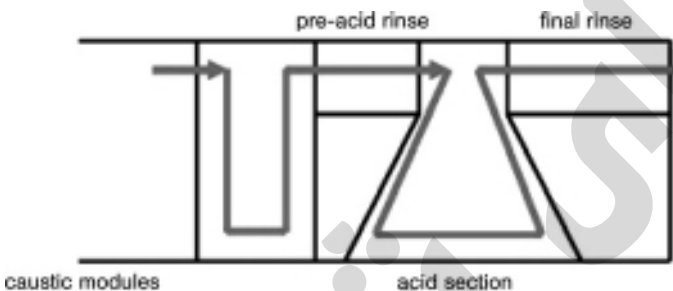


Figure 6.4 A type of acidic section inside the bottlewasher.

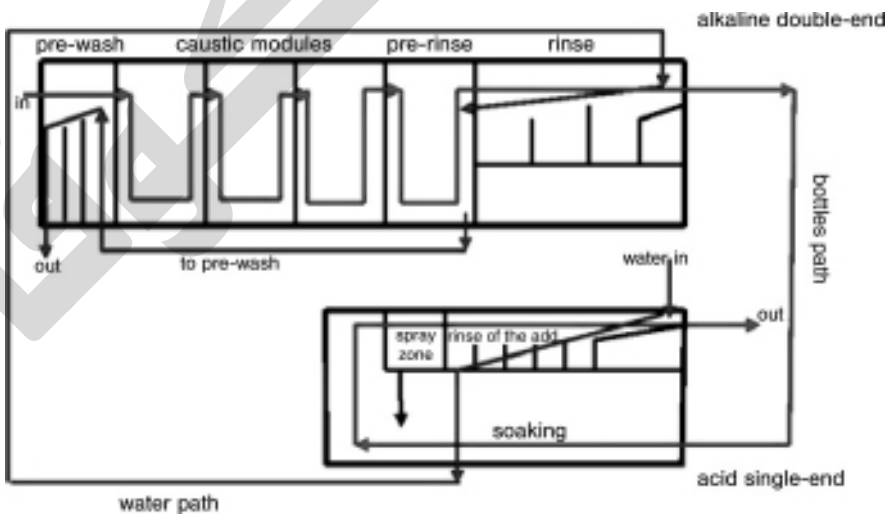


Figure 6.5 Acidic section coupled to the caustic section.

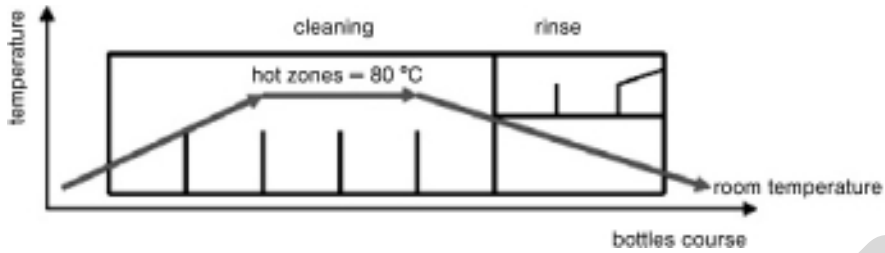


Figure 6.6 Temperature gradient.

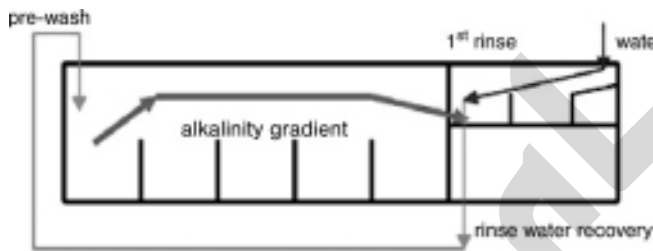


Figure 6.7 Alkalinity and temperature are recovered from the first rinse and re-used in pre-wash.

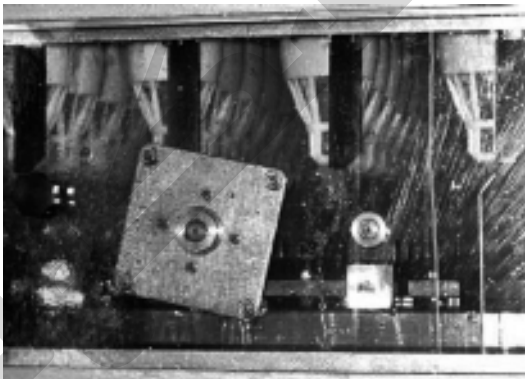


Figure 6.8 Example of spray in bottlewasher.

- **The alkalinity gradient** (Figure 6.7) exists in the modular units in order to exploit as much alkalinity as possible before disposing of it.

The caustic sections contain spray equipment. Sprays play an important role since they provide the cleaning solution with mechanical force oriented toward the inside of the bottle, as shown in Figure 6.8.

Several types of contamination, such as dry organic residue, molds, and larvae, are removed by the aid of mechanical energy. Frequent checks of the spray nozzles enable an effective spray to be kept free of pulped and torn labels, limestone build-up, and broken glass. At the same time, suitable defoamers are needed to suppress foam below a critical level [1]. Foam keeps labels still inside it, slows extraction down, and increases pulping. Foam alters the signal of the electronic controllers (probes and detectors of the solution volume) and causes pumps to cavitate. A bottlewasher is sensitive equipment, the steady condition of which is subject to a complex balance between chemicals and machine management.

6.1

Pre-washing

Pre-washing provides the bottles with the first contact with water coming from the rinse. The rinse carries residual alkalinity and has a warm temperature. Inside the pre-wash, a moderate temperature (~35 °C) protects glass from thermal shock, bottles receive a rough cleaning, and labels undergo the first wetting. As the chemical composition of the pre-wash solution corresponds to the first final rinse, the solution transfers the rinse problems to the pre-wash module (pH condition, tendency to scale, and sequestrant concentration). All these parameters will be discussed in the rinse section. Nevertheless, negative results of cleaning cannot be ascribed to this zone.

6.2

Caustic Zone

The alkaline soaks constitute the zones where cleaning and disinfection are accomplished. As already mentioned, cleaning involves the removal of labels, molds, fly eggs and larvae, glue solubilization, soil removal and dispersion, aluminate and scale control, prevention of pulping of labels, suppressing foam, glass protection, chemical stress cracking, and haze prevention. Each of these will be discussed in the next paragraphs.

The microbiological investigation checks that the bottles are sterile when they come out of the caustic section, and the caustic solution is polluted even if running at high temperature and alkalinity. The microbiology of the bottles usually corresponds to Table 6.1, taken from Ref. [2].

Microbes and spores, on the contrary, continuously enter the running caustic solution. When analyzed, an average of between 2 and 10 ufc/100mL can be detected although it is running steadily (e.g., 1.5% NaOH and 80 °C). The contact time explains this. While bacteria are rapidly killed, spores last long enough to keep them surviving until completion of the microbiological procedure, which starts by decreasing the temperature and neutralizing the causticity. Thus, pollution in caustic baths depends on the continuous contribution of spores from

Table 6.1 To read the table, for example, 71 °C and 9 min contact need 0.5% alkalinity to give sterility. Courtesy of Niven [2].

Contact time (min)	Temperature (°C)					
	43.5	49	55	60	67	71
	NaOH concentration (%)					
1	11.9	7.9	5.3	3.5	2.4	1.6
3	6.4	4.3	2.9	1.9	1.3	0.9
5	4.8	3.2	2.2	1.4	1.0	0.6
7	4.0	2.7	1.8	1.2	0.8	0.5
9	3.5	2.3	1.6	1.0	0.7	0.5
11	3.1	2.1	1.4	0.9	0.6	0.4
13	2.8	1.9	1.3	0.8	0.6	0.4
15	2.6	1.7	1.2	0.8	0.5	0.3

the soiled bottles. The same solution does not in fact show any microbiological activity one hour after stopping the wash.

6.2.1

Modifications Induced by Alkalinity

When alkalinity is related to detergency, it can be divided into four zones:

- pH from 7 to 8.3 → Field of raw water and neutral detergents
- pH from 8.3 to 10 → Calcium salts show the greatest adherent behavior
- pH from 10 to 12 → Sequestrants manifest the greatest difficulty in controlling scale (higher concentrations are required to prevent deposition [critical pH])
- pH above 12 → Less adherent behavior of calcium salts, which form flocs. The strength of the hydroxy ion is so high as to modify everything and promote intense cleaning.

Besides soil and salts deposition, alkalinity also influences the following processes:

- sequestration
- aluminium dissolution
- pulping of labels
- glue dispersion
- new glass bottles
- plastic bottles recovered (REF)
- glass hydrolysis

- carryover to rinse section
- soil and mud from road haulage.

Sequestrants prove to be sensitive to pH. The more the pH rises, the more they increase the sequestering power. While hydrogen ion affects the stability of complexes by replacing ligands, the hydroxyl ion takes a positive part in the coordination bond and contributes to forming and stabilizing the steric molecular structure of the single and complete framework of complexes. However, some metals (e.g., iron and aluminium) preferentially form stable complexes with the hydroxyl ions (OH^-). As sequestrants have difficulty in competing with the ionic strength of the hydroxyl ligands, the caustic solutions promote the hydroxy structure for those metals. It follows that scale prevention is accomplished by dispersing and suspending the hydroxy salt rather than keeping the metal ions soluble (sheer sequestration).

The hydroxyl ions ($\text{pH} > 12$) transform everything into 'hydroxo-macromicelles' aggregated in flocs temporarily suspended in solution. Calcium carbonate coagulates as amorphous hydroxy-carbonate $[(\text{CO}_3)_x(\text{OH})_y]$, calcium orthophosphate as amorphous hydroxy-phosphate $[(\text{PO}_4)_x(\text{OH})_y]$, and aluminium as hydroxyaluminate $[\text{Al}(\text{OH})_4^-]$, and starches and proteins are hydrolyzed and their chains swollen and transformed into an anti-caking material useful for preventing rocky deposits. Thus, theoretically speaking, the cleaning of the recovered bottles (glued labels) could be only accomplished by caustic soda. Starch and casein dispersed from the label glue prevent the hydroxy-inorganic matter from compacting. However, the non-adhesion of the inorganic matter in caustic solution is only a temporary condition. It changes into a compact deposit if left to rest. Moreover, increase in aluminate and foam, label detaching, and mold removal are quite impossible to achieve by anything other than caustic soda. Hence, specific formulated detergents are justified and demanded.

Causticity affects sequestrants. Sequestrants having several hydroxyl groups in a relatively small molecule maintain optimum activity even at extreme pH (>13). Gluconate and ATMP are consistent examples. The molecular structure of HEDP should also be effective, but it represents a strange exception. HEDP loses activity both in caustic systems and in the presence of chlorine, although it should theoretically be stable in both. Conversely, HEDP is the most effective threshold sequestrant for neutral pH (<10).

The graph in Figure 6.9 shows the trend in preventing calcium deposition for some chemicals as a function of alkalinity (Figure 6.9).

Causticity and temperature hydrolyze polyphosphates to orthophosphate. Orthophosphate precipitates hard deposits below the transition pH (<12). The change in pH is typical of the rinse zone in bottlewashers. The alkalinity carryover to the rinse makes the pH decrease down to neutrality. Calcium phosphate deposition is effective in the rinse section.

Aluminium is thermodynamically unstable in alkaline solution. The instability allows the aluminium labels on the recovered bottles to be removed and foil to be dissolved. The solution, with 1.5% alkalinity and at a temperature of 80°C , takes

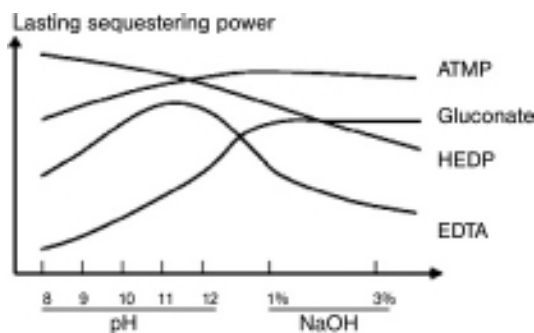
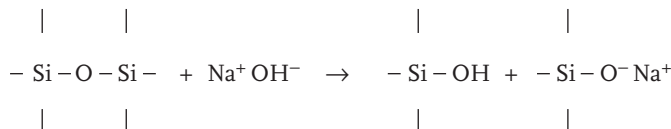


Figure 6.9 Prevention of calcium deposition as a function of alkalinity.

from a few seconds to minutes to solubilize aluminum foils and labels as a function of the weight and of the varnish and dye which cover them. The reaction produces hydrogen, which is scavenged from the machine through funnels to prevent risk of explosion. From stoichiometry, 1 kg of Al consumes 1.48 kg of caustic soda, releases 0.11 kg of hydrogen and leaves 3.07 kg of aluminate (NaAlO_2). Gluconate and polyphosphates help dissolution and prevent the aluminate deposition. Conversely, silicate, being an aluminium corrosion inhibitor, slows down the chemical attack and causes a delay in the label detachment and foil dissolution. Moreover, silicate carries a risk of glass corrosion if it dries on and promotes scuffing. Long stoppage of the bottlewasher can lead to an irreversible haze on the bottles in the presence of silicate.

Although recovered bottles carry soil, labels, and glue, new ones use up more alkalinity. Because of the caustic soda reaction with the film protecting new glass, new bottles might consume up to 0.5% alkalinity more than recovered ones in one day of cleaning. Coatings include tin and titanium oxides, polyethyleneoxide monostearate, polyethylene wax, oleic acid, and graphite [3–6]. Alkalinity slowly solubilizes them (more cycles of cleaning are needed). Several bottling processes use new and recovered bottles in the same machine. A homogeneous spray of protective film on a bottle just molded in a glassworks is crucial to provide the film with stability, damage-free cleaning, and a coating that can be reliably and consistently removed. Figure 6.10 shows the ugly consequence of cleaning due to a wrong spread of the protecting film in the glassworks.

Although glass is one of the most resistant materials, caustic soda and sequestrants slowly but constantly corrode it at every cycle of washing. Alkalinity attacks the Si–O bond and causes depolymerization [7]:



Alkaline ions (e.g., Na^+ and K^+) are extracted (leached) at the glass-liquid interface and leave the outer surface weaker.

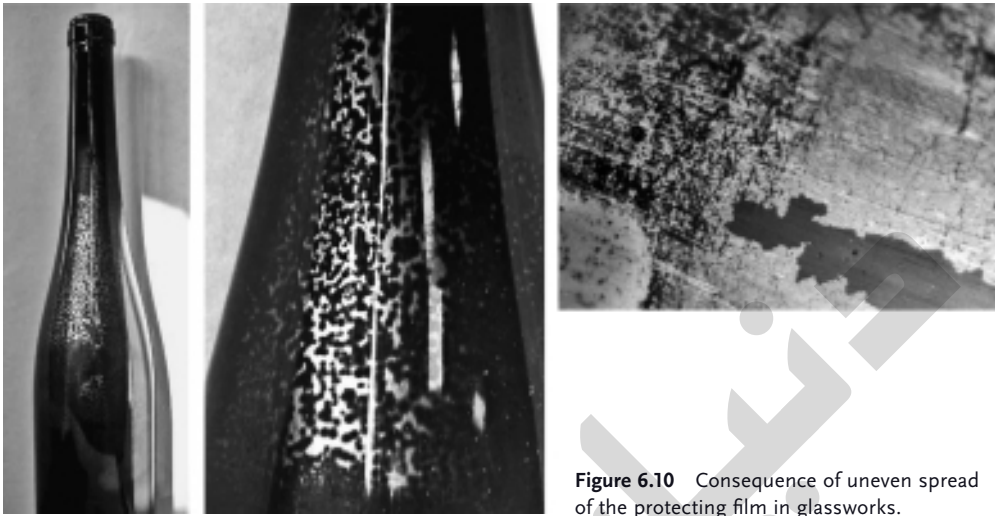


Figure 6.10 Consequence of uneven spread of the protecting film in glassworks.

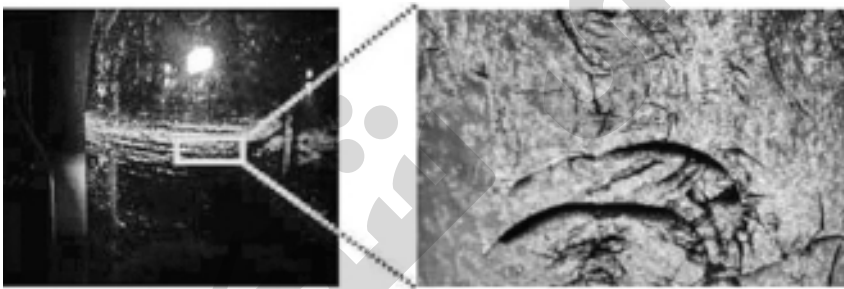


Figure 6.11 Scuffing on glass bottle and its magnification (photomicrograph).

It has been calculated [8] that a one liter bottle immersed in a 0.5% solution of caustic soda at 80°C for a week undergoes a weight loss of ca. 2 g. The leached matter is transformed into silicate sludge, which contributes to dulling the brilliance of the glass. Sequestrants can increase the corrosion rate (e.g., EDTA, STP, and gluconate) or reduce it (e.g., phosphonates [9] and acrylic (co)polymers).

Whereas caustic soda opens the Si–O bond, sequestrants act directly on the polyvalent metals, pull them out of the glass, leave micro-holes, and weaken the surface. The corroded surface undergoes scuffing faster, which makes it look older. EDTA is the worst sequestrant for damaging glass integrity.

Soft water enhances glass corrosion [4]. Even specific inhibitors become ineffective below 5 dF hardness. The combination of chemical attack on the glass ('etching') and mechanical abrasion (bottles running on the track) leads to weakening of the surface and promotes deeper scuffing, as seen in Figure 6.11.

Haze and scuffing diminish the aesthetic appearance of the bottle and shorten its life (even 50% less). Ruf [10], Dullinger [11], and Braune [6] developed the first

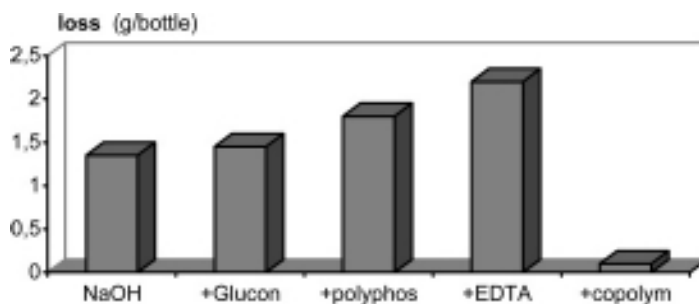


Figure 6.12 Conditions: alkalinity 1%, additive 1 g L⁻¹, 75 °C, 30 cycles. Copolym: acrylic maleic terpolymer 3000 MW.

approach to the prevention of scuffing. They attempted to add an external treatment based on organic polymers (e.g., polyethylene and silicone derivatives) after washing to restore a sort of protective film. The evolution of anti-scuffing technology focused on damage prevention only during the bottle washing. The ability of particular sequestrants to inhibit leaching is now exploited in the caustic modules to preserve glass and keep bottles looking new for longer. Figure 6.12 shows the loss in weight of glass caused by some chemicals.

Etching is considered to be the main cause of scuffing because of its responsibility for increasing the glass porosity and decreasing its resistance to friction and impacts on tracks. Thus, a decrease in glass etching adds brilliance and prolongs the life of the bottle. The surface tension of the bottle can check the etching intensity. Etching promotes porosity and increases surface area and retention of surfactants on glass. Residues of surfactant (even traces) are undesired in bottles. Breweries, in particular, are concerned about their presence (collapse of beer froth). It is calculated that 20 µg of nonionic defoamer can reduce the amount of froth on a beer by 10%. It is therefore crucial to rinse off surfactants as much as possible. Although quantitative procedures cannot directly determine surfactants on the glass, the surface tension can indirectly disclose their presence. The lower the surface tension, the more the surfactants are adsorbed on glass. Comparison of the behavior of bottles in contact with polyphosphate, gluconate, EDTA, and additives containing corrosion inhibitors (e.g., phosphonates and acrylic copolymers) reveals remarkable differences in surface tension after 30 cycles of cleaning, as shown in Figure 6.13.

However, the closer the surface tension is to that of pure water, the more rinsing is required. As a complete absence of surfactants requires practically endless rinsing, many authors recommend values of >60 mN m⁻¹ as an acceptable goal [12].

6.2.2

Label Removal

Label removal is one of the objects of washing and is often crucial to achieving a good cleaning operation. Labels must come off at a precise point in the machine

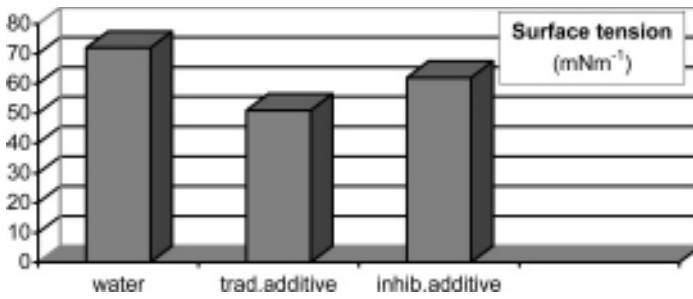


Figure 6.13 Surface tension on bottle.

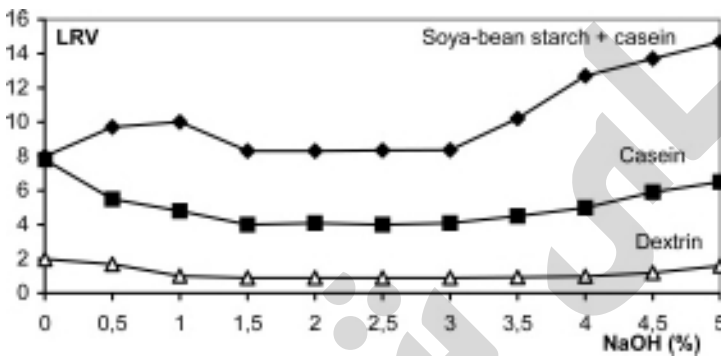


Figure 6.14 LRV = Label Removal Number (minutes), 45°C to magnify differences.

in order to be properly extracted without pulping or dragging. Type of glue, percentage of caustic soda, temperature, quality of paper, dyes, and coatings of wax and varnish affect the detachment process.

The efficiency of label removal is quantified as the LRV (label removal value), which is the statistical result of 15 tests repeated for each chemical and analyzed by the technique known as analysis of variances (ANOVA) as in the Table 6.2.

Glue affects the removal, depending on the mixture of starch and casein, as shown in Figure 6.14.

Figures 6.14 and 6.15 show the peak of NaOH activity between 1.5 and 3%. Above this interval the viscosity of solutions slows down the rate of removal. Only 15% alkalinity and more restores the activity to the value at 2%.

Temperature is one of the key factors in label detachment. Labels are not removable at low temperatures (below 60°C) unless, being labels made of weak paper, they are immediately wettable (not coated) and liable to pulp.

Although the removal of low-quality labels is attained below 80°C, nobody risks temperatures below 70°C as a steady condition. Because of several variables in structure, contamination and microbiology, the detachment follows statistical rules. Statistics indicate that the sensitiveness is so high that the process is affected even by small changes in the cleaning factors. As temperature is one of

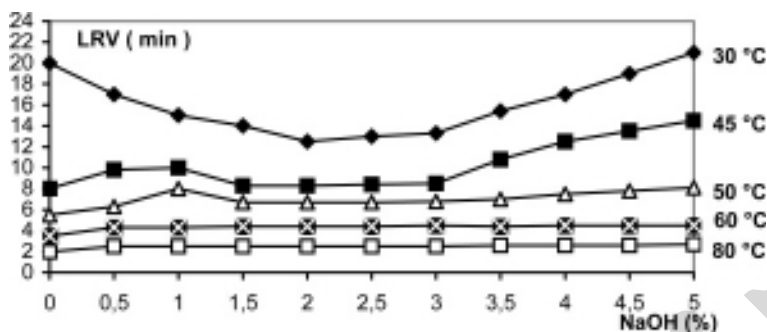


Figure 6.15 LRV = Label Removal Number. Glue = Soybean starch and casein.

the most sensitive parameters, detachment problems at steady temperature (80°C) often imply non-ideal materials forming labels. The manufacturers of labels are asked to

- minimize polluting components, such as heavy metals and halogenated solvents as well as organic components causing high COD
- minimize the resistance to alkali and enhance the penetration of the alkaline solution into the paper fibers
- set competitive prices and keep an acceptable aesthetic quality. [13]

When the behavior of a label is assessed for suitability for the cleaning process in a bottlewasher, the following variables are investigated:

- **Wettability:** time taken by 1% alkaline solution to penetrate the label. Wettability depends on the finish on the label.
- **Resistance of the paper structure:** force applied to tear a label after 5 min immersion in 1% caustic soda solution at 60°C. The resistance depends on the paper thickness, and the cellulose specifically treated to reduce tearing in caustic solution [3].
- **Inorganic coating:** a good label retains its inorganic coating undissolved. While kaolin (silicate coating) contributes to the label integrity, gypsum (sulfate coating) proves to be harmful to the machine management and the glass shine. If a label loses gypsum, this remains undissolved and produces so a thick mud as to endanger the process and the cleaning solution. The coating quality is assessed by a sulfate determination after stirring in 1% caustic soda solution at 60°C for 5 min.
- **Dye, wax and varnish:** dyes affect wettability. A colored portion of label can resist the detachment, being less wettable than the remaining zones [14]. The final layer of varnish and wax provides labels with shine but can also stop wettability. The first instant of soak gives empirical information on wettability: the less the label curls, the more wettable is the coating.

A good label extraction process roughly follows the empirical rule of 9, which is that 90% of labels come out of the first module, 9% of the second and 0.9% of third. It is obvious that the rule of 9 is only a rough guide to understand the concept of extraction. 90% could also mean a number between 60 and 90% and 9% a number lower than the first one.

Pulping releases paper fibers and leads to faster clogging of filters. Clogged filters need frequent manual cleaning in order to keep the bottlewasher efficient. The carryover transports fibers to the rinse. The risk of finding fibers inside the clean bottles increases proportionally to the quantity of fibers. Moreover, pulping from aggressive agents (e.g., EDTA) releases not only fibers and gypsum but even dye and ceramics. Dye and ceramics could include heavy metals such as cadmium (red color), copper and zinc (gold color), chromium (green color), aluminium (silver color), lead, and tin [15]. The use of gluconate, NTA, STP and phosphonate better preserves the label integrity. A less polluted solution is less likely to lead to finding heavy metals in the outcoming bottles and in the bottled drink.

Too resistant paper and slow wettability delay the detachment time and cause the labels to be left on the discharged bottles. Plotting all of this in the Figure 6.16, it is possible to define the quality of a label from its position.

The graph explains one of the laboratory procedures to assess labels. Paper resistance in the range 500–1000 g and wettability <40 s ensure label removal and machine management with the best balance.

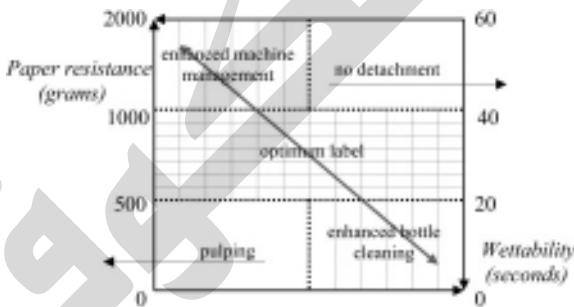


Figure 6.16 A laboratory test to determine the quality of a label.

Wettability is the essential requisite. Differences in wettability lead to considerable differences in time of removal while the paper resistance relates to the label pulping. The solution to the problem of label detachment often consists in asking the label manufacturer either to decrease the thickness of the finish (varnish or wax) or even to change the composition of the outer coating. Figure 6.17 shows the behavior of various coatings.

Some chemicals help temperature and alkalinity to decrease the removal time. In order to make evident differences in time, the test is carried out at low temperature (45 °C) with average labels glued on glass bottles with a blend of casein and soy-bean starch. A slow 180°-alternated course moves the bottle in 1% alkalinity solution prepared from a powder base consisting of NaOH 82% + Na carbonate 16% + defoamer 2% to which 9% of the chemical agent is added. Reporting time (minutes) in decimal form, LRV values are listed in Table 6.2.

Chemicals with LRV values lower than the base help the label to be detached. LRV is lower for chemicals containing nitrogen and for carbohydrates such as gluconate, sorbitol and dextrose. According to the affinity rule, nitrogen compounds are mainly active on proteic constituents (casein) while carbohydrates prefer starches and cellulose. Thus, when labels are wetted, chemical affinity allows the glue to be soaked in quickly.

The higher the percentage of the active agent, the better the label removal. However, the minimum concentration of activity starts near 300ppm. Examples are given in Figure 6.18.

Nitrogen compounds give good performance at low concentration because of their surfactant (wetting) properties. However, while ethoxy amines are foam makers, carbohydrates are not. Among these, gluconate has a remarkable sequestering activity on the dissolved aluminium. It follows that gluconate is considered the most versatile and satisfactory builder for the bottlewashing process. EDTA is effective to detach labels but glass corrosion and label pulping counterbalance its efficacy. NTA supplies a balance: good time of detachment and low corrosivity on glass.

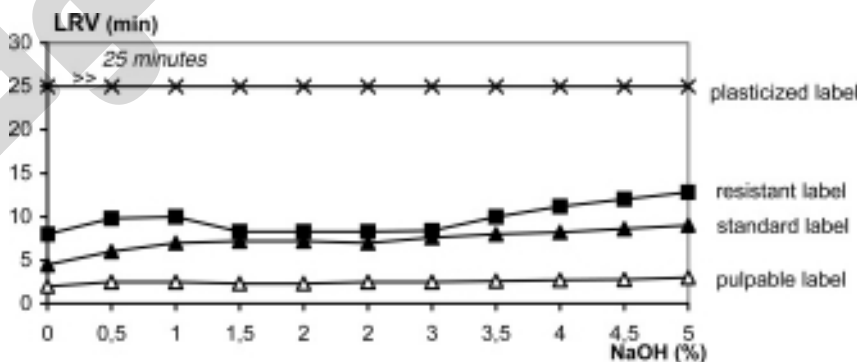


Figure 6.17 Different coatings influence label detachment.

Table 6.2 LRV of chemicals.

Chemical description	Commercial name	LRV
Polyoxyethylene(15)laurylamine	Ethomeen C25	8.00
Alkyl(8–22)aminopolyoxyethylene(11)	Noramox S11	8.48
<i>N,N</i> ,tris(2-hydroxyethylene)- <i>N</i> -tallow-1,3-diaminopropane	Ethoduomeen T20	8.50
Polyoxyethylene(15)oleylamine	Ethomeen S25	8.69
Sorbitol	Sorbitol	8.76
Na gluconate	Na gluconate	8.78
Dextrose	Dextrose	9.01
ATMP	Dequest 2000	9.20
Urea	Urea	9.24
NTA	Trilon A	9.44
Polyoxyethylene(15)tallow-amine	Ethomeen T25	9.46
EDTA	Trilon B	9.48
Na citrate	Na citrate	9.53
EDTMP	Dequest 2041	9.55
2-Butoxyethanol	Buthylcellosolve	9.66
Alkylpolyglucoside	Triton BG10	9.74
Imidazoline amphoteric surfactant	Amphotensit CB	9.94
2-ethylhexyl sulfate	Lumuro! FA40	9.98
Octyl sulfate	Mouillant B4007	10.00
Na toluenesulfonate	Eltesol TA	10.04
Na tartrate	Na tartrate	10.08
Na dodecylbenzensulfonate	Nansa HS80	10.11
Na xylenesulfonate	Eltesol SX93	10.12
2,4,6-Triamino-1,3,5-triazine	Triaminotriazine	10.16
Na dioctylphthalate	Vestinol AH Spezial	10.22
Ethylene glycol	Ethylenglycol	10.25
NaOH 1%	Caustic soda	10.31
Morpholine	Morpholine	10.33
Alkyl(8–22)aminopolyoxyethylene(7)	Noramox S7	10.35
Phosphoric ester	Berol 548	10.35
Defoamer	Erdef 2	10.36
Triethanolamine	Triethanolamine	10.38
Nonylphenol 12EO	Empilan NP12	10.39
Ammonium nitrate	Ammonium nitrate	10.44
DTPMP	Dequest 2060	10.45
Fluorinated surfactant	IIF Fluorate	10.52
Na formate	Na formate	10.53
Fluorinated surfactant	FC 129	10.62
Cetyl oleic alcohol 9EO	Chimipal CO9	10.63
Isopropyl alcohol	Isopropyl alcohol	10.65
Paraffin solvent	Isopar H	10.70
Cocodiethanolamide	Empilan CDE	10.74
<i>N</i> -oleic-1,3-diaminopropane	Duomeen OX	10.82
Oleic-stearic alcohol 10EO	Chimipal OS2	10.85
Block copolymer PO EO	Pluriol 6820	10.91

Table 6.2 (Continued)

Chemical description	Commercial name	LRV
HEDP	Dequest 2010	10.93
Alcohol (13–15) 9EO	Chimipal AC9	10.97
Polyvinylpyrrolidone	PVP	11.09
Alkylacetal	Degressal CD10	11.09
1% Basic solution (NaOH 82% + Na carbonate 16% + defoamer 2%)		11.11
Na tripolyphosphate	Na tripolyphosphate	11.12
2-Methylaminopropanol	2-Methylaminopropanol	11.16
Alkyl(12)oxydiphenyldisulfonate	Dowfax 2A1	11.17
Imidazolinebetaine amphoteric surfactant	Empigen CDR10	11.23
Cocoimidazoline amphoteric surfactant	Miranol C2M/SF	11.25
Phosphoric ester	Triton QS30	11.29
Caprilidicarboxylicimidazolin amphoteric surfactant	Amphoterge K2	11.38
Fluorinated surfactant	FC 170	11.42
N-EO PO defoamer	Triton CF32	11.54
Fatty acid EO	Lutensit AFK	11.55
Na polyacrylate 4500 MW	Acusol 445	11.56
Alkylpolyamide dimethylamineoxide	Aminoxid WS35	11.58
Quaternary ammonium compound	Empiquat BAC	11.62
Phosphoric ester	Chimin P1	11.65
Trisodium phosphate	Trisodium phosphate	11.73
Na hexametaphosphate	Na hexametaphosphate	11.99
Monooleatesorbitan 20EO	Tween 80	12.39
Na pyrophosphate	Na pyrophosphate	12.45
Polyacrylic acid >100 000 MW	Goodrite K722	12.46
Galactomannan EO	DPN 610	12.48
Carboxymethylcellulose	CMC	12.73
Ethylene-maleic copolymer	EMA 91	12.79
Xantane	Actigum CX9	14.27
Phosphoric ester	Hostaphat MDSA	14.38

Given that high temperature means high cost in energy, cleaning bottles at lower temperature was one of the most interesting investigations carried out in the past. It is calculated that a decrease from 60 to 40 °C would reduce the energy requirements by 47% [16]. In spite of this, it was also demonstrated that labels, bio-soil removal and bottle sterility basically depend on temperature. For this reason, cleaning bottles at low temperature remained a good theoretical exercise.

Glue has no practical effect on the label removal at the steady condition of washing. In some case, a type of glue based on starches and acrylic polymer compounds, also known as synthetic glue, can affect the foam control. The

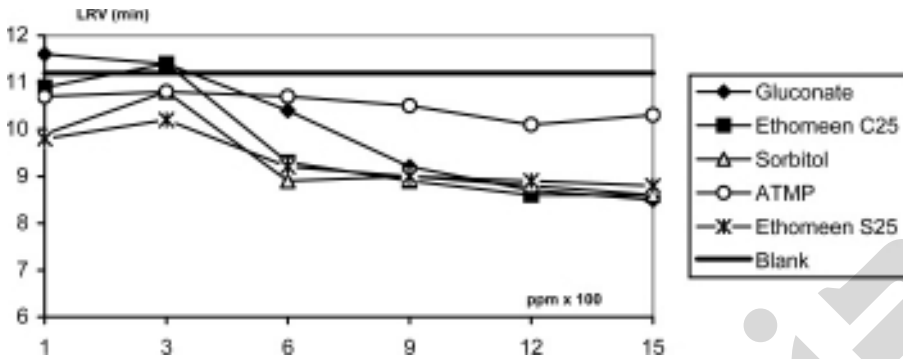


Figure 6.18 Efficiency of label removal promoters.

traditional defoamers have difficulty in suppressing such foam. Particular care in applying suitable detergents and ancillary defoamers is required to wash recovered bottles so glued.

6.2.3

Self-Adhesive Labels

Self-adhesive labels have 6 different layers. Three of them correspond to traditional labels (protective varnish, ink and front paper), and the other three provide the self-adhesive behavior (synthetic adhesive and basic paper covered with anti-adhesive resin). The front structure is plastic in the new generation of synthetic labels.

Stickers and self-adhesive labels suffer by ageing. The more they age, the more the adhesion is chemically irreversible. Therefore, the current chemicals of cleaning have no effect in removing the standard self-adhesive labels even after repeated cycles of cleaning.

The synthetic glue is constituted of caoutchouc and acrylic rubber [14] and behaves like plastic. It does not undergo chemical reactions with the usual detergents [17]. The glue is only sensitive to strong solvents, but unusable in the food industry (e.g., chlorinated solvents), and at temperatures which soften but do not remove the label. The detachment problems even come from small stickers placed on the paper labels. Although stickers cover a small area, they make the contact point non-detachable. For these reasons, self-adhesive labels are typical labels devoted to one-way bottles (non-returnable). In these terms, the traditional synthetic labels cannot be treated in a bottlewasher. Laboratory tests demonstrate that their LRV indicates at least three times the permanence than can be accommodated in the washing machine. Moreover, the best result in removal is accomplished by highly foaming and eco-harmful surfactants such as ethoxyl-kylphenols, which are no longer permitted.

The investigation into synthetic labels suitable for the cleaning in the bottlewasher has led to labels based on plastics sensitive to heat and caustic.



Figure 6.19 Experimental thermoplastic labels (courtesy of Steinbeis Co. and Simonazzi).

Thermoplastic polymers achieve label removal through thermal deformation (shrinkage). This takes off the acrylic polymer adhesive and allows removal in a few minutes. Figure 6.19 clearly shows what happens.

The second type of synthetic sticker is sensitive to causticity and consists of regenerated cellulose film (RCF). Although the method of detachment is similar to that of the thermoplastic polymers, slower shrinkage proportionally delays the removal time.

Hardening after the thermo-contraction was the common flaw of the first generation of plastic labels. The bottlewasher has difficulty in extracting them. New generations of labels remain softer and more compatible with the bottle-washing process, as can be seen in Figure 6.20.

Nevertheless, synthetic labels are expensive. They are regarded as interesting but only practicable on goods having a well-defined high value.

The adhesion of the synthetic glue needs a dry surface. As the carbonation of beverage depends on cold temperatures, the adhesion needs to take place at very low temperatures, but ambient moisture condenses on the bottle and disturbs the attachment. Thus, equipment aiming at keeping containers dry (hot air blowers) is often found before labeling. Example of blowers are shown in Figure 6.21.

6.2.4

Ceramic Labels

The excellent appearance and the peculiar personalization of containers make ceramic labels (AC labels) increasingly popular in the market.

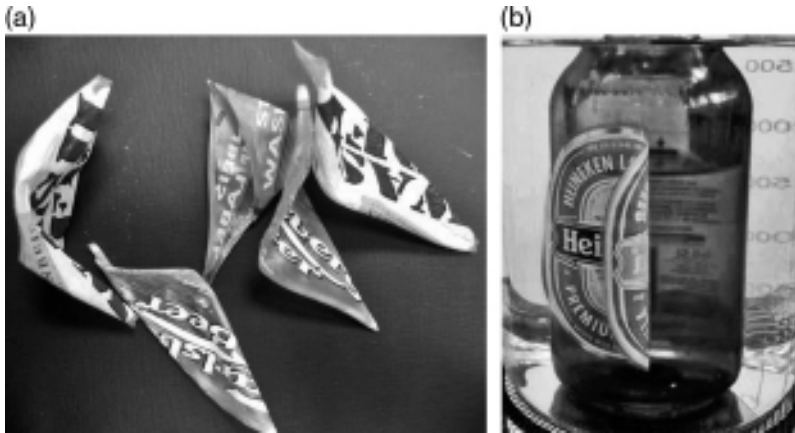


Figure 6.20 (a) Stiff labels after detaching and (b) flexible synthetic label.

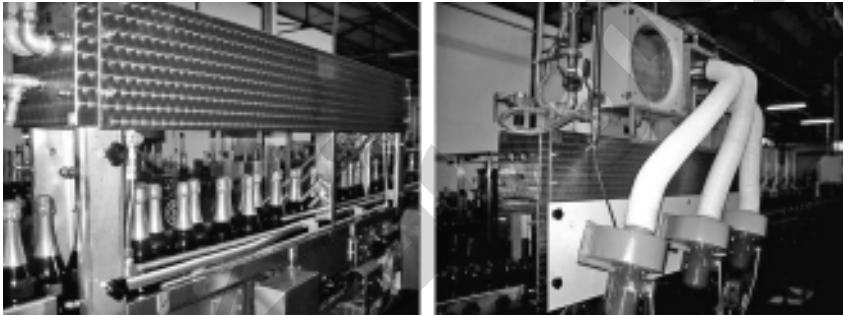


Figure 6.21 Hot air blowers.

One type of bottle is planned for single use (e.g., wine). The chemical treatment before filling is carried out through a single rinse or a combination of rinse and disinfection. In this case, the ceramic label is assembled having in mind simply the lowest cost in manufacturing and without worrying about being cleaning-proof. Conversely, a second type of bottle is intended to be recoverable to be cleaned and re-used. These carry a more resistant ceramic. However, molds grow well on their fertile residual contamination. Molds require strong chemicals to be removed. Although the latter ceramic is suitable to undergo caustic cleaning, strong sequestrants (e.g., EDTA) can pull heavy metals out of ceramics. Traces of solubilized heavy metals are carried over (e.g., lead, chromium) and are found even in the cleaned bottles. This exposes consumers to health danger. Then, either the AC labels have to be changed to ceramics free of heavy metals, or milder detergents must be applied. The use of less aggressive NTA, gluconate, and phosphonate instead of EDTA enables the amount of heavy metals dissolved to be reduced without losing efficiency of bio-dirt removal. Besides mild cleaning, specific sequestering additives to the rinse section have been developed to promote

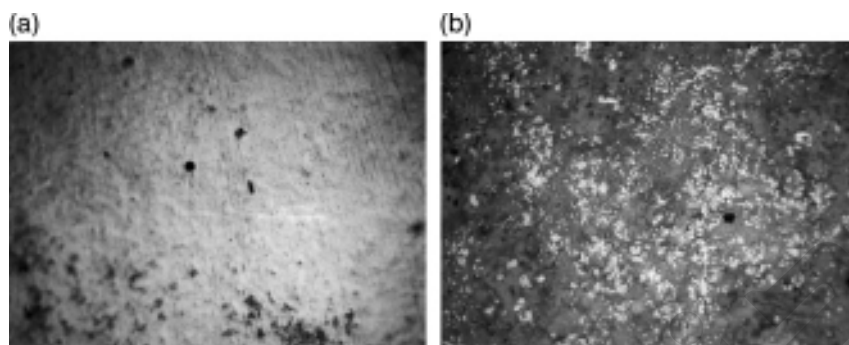


Figure 6.22 (a) Ceramic label protected with varnish (photomicrograph). (b) Same label after a 70 °C and 1.8% alkalinity cleaning.

the thorough removal of heavy metals from the inside of the bottle (e.g., EDTA and sodium salts of citric and tartaric acids are added to the softened rinse water).

Particular applications, such as glass bottles for the aseptic filling of sweet wine, need careful cleaning to prevent excessive foam generation during the filling operation. As the integrity of the one-way bottle is sensitive to temperature and caustic chemicals, ceramics are often protected with varnish. The standard conditions of cleaning (temperature and alkalinity) damage the varnish and cause its partial removal. Besides losing shine, the porosity of unprotected ceramics adsorbs alkalinity. The alkalinity inside the porosity undergoes carbonation (atmospheric CO_2) and becomes visible on the label as whitish marks (sodium carbonate). As a consequence, the unprotected single-use ceramics cannot be washed in caustics. Bottles are either disinfected at room temperature (peracetic acid) or hot-rinsed. Figure 6.22 shows the negative result of the caustic cleaning on the varnish protecting one-way AC labels.

The competition between mold removal and label protection necessitates a balance between chemicals and temperature.

Aging considerably improves the resistance of AC labels. Varnish and ceramics need time to attain a complete and stable polymerization and adhesion. Thus, in order to assure enhanced durability, it is recommended to use bottles with aged ceramics and varnish (sufficient time between manufacturing and bottling).

6.2.5

Mold Removal

Molds are one of the hardest types of soil to clean off the inside of the bottles. The mold hyphae adhere to the surface with glyco-proteinaceous cementing substances and calcium salts. Figure 6.23 shows the tangled hyphae with their organic metabolic substances [18].

Cleaning needs the application of efficient detaching chemicals. However, the more robust the cleaning, the more the glass is etched. In practice, it is proved

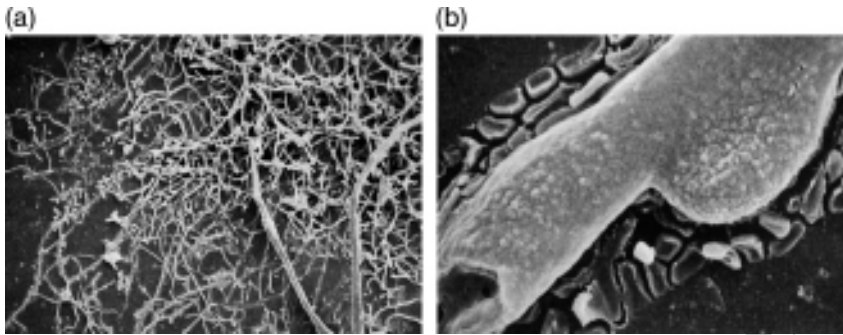


Figure 6.23 (a) Mold on PET and (b) a dried hyphae surrounded by proteinaceous cementing substance. Electron microscopy, courtesy of Diversey Co. [18].

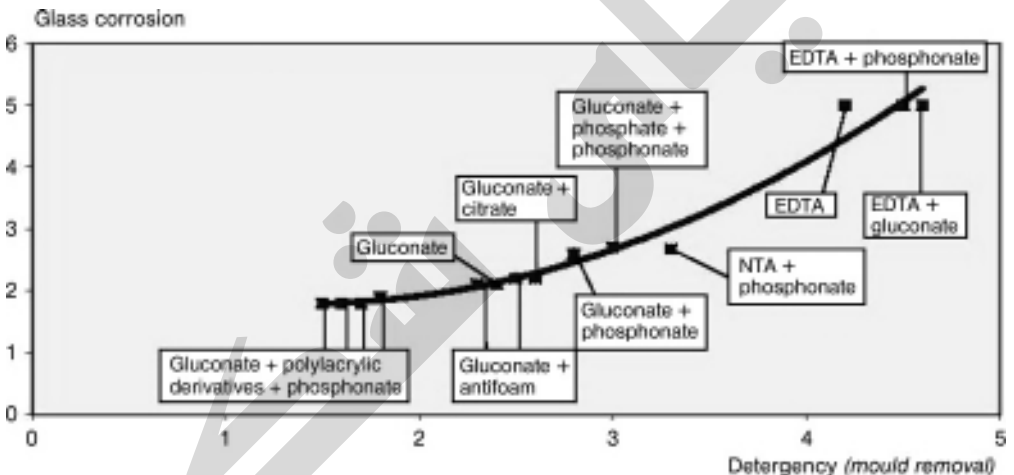


Figure 6.24 Mold removal is directly proportional to the glass corrosion.

that the efficacy in removing a severe contamination of molds is directly proportional to the glass corrosion, as shown in Figure 6.24.

The graph gives the sequestering components in 2% alkalinity solution. Detergency (mold removal) correlates with leakage from the glass, which in turn correlates with the metal binding strength of the sequesterant. Caustic soda and sequesterant promote Si–O–Si hydrolysis (glass corrosion), which enhances the release of mold. As the mold adhesion with glycoproteic compounds from hyphae secretions is loosened when traces of glass are solubilized, mold removal from glass is less problematic than mold removal from plastic (e.g., PET). On the other hand, unlike plastics, glass suffers etching from this, so that haze and scuffing are speeded up. EDTA is at the top position for both detergency and etching. Its strength does not weaken even when it is formulated together with

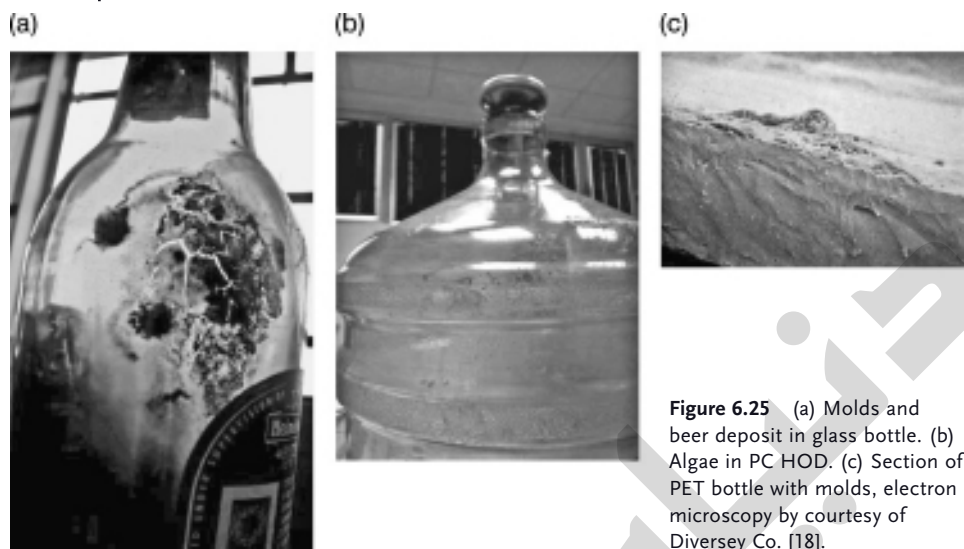


Figure 6.25 (a) Molds and beer deposit in glass bottle. (b) Algae in PC HOD. (c) Section of PET bottle with molds, electron microscopy by courtesy of Diversey Co. [18].

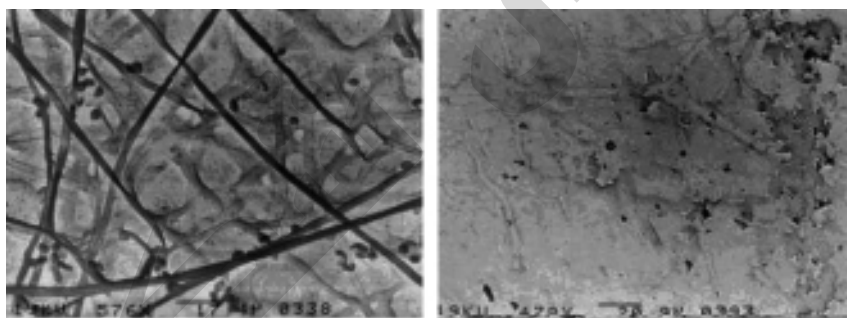


Figure 6.26 SEM view of molds and their tracks. Courtesy of JohnsonDiversey [18].

glass-protecting chemicals (co-polyacrylic derivatives and phosphonates). The difficulty in removing molds (Figure 6.25) is common to all types of bottles (glass, PET, PC, PEN). Troublesome failures of cleaning are difficult to detect before filling even with electronic devices and, therefore, extremely risky.

Molds do not penetrate the surface. They cling to it by a self-protected layer of organic and inorganic compounds (biofilm) and remain glued whether they are alive or dead. Figure 6.26, from the JohnsonDiversey Microbiology Department, shows a biofilm with molds and a portion of surface with microscopic traces (tracks) where the molds were once attached.

When molds are statistically significant in the recovered bottles (usually after long exposure to an open environment), it is worth accepting mild etching of the glass and a little enhancement in haze on PET and PEN in order to prevent the bottles from being rejected because of any flocs of dead mold inside. Figure 6.27

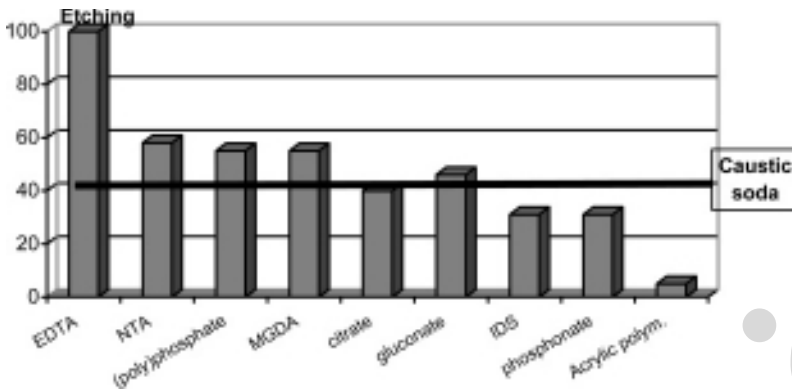


Figure 6.27 Etching strengths of various sequestrants (EDTA set at 100).

compares the etching strength of typical sequestrants used to help caustic soda in bottlewashing.

Safe cleaning, low etching, operational costs and risk assessment are components of a pre-calculated balance for every washing plant.

6.2.6

Plastic Bottles

The transportation benefits deriving from their negligible weight have made plastic bottles (PVC, PET, PEN, and PC) so interesting as to become the prevalent packaging. Their ready acceptance has induced a rapid growth in the use of plastics in the food industry despite the fact that traces of bisphenol A monomer from PC and acetaldehyde from PET are suspected to be toxic to the endocrine system [19].

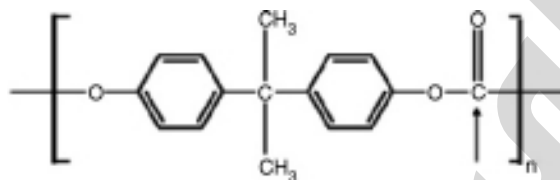
Later, cost and environmental issues have made their recovery and re-use attractive. Investigation of various types of biodegradable plastic polymers is ongoing, these including cellulose derivatives and polymers from renewable sources (e.g., polylactic acid [PLA] and polyhydroxyalkanes [PHAs]) [20]. PLA is particularly attractive as a sustainable alternative to petrochemical-derived products. Although fossil fuels are still needed to produce PLA, the process requires 20–50% less fossil resources than plastics from petroleum. Lactic polymers are more hydrophilic than PET, have a lower density, are stable to ultraviolet light, offer low flammability, and can be bio-adsorbed (medical industry) [21]. PLA is fully compostable in composting facilities, converting into the monomer, which can be converted back into polymers. Alternatively, it can be biodegraded in water. PLA releases carbon dioxide and methane during this process.

PET currently remains the main plastic, although PEN gives better performance, as the Table 6.3 indicates [22].

PEN containers provide superior mechanical resistance to abrasion and haze, do not suffer stress cracking in contact with chain lubricants [23], prove less

Table 6.3 Tests of plastics for use in bottle manufacture (courtesy of Centurioni [22]).

Parameters	PEN	PET
Permeability to O ₂ (cm ³ μm/m ² /day/ate) (film = 25 μm)	500	1400
Permeability to CO ₂ (cm ³ μm/m ² /day/ate) (film = 25 μm)	2400	8500
Permeability to H ₂ O steam (g/m ² /day) (film = 25 μm)	6.7	21.3
Monomer extraction with chloroform 1 h 23 °C (mg/m ²)	0.8	20
Monomer extraction with chloroform 15 h 23 °C (mg/m ²)	3.3	100
Contact angle (°) H ₂ O in air	70	70
Adhesion to aluminum (peel test) (g/inch)	120	110
Specific gravity (g/cm ³)	1.36	1.40
Average refractory index	1.67	1.61
Water adsorption (%)	0.4	0.5

**Figure 6.28** Ester of 2,2-bis(4-hydroxyphenyl)-propane (Bisphenol A) and carbonic acid.

permeable to oxygen and carbon dioxide, and are safe from the point of view of monomer extraction. In spite of this, cost and availability of 2,6-naphthalene-dicarboxylic monomer currently limit the spread of PEN.

Polycarbonate (PC) bottles have already been in use for several years as containers for milk, yogurt, and other occasional applications. At the same time, a specific configuration of returnable containers for non-carbonated water was developed and well accepted in the market (5 gallons HOD [20 liters]). Polycarbonate is an amorphous and crystal-clear thermoplastic polymer with almost 90% light transmission, the structure of which is given in Figure 6.28 [24].

It produces containers with a brilliant appearance and permits optimum control of cleanliness during filling and packaging. The ester carbon is the weak point of the structure, being accessible to caustic attack (OH⁻), which disrupts the polymer. The damage leads to haze and stress cracking. Figure 6.29 shows the layout of an HOD washing machine [25].

The different typologies of plastics have similar problems of cleaning. Hence, the investigation on PET can be also applied to the others, which differ in being more sensitive to one aspect compared to another. For instance, PC undergoes more rapid stress cracking than PET, while PEN is far more resistant.

Figure 6.30 show the molding process (adapted from Ref. [26]).

The sequence (Figure 6.31) starts with ‘candles’, which are heated and blow molded. The bottles formed are then ready to be filled or warehoused.

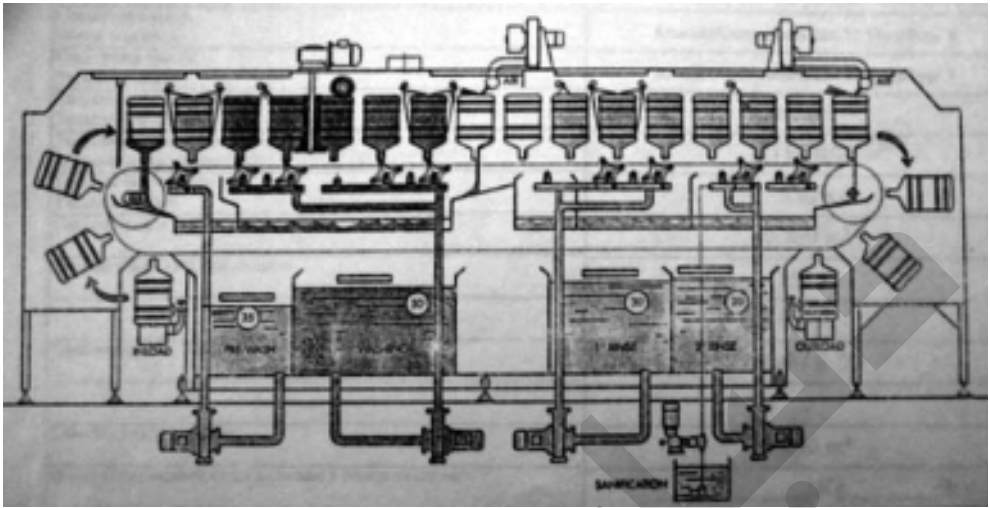


Figure 6.29 Layout of an HOD washing machine.

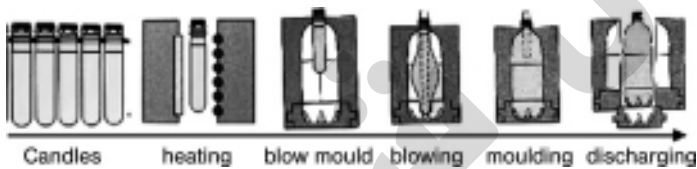


Figure 6.30 Blow molding process (Courtesy of Kronos [26]).

When PET degrades, several events happen, mainly the formation of acetaldehyde and cross-links (gel or fish-eye formation). Acetaldehyde is a colorless gas with a fruity smell. Although it occurs in nature and is agreeably accepted in fruit, acetaldehyde adds an off-taste to the bottled water. It is formed by abuse of the material. High temperatures (PET decomposes above 300°C), high pressures, high extruder speeds (friction), and long periods of barrel residence contribute to the generation of acetaldehyde. When acetaldehyde is produced, some of it stays dissolved in the container wall and then diffuses into the product stored inside, altering taste and aroma. Acetaldehyde is not a problem for fruit juices (already containing acetaldehyde), non-consumables (e.g., shampoo) and strong-tasting drinks (soft drinks). However, keeping water acetaldehyde-free is quite important, because even an extremely low concentration (10–20 ppb) can be detected.

The REF-PET bottlewashing process is broadly similar to the one for glass bottles. The soil is comparable as well as the role of the bottlewashing chemicals. The difference comes from its greater sensitivity to temperature and chemicals, sodium hydroxide included. The temperature is roughly set at $\leq 60^{\circ}\text{C}$, since

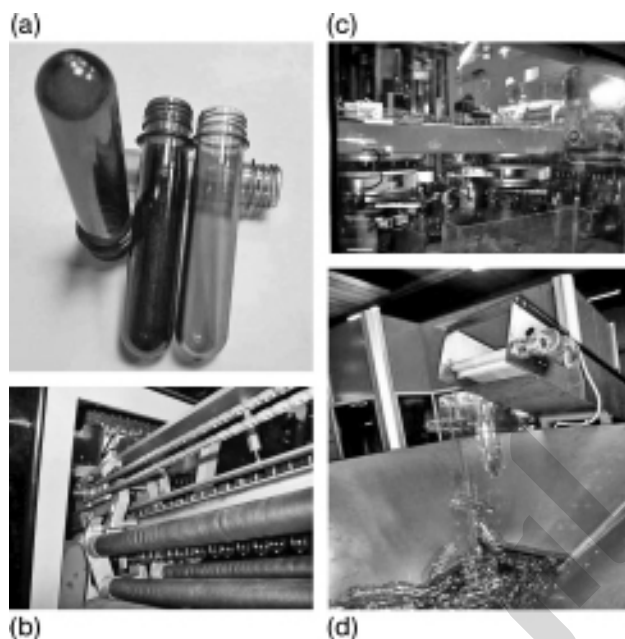


Figure 6.31 (a) Candles, (b) Candles to heating, (c) Candles heating and molding, (d) Discharge of molded bottles.

higher temperatures would affect the structural integrity of the polymer. Polycarbonate needs temperatures not exceeding 62°C and should only be exposed to caustic-free detergents to prevent haze. PC is safe with silicate, nitric and phosphoric acids, and mildly alkaline salts, but is damaged by caustic soda and potash, ammonia, fatty amines, and condensed surfactants. However, and in spite of reducing the container shelf life, more stressed conditions of cleaning (higher alkalinity) are required if contaminations include algae and molds. The turnover of containers is directly proportional to the stress conditions of cleaning and disinfection.

PET suffers from haze, usually caused by caustics, and stress cracking caused by co-formulants such as alcohol, glycols, alkanolamines and, chiefly, condensed surfactants (EO group). Bottlewashers for PET (like glass bottle washers) are affected by foam problems. Defoamers are required although defoaming surfactants are known to be responsible for PET stresscracking. It follows that comprehensive tests must be used to select the best balance among biodegradability, rinsability, defoaming efficiency, haze suppression, and prevention of stress cracking. Tests reproduce the field conditions. Different methods, tailored to types of plastic and sectors of application, are described below.

6.2.6.1 Procedure for Testing for Stress Cracking due to Cleaning Solutions

- At least 10 pressurized bottles are needed.
- Immerse the base of a PET bottle in a 1 L beaker containing about 200 mL of caustic solution prepared with 2.5% caustic soda and a suitable quantity of additive in order to have 250 ppm of defoamer in solution.
- Cover the bottle and beaker with a plastic bag to prevent evaporation.
- Incubate at 50°C.
- Examine the bottles daily for stress cracking.
- Plot the number of failed bottles against time.

An example of a result is given in Figure 6.32.

Bottles remain in contact with the washing solution for less than 10 min per cycle of cleaning. When a tested surfactant has been in continuous contact for two days without causing failures, it is considered plastic friendly.

The attainable number of cycles before failing depends on the type of chemicals. The choice of friendly defoamer influences the bottle turnover. While in the laboratory test cleaning based only on caustic soda theoretically guarantees bottles up to 70 cycles, additives to caustic soda may reduce number of cycles to 50. An experimental result is given in Figure 6.33.

The choice of suitable chemicals can prolong the life of the bottles, even by 50%.

Some defoamers succeed in reducing the haze caused by the caustic attack as if they provide the cleaning solution with a sort of inhibition due to a protective barrier. One of the procedures to assess such behavior is given below.

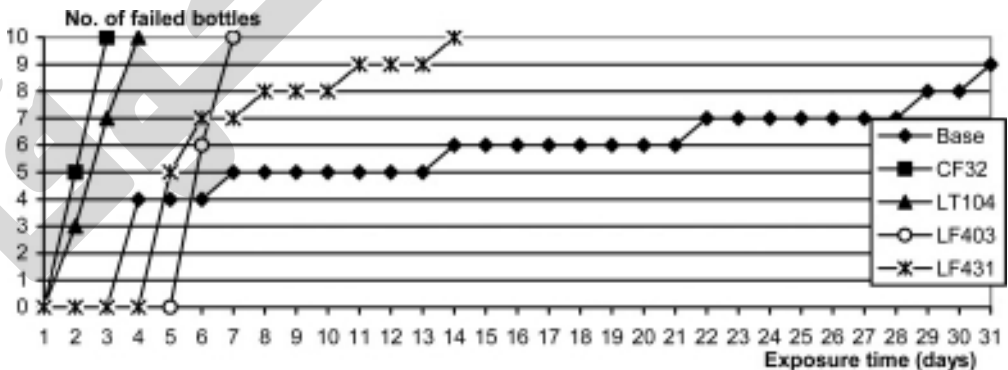


Figure 6.32 Results of test Base = NaOH + gluconate + ATMP + Triton H 66. Surfactants = Triton CF32, Dehypon LT104, Plurafac LF403, Plurafac LF431 (Triton® is Union Carbide, Dehypon® is Henkel, Plurafac® is BASF trademark).

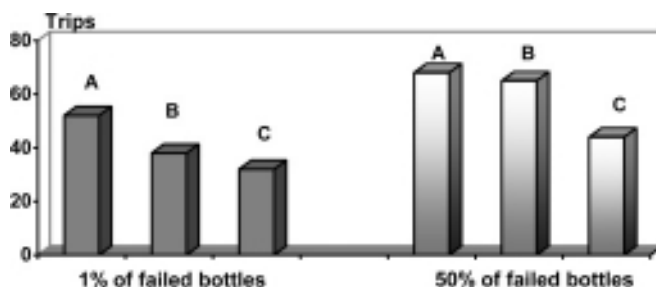


Figure 6.33 Results of test of influence of various surfactants on bottle failure. Number of trips to obtain 1% or 50% of failed bottles. A = Caustic soda B = friendly additive C = aggressive additive.

6.2.6.2 Procedure for Testing for Haze Suppression

- Immerse 6 bottles in 2.5% caustic soda solution (made with softened water) containing 0.7% of additive and 250 ppm of defoamer.
- Set the temperature at 60 °C.
- Remove 2 bottles after 50, 100, and 150 min.
- Examine for white haze on the neck and base of the bottle and compare the results.

The adsorption of specific defoamers on plastic material is beneficial for haze suppression. However, defoamers can add problems to the washing process. Although a bottlewasher rinses glass and plastic bottles in quite similar ways, the time available for the HOD rinsing process is shorter than that for glass. Thus, traces of surfactant could remain inside the plastic containers. For this reason, defoamers are also investigated for their rinsability.

6.2.6.3 Procedure for Screening Defoamer Rinsability

- Immerse a plastic bottle in 2.5% caustic soda solution containing 0.7% of additive and 250 ppm of defoamer.
- Set the temperature at 60 °C.
- Stir for 7 min.
- Remove the bottle, drain, and immerse in a static water bath at 38 °C for 30 s.
- Remove the bottle, drain, and immerse in a static water bath at 22 °C for 30 s (perform rinsing without agitation).
- Gently pour 1.5 L of carbonated water into each washed bottle, noting any types of foaming.
- Observe
 - whether foam is formed in the bottle during rinsing
 - whether there is a visible residue on the bottle after rinsing
 - whether there is excess foaming when the bottle is filled with carbonated water
 - whether the carbonated water in the filled bottles becomes cloudy.

Table 6.4 Foaming behavior of defoamers.

	Foam during rinsing	Visible residue after rinsing	Excess foam during filling	Haze in filled bottles
Triton® CF32	No	Slight	Yes	No
Dehypon® LT104	No	Slight	Yes	Slight
Plurafac® LF403	No	Yes	Yes	Yes
Plurafac® LF431	No	Slight	No	No
Plurafac® LF221	No	Slight	No	No

Table 6.4 gives some examples.

It being impossible to obtain adequate cleaning with caustic soda only, the combination of chemicals results in haze suppression, stress cracking prevention, rinsability, and defoaming efficiency, leading to a satisfactory balance applicable in the field.

Respect for the integrity of the bottle must not divert attention from the cleaning issues. Thus, a certain decrease in shelf life of the bottle is unavoidable and to be expected in the field. Molds represent one of the most resistant soils in bottling. The cleaning of bottles recovered in the hot season is more difficult because beverages leave residues rich in sugar, starch, and proteins that provide nourishment on which molds grow easily. The cleaning approach to mold removal has been discussed in Section 6.2.5 and is applicable to every type of container.

6.2.7

Exhausted Solution

The decision when to replace the caustic solution depends on different factors. In terms of cleaning efficiency, the life of the caustic solution should be regarded as indefinite, since

- casein, starch from glue, and cellulosic fibers from labels transform the contamination into inert material which does not disturb the cleaning efficacy. The sludge formed is even able to aid antideposition. The additives to caustic soda help dispersion and suspension.
- The equilibrium between dirt and carryover governs the growth of sludge until the amount remains steady.
- The caustic solution and temperature maintain the sterilizing power even in the presence of considerable contamination.
- A suitable rate of rinsing removes all the constituents of the carryover.
- Devices such as filters, centrifuges, and nanofiltration can keep the detergent solution cleaner.



Figure 6.34 Centrifuge added to the caustic bath in mineral water bottling.

Thus, the alkaline bath need never be disposed of. It is sufficient to transfer it to an outside tank just for the time required to remove the broken glass and clean the machine. Afterwards, the alkaline solution is reintroduced into the bottle-washer and the quantity lost is restored. Machines provided with a broken glass collector prolong the operational time even more. Users are nevertheless in the habit of replacing the alkaline solutions. Various suggestions for criteria for deciding when to dispose of or restore the caustic solutions are summarized below.

- Replace the caustic bath after 120–180 h operation. Bottlewashers are usually small plants whose cost in comparison to that of production and disposal is not significant.
- Move the caustic solution to an outside tank, clean the bottlewasher, and re-use the solution. Only a small quantity of liquid is lost.
- Transfer the alkaline bath from one module into another, moving the oldest one to the outside to be purged. After cleaning the emptied module, a new solution is prepared. The old bath purged in the outside tank is re-used to restore all the alkaline modules when operating.
- Provide the bottlewasher with a device (centrifuge, microfiltration, nanofiltration). The caustic solution is purified in a closed cycle (from module to physical treatment to module again). The process is carried out on the operating machine. The caustic solution is only removed when the machine needs to be cleaned (Figure 6.34).

Recovery of the caustic solution is done to save money, pressure to preserve the environment, and to control the waste water process.

6.2.8

Sequestrants in Washing

Alkalinity, which is usually in the range 1.5–2.5%, has $\text{pH} > 13$. Such pH directs the choice toward sequestrants suitable to perform and maintain acceptable

activity in these extreme conditions. As already described, casein and starch from glue behave as generic dispersants and help sequestrants to prevent deposits. Rather than complexing polyvalent metals, sequestrants are used to keep the inert matter and salts dispersed (preventing adhesion), to enhance the detergent activity on molds, insect eggs, and larvae, and to control aluminate and to detach labels. Different classes of sequestrants and suitable combinations of them ensure that they will perform as described.

6.2.8.1 Polyphosphates and Phosphates

The history of bottlewashing sequestration is based on tripolyphosphate in alkaline baths and hexametaphosphate in the rinse. The chemistry and behavior of polyphosphates have been already described (Section 3.4.1). Although polyphosphates do not improve label removal, they provide for threshold and dispersing efficiency as well as a high degree of detergency. Unfortunately, they undergo hydrolysis to orthophosphate. As mentioned (Section 1.1.4.2), orthophosphate is sensitive to pH and, although TSP does not present problem in alkaline modules, it proves to be dangerous in the rinse zone, where it is carried over. The pH of the rinse is lower than that of the caustic, and the amorphous calcium hydroxyphosphate becomes crystalline calcium phosphate and scale. Hexametaphosphate gives the same problem when added to the rinse to prevent limestone. Phosphoric acid, often formulated as a stabilizer in additives to caustic soda, behaves similarly. As STP is not as effective as gluconate in preventing aluminate deposition and detaching labels, STP is customarily blended with gluconate. Tripolyphosphate and gluconate are also used to derust and remove insect eggs and larvae when unacceptable pulping, glass etching, and solubilization of heavy metals do not permit the use of EDTA. Polyphosphates and even orthophosphate (i.e., additives based on phosphoric acid) prevent dull film, white ring and flash spots on bottles when a machine stoppage extends beyond several minutes.

6.2.8.2 Gluconate and Gluconic Acid

Sodium gluconate and gluconic acid have in practice replaced heptonate, glucoheptonate, and boroheptonate in bottlewashing. Gluconate proves to be the real polyfunctional sequestrant for alkaline baths. As described (Section 3.4.3), its efficacy increases and reaches a peak within the 1–3% alkalinity range, where it intensifies sequestration, dispersion, and suspension activity specifically toward aluminium and its salts, label detaching, and larvae removal. Furthermore, it assists EDTA and STP in solubilizing rust from the contamination of bottlenecks shown in Figure 6.35.

Gluconate carryover to the rinse zone promotes a rapid draining of the water film on the outcoming bottles. It contributes to dispersing the water salinity and enhances the glass shine. Citric and tartaric acids perform even better on salinity dispersion and bottle shine, and are therefore components of special additives to the rinse (rinse of traces of heavy metals). However, the decrease in pH makes gluconate less active, releasing those polyvalent metals complexed in the caustic modules. Care is due in setting the sequestrant concentration in the rinse section

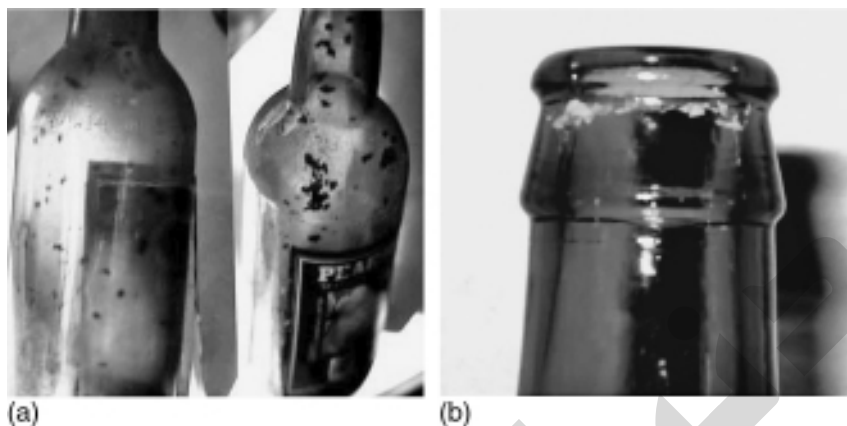


Figure 6.35 (a) Fly eggs and larvae, and (b) rust on neck.

if aluminium concentrates in the caustic solutions and is carried over to the rinse as an aluminium-gluconate complex (Section 6.3.1).

Unlike EDTA, gluconate does not interfere with the etching inhibitors (glass protectors) such as acrylic (co)polymers and phosphonates. Thus, gluconate, in combination with NTA, MGDA, GLUDA and IDS, is an acceptable alternative to EDTA when resolute action against tenacious soils is required without affecting the integrity of the glass. For this reason, gluconate is the fundamental component of primary and ancillary cleaning additives.

When phosphorus-free additives to the caustic solution are asked for, gluconate alone answers the need.

6.2.8.3 Phosphonates

This important group of sequestrants has been discussed in Section 3.4.2. Phosphonates exhibit one of the greatest threshold abilities, which is exploited during the infinite dilution typical of the rinse. In alkaline solutions they normally work in stoichiometric conditions, develop direct sequestration of the metal ions, disperse their salts, and provide detergency. Since ATMP enhances its efficiency at caustic pH, it is suitable for every sector of the bottlewasher, including alkaline soaking and the rinsing section. PBTC and HEDP help or replace ATMP in those cases of low pH in the first rinse (<10) combined with high water hardness (>25 dF). ATMP could precipitate itself as the calcium salt (turbidity zone) in a non-caustic situation.

The association of phosphonates and stoichiometric sequestrants generates the typical carrier mechanism where thresholds allow stoichiometrics to maintain their sequestering capacity even in sub-stoichiometry.

Although the presence of nitrogen places ATMP in the category of molecules promoting label removal, such as NTA and EDTA (Section 6.2.2), its primary benefit remains the threshold sequestration. Therefore, the use of phosphonates

in bottlingwashing is for dispersion of mud and metals in alkaline baths (preventing deposition) and threshold sequestration in the rinse. The primary task of label removal is assigned to gluconate, EDTA, and ethoxy condensed amines.

6.2.8.4 Phosphono-Carboxylate Polymers

Phosphono acrylic and maleic polymers have been synthesized in an attempt to prevent scale in competition with (and as an alternative to) phosphonates and phosphonate-polyacrylate mixtures. They maintain the dispersing and suspending capacity of acrylic polymers and improve their sequestration due to the presence of phosphonic groups. In practice, even if they do not reach the specific efficiency of phosphonates (ATMP and PBTC in particular), the addition of phosphono groups to acrylic (PPA) and maleic (PPAM) polymers confers a notable improvement in scale control, as described in Section 3.4.4. Besides this, phosphono-acrylates prove to be even more stable to chlorine than the equivalent homo-polyacrylates. For all these reasons, they can be formulated together and as an alternative to phosphonates and polyacrylates. Furthermore, they become ideal sequestrants in the rinse when low-phosphorus additives are required. Although PPAM performs a little better than PPA at lower pH (neutral pH), the latter is preferred in the presence of chlorine (for stability reasons). PPA and PPAM do not prevent aluminate deposition, so they cannot replace gluconate in bottlingwashing.

6.2.8.5 Acrylic Polymers

Being aware that a polymer suitable for all purposes does not exist and that polymers have to be tailored to each specific washing condition, the investigation (Section 3.4.4) shows that a molar mass of 4000–5000 is the best compromise. Such a molar mass positively meets all needs and maintains performance adequately at every pH used in food cleaning. Not only homopolyacrylates but also the modified ones work at the peak of activity at 4000–5000 MW. Adding the fact that the 4500 MW homopolymer also provides better stability to chlorine, this currently represents the chemical of reference in food detergency. Generally speaking and according to the overall result and cost-in-use, homopolymers have to be preferred even though they lose part of the inhibition of crystal growth at high temperatures in comparison with the acrylic-maleic polymers [27].

Phosphorus restrictions have led to a search for alternative technologies as effective as tripolyphosphate. This is attained by co-formulating polyacrylates with phosphonates and phosphono-acrylates, the latter mainly as an additive to the rinse.

Polyacrylates assist gluconate and phosphonates in keeping calcium aluminate, calcium phosphate, gypsum, and carbonate mud dispersed.

6.2.8.6 EDTA and NTA

EDTA and NTA are progenitors of the stoichiometric sequestrants. They show the strongest stability constant and are able to compete with the most powerful precipitants for metals. Stoichiometry means a sequestrant effective only when

the sum of the covalent and dative charges exceeds the metal concentration in the system. As metals also come from soil, it is not easy to calculate the overall concentration of charge. Thus, the exclusive use of EDTA and NTA represents a risk. The combination of these with threshold sequestrants becomes mandatory. Owing to its strong activity even on precipitated salts, EDTA acts on the layer of kaolin, gypsum and calcium carbonate deposited on the label structure and weakens its paper fibers (causing pulping). Moreover, AC labels suffer leaching and release heavy metals in solution (e.g., lead, cadmium, chromium and copper-forming dyes). For this reason, it is not recommended to base the primary cleaning on EDTA in bottlewashing. EDTA usually constitutes a secondary additive. The secondary additives are added to the basic systems of cleaning, aiming at improving specific aspects of washing such as the removal of molds and larvae, detachment of labels and solubilization of rust. In a few cases, EDTA represents the extreme attempt to detach very firmly attached labels from glass. On the other hand, the cleaning of refillable plastic bottles (mold removal) benefits from the use of EDTA.

NTA is an alternative to EDTA in all the cases where EDTA is not permitted.

IDS, GLDA and MGDA are alternatives to NTA when customers prefer chemicals completely free of harmful properties (above 1%, NTA products must be labeled as potentially carcinogenic).

Although glass is one of the most resistant materials, it is corroded by caustic soda at every cycle of cleaning. Sequestrants increase the corrosion rate and, among them, EDTA is so corrosive that even specific etching inhibitors do not perform in its presence. Cation extraction (leaching) and depolymerization of silicate (chemical etching) weaken the glass surface. After the chemical attack, bottles more readily suffer scuffing (mechanical etching) as a consequence of mechanical clash and friction on tracks (Figure 6.36).

Etching and scuffing diminish the aesthetic appearance and shorten the bottle life. As EDTA is a proven sequestrant causing etching, it must be used in glass washing only when strictly necessary (e.g., serious problems of removal of molds



Figure 6.36 Scuffing in the life of a bottle.

and larvae). NTA, MGDA, and GLDA occupy an intermediate position and represent a good balance when enhanced cleaning and glass protection are required simultaneously.

6.2.8.7 Polysaccharides and Bentonites

This group of compounds keep surfaces clean by means of an irreversible inertization of the dirt. Rather than performing sequestration, they act as flocculants, dispersants, and anti-redepositing agents. As reported in Section 3.4.6, dirt takes an active role in the cleaning solution. In order to obtain a clean surface, it is crucial to remove it from the system. The soil removal is attained not only by mechanical devices, but also by making the contamination inert and keeping it in this condition, that is, no longer able to re-deposit. As a consequence, dirt is adsorbed into agents that produce a sort of wrapping and is transformed into matter that is indefinitely inactive and suspended in solution. Carrageenans, alginates, xanthans, galactomannans, starches, cellulose derivatives, and bentonites lead to inertization of the soil. Inertization becomes visible as flocs and mud physically removable by centrifuges, settlers, and filters. The treatment makes the cleaning solution last longer, there being no theoretical time limit. Unfortunately, such molecular structures are insoluble and unstable in traditional liquid detergents, though they can be managed in powder detergents and slurries. Instability and difficulty in handling their viscosity do not allow this group of chemicals to be commonly used.

6.3 Rinse Section

The primary object of the rinsing zone is the removal of the caustic carryover from the bottle.

Since warm temperatures, high humidity, and a pH close to neutrality are the features of an ideal environment for microbial growth, suitable disinfectants (chlorine, chlorine dioxide, peracids, hydrogen peroxide, and ozone) are used to keep the microorganisms under control, limiting their growth (bacteriostatic action). A reduced growth rate leads to a relatively low concentration of microorganisms, so that the final potable spray can rinse them off, depending on the statistic ratio between microbial concentration and volume of water entering the machine. Microorganisms are always and inevitably present in the rinse section. Each industrial unit has a typical microbial population surviving in every zone [28], including the rinse. The Figure 6.37 shows examples of the remarkable variety of microorganisms collected in a winery environment.

Frank [29] reported the presence of molds and yeasts in a brewery room (Figure 6.38).

Bottles leaving the caustic zones are sterile, but the series of rinses re-contaminates their internal surface. The planktonic microorganisms do not immediately stick to the surface and are still removable by means of a suitable volume of pure

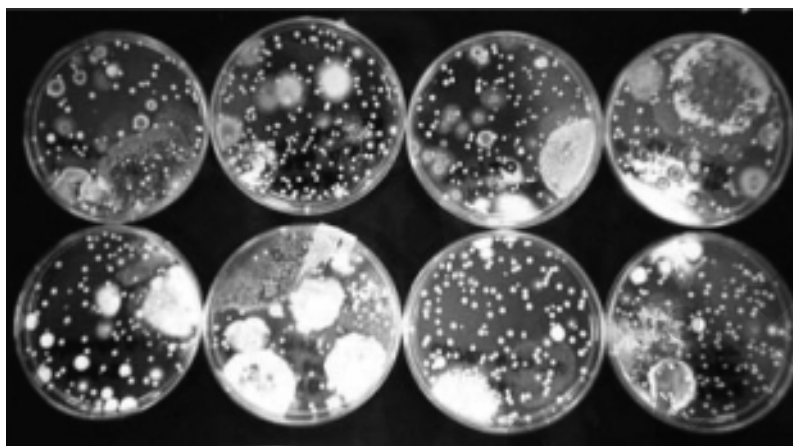


Figure 6.37 Colonies of microbes grown after 1 h of exposure in wine factory environment.

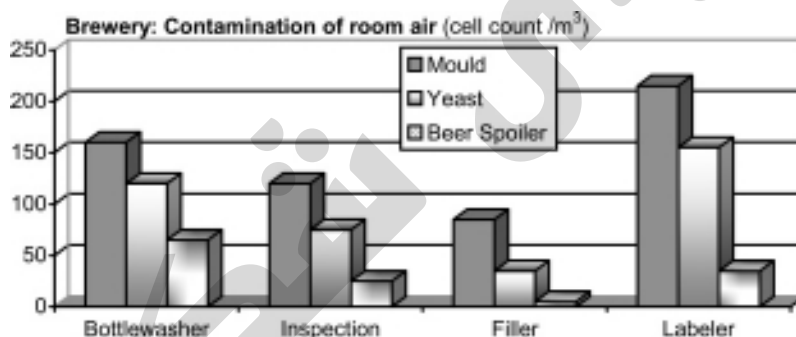


Figure 6.38 Molds and yeasts in a brewery room.

water. The final potable spray succeeds in eliminating them only if they do not exceed a limit which varies as a function of the volume of water per bottle entering the rinse. Disinfectants can never sterilize the rinse section. Their job is to keep the concentration of microbes below the prescribed limit, usually $\leq 3 \log/100 \text{ mL}$.

Carryover causes a pH gradient across the alkaline first rinse (ca. 12 pH units) down to neutrality in the final one (entering water). The gradient is severe and can affect the sequestrants. These are expected to behave initially as stoichiometric sequestrants and finally as thresholds. The first rinse induces precipitation of calcium carbonate, while the neutral one may cause precipitation of calcium sequesterant (transition zone for thresholds). The precipitation of salts causes scaling in the rinse section and clogs the spray nozzles, making them no longer able to remove alkalinity and microbes. Thus, it is wise to keep this zone of the bottlewasher under close surveillance, as it is often responsible for troubles that are mistakenly attributed to cleaning.

6.3.1

Rinse Design and Chemicals Application

In order to reduce the alkalinity carryover to the rinse and the volume of water to rinse it off, it is customary to provide bottlewashers with a pre-rinse module (static bath) whether they are single- or double-ended, as schematically shown in Figure 6.39.

One of the critical phases of bottlewashing is the transition from the caustic section to the rinsing section. Caustic solution (ca. 13–15 mL) is carried over on each one-liter bottle (ca. 25 mL on the whole box). Whether the volume of the entering water is sufficient to accomplish the rinse depends on the caustic soda carryover. Considering that

- the volume of entering water is unchangeable and usually predetermined within the range of 0.3–0.5 liters per bottle, and
- the decrease in pH follows a logarithmic scale (a 10-fold dilution giving a reduction of 1 pH unit),

several bottlewashers are provided with a pre-rinse module to hold up the alkaline carryover. The pre-rinse accumulates alkalinity and is either discharged every day or diluted with fresh water or water coming from the first rinse.

Another expedient to reduce the alkalinity is to add acid directly into the second rinse to neutralize part of alkalinity. Sulfuric acid provides the best balance in terms of activity, cost, and environmental compatibility. Phosphoric acid readily forms a precipitate with calcium. Hydrochloric acid corrodes (chloride). Carbon dioxide adds a co-precipitant (carbonate) to the system and makes the scale worse. The last three chemicals are therefore not recommended as acids to be added to the rinse.

Pre-rinse and addition of acid also allow the sequestrant concentration to be reduced. A decrease in alkalinity shifts the pH below the critical value (<10) so that a lower concentration of sequestrant is needed to prevent scale. In practice, the pre-rinse accommodates different concepts of treatment according to how it is managed. It can be regarded as a static rinse where the water has a constant composition for long periods (renewed every day, every shift at least). Pre-rinse

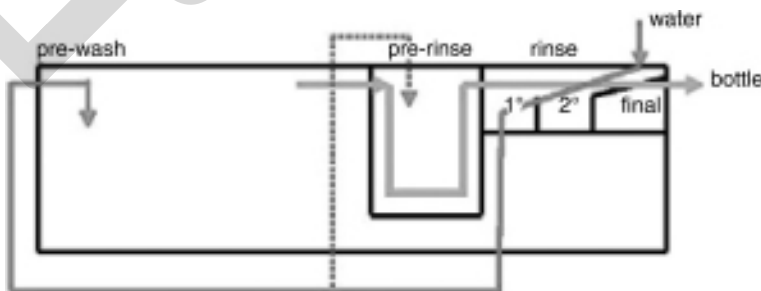
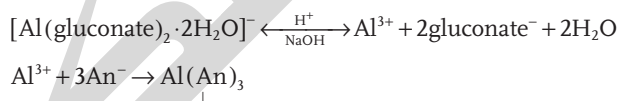


Figure 6.39 Water path in a bottlewasher.

each time starts as raw water and each time requires an amount of sequestrants proportional to the water hardness. Afterwards, its alkalinity progressively rises and, according to the number of bottles passing through per hour, could reach over 0.5–0.8% NaOH within a few hours of running. An alkalinity above 0.5% makes the pre-rinse behave as an alkaline module at the critical pH where scale control is increasingly difficult. Therefore, in order to keep the alkalinity below 0.5%, new water or water coming from the first rinse is continuously added to dilute it, which means changing the static module into a continuous rinse, which needs the same sequestering treatment as the final rinse section. Bottlewasher manufacturers should therefore not regard the pre-rinse as an undefined area segregated from the rinse. They should plan the pre-rinse in the same way as the final rinses and provide for a continuous addition of water from the first rinse. As the first rinse is already treated with sequestrants, the management of the bottlewasher will be unchanged and an equal water saving will be achieved.

The concentration of the sequestering additive in the rinse section not only deals with the water hardness but also with the carryover of metals from the caustic modules. A good detergent usually provides the bottlewashing with gluconate, which is used for label removal and metal dispersion, aluminium in particular. The gluconate complexes with metals become more stable as the alkalinity increases (enolate group activation). When the caustic solution reaches the rinse zone it is diluted, the pH falls, and the stability of the metal-gluconate complex rapidly decreases. It follows that polyvalent cations are released and again become available to react with the precipitant anions and yield scale. If we assume a complex with 2 moles of gluconate per each mole of trivalent metal [30], the following reactions will occur:



No longer sequestered, metals (e.g., aluminium and calcium) will precipitate according to the solubility product of the precipitant anions (An^-), such as carbonate, hydroxyl, phosphate, and sulfate. Precipitation is primarily visible on the bottles, which come out of the rinse dusty and striped. Afterwards, the entire rinse zone becomes covered with a gray-white scale. Thus, an increase in the concentration of threshold sequestrants is mandatory to control water hardness and carryover of metals. A example of calcium carbonate deposition in the rinse and discharge is shown in Figure 6.40.

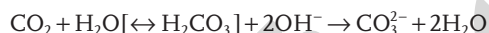
The more the hardness increases, the more the rinse becomes critical. All is related to the water volume and its hardness. The lower the volume of water entering (<0.5 liters per bottle), the more care must be taken over the arrangement of the entire series of rinses including the pre-rinse and the final rinse. Although theoretically the concentration of sequestrant can increase indefinitely, in practice when the sequestering additive reaches concentrations of 400 ppm and over (hardness >30 dF), the sequestrant alone causes the calcium control to be unpredictable and the application expensive. So, there are two possibilities:



Figure 6.40 Limestone in rinse section and discharge (mineral water bottling).

- Soften the water. More equipment (i.e. a softener) is installed and managed.
- Add acid to the rinse. The pH shifts toward neutrality (<10). The decrease in sequestrant concentration follows the pH reduction.

As already mentioned, the cost-in-use directs the choice to sulfuric acid. Carbon dioxide is not recommended although it is widely available (e.g., from a brewery). Although CO₂ decreases the alkalinity



the added carbonate ion is a co-precipitant. Carbon dioxide makes the control of the metal ions unpredictable and non-reproducible. If the emission of carbon dioxide to the environment has to be limited, it can be diverted to the rinse section, bearing in mind that the concentration of the sequestrant will have to be adjusted to suit the new condition.

6.3.1.1 Second Rinse

The second rinse is usually accompanied by the addition of a disinfectant in order to achieve a bacteriostatic effect.

Keeping bacteria below 3 log enables the final rinse to remove them and leave bottles containing only the small microbial charge present in the entering potable water. The potable water bears a microbial charge [31] which grows at an acceptably low rate in the bottles [32, 33], as Rizzo [34] reports in Figure 6.41.

Baldini [35] claims that the microbial charge reaches 2×10^3 and 1.3×10^4 at 37 and 20°C respectively within 6–8 days in glass bottles and even more in plastic ones. In order to keep the charge as low as possible, the microbial state of the outgoing bottles must correspond to the final rinse one, which should be potable, at least. One-way bottles can be a source of foreign microbial contamination, the survival of which depends on the type of microorganisms and the water (natural or carbonated). Guerrieri [36] reports the ability of *Micrococcus spp* and *Penicillium spp* to survive in carbonated and uncarbonated mineral waters at room temperature. Microorganisms survive longer in non-carbonated water and disappear within a few days if the water is carbonated.

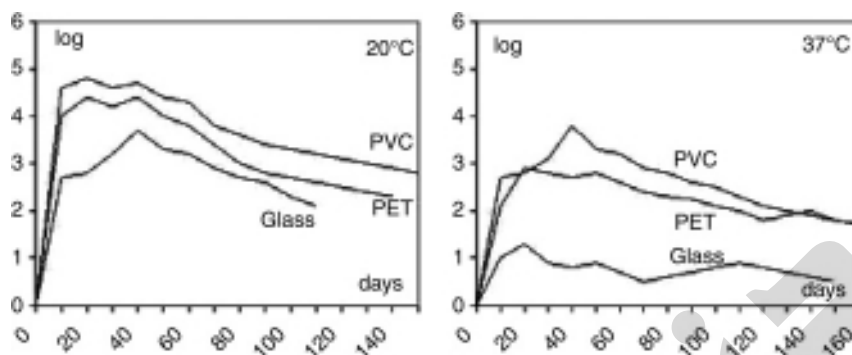


Figure 6.41 Development of the microbial charge in waters bottled in different materials.

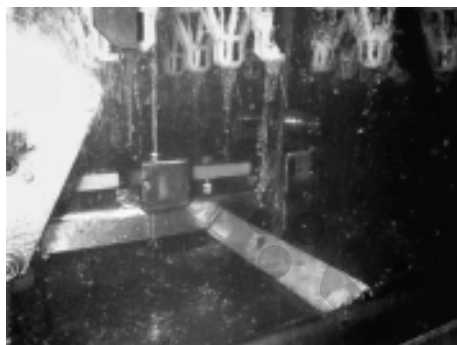


Figure 6.42 Absence of scale in a rinse with ATMP.

The head is the dead space of a bottlewasher, and is highly favorable to microbial growth. If the head of the machine is not regularly disinfected, the addition of a disinfectant to the second rinse could well be insufficient to keep the rinse environment in a bacteriostatic condition. A daily disinfection is recommended.

The head space of the bottlewasher should be provided with a device able to nebulize disinfectant immediately after the daily cleaning or once a week at least. In the absence of an automatic device, the headspace is cleaned and disinfected with foam or spray sanitizing products (e.g., chlorinated alkali or alkaline disinfectant). This good practice will prevent dead spots harboring microorganisms potentially responsible for microbial pollution of bottles.

6.3.2

Sequestrants of Rinse

The rinse employs sequestration without any opportunity to exploit dispersion and suspension (Figure 6.42). Depending on the size of the bottlewasher, the

sequestrants must treat water flowing at a rate of $5\text{--}30\text{ m}^3\text{h}^{-1}$, which continuously renews the rinse conditions and makes pH move rapidly from alkalinity to neutrality. Apart from the historical use of hexametaphosphate, rinse additives now give a balance between efficiency in controlling precipitants and cost of application. Phosphonates, polyacrylates, polymaleates, phosphono-polyacrylates, and their blends provide solutions to every practical demand.

Phosphonates exhibit one of the greatest efficiencies during the infinite dilution typical of the rinse (e.g., ATMP and PBTC). Although (co)polyacrylates, (co) polymaleates and phosphono-(co)polyacrylates perform well in these conditions, they require a concentration higher than that of phosphonates to be effective (Table 6.5).

The superior activity of phosphonate is confirmed when they are blended with polymers. Blends are always less effective than the phosphonate alone, as Table 6.6 proves.

Table 6.5 Tests of rinse sequestrants. Rating: – insufficient, + sufficient, ++ good, +++ excellent hardness control. Condition: hardness 40dF, pH 12, temperature 70°C , 16 hours of rest, glass slides. Raw materials reported to 40% of active matter.

Chemicals (40% active)	Sequestrant (ppm) to control 40dF at pH 12						
	100	200	300	400	500	600	700
PBTC	–	–	++	+++	+++	+++	+++
HEDP	–	–	–	–	++	+++	+++
ATMP	–	–	+++	+++	+++	+++	+++
PPA	–	–	–	+	+++	+++	+++
PPAM	–	–	–	+	+++	+++	+++
PA4500	–	–	–	–	–	–	–
mPA4000	–	–	–	–	–	–	–
PM	–	–	–	–	+	++	++

Table 6.6 Same conditions as the previous table.

Ratio	Sequestrant (ppm)				Ratio	Sequestrant (ppm)			
ATMP:PA4500	400	500	600	700	ATMP:mPA4000	400	500	600	700
0:100	–	–	–	–	0:100	–	–	–	–
10:90	–	–	+	+	10:90	–	–	–	–
30:70	–	–	++	+++	30:70	–	–	++	+++
50:50	–	++	+++	+++	50:50	–	++	+++	+++
70:30	–	+++	+++	+++	70:30	–	+++	+++	+++
90:10	++	+++	+++	+++	90:10	++	+++	+++	+++
100:0	+++	+++	+++	+++	100:0	+++	+++	+++	+++

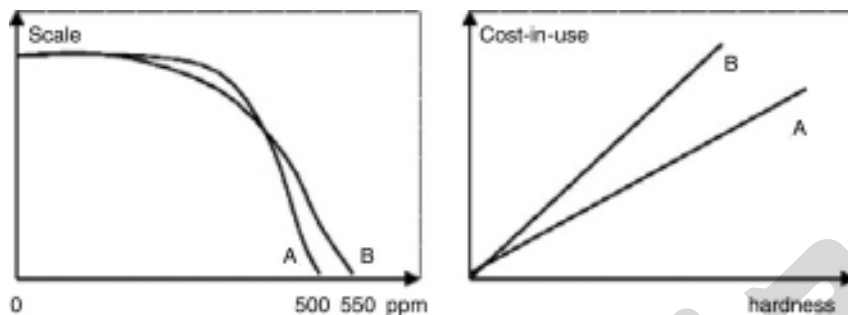


Figure 6.43 Results of tests of phosphonate additives to rinses. Condition: 40 dF, 60°C, glass slides, 16 hours of rest; A: sequestering additive based on ATMP 20% active matter; B: sequestering additive based on ATMP 10% + HEDP 10% active matter.

ATMP is suitable for every sector of the bottlerwasher, both caustic soaks and rinse. It proves to be the most effective phosphonate and offers the best cost-effectiveness balance. When high hardness (>25 dF) is associated with low pH (<10), ATMP falls in the transition zone of activity (turbid zone), where it precipitates out in the form of calcium phosphonates. Hence, HEDP and PBTC are the most suitable phosphonates for rinses of pH < 10. The behavior described would suggest adding HEDP or PBTC to ATMP in order to obtain a sequestering additive suitable for all conditions. The combination (Figure 6.43) in fact solves the precipitation problem but changes the cost-effectiveness ratio.

PBTC performs like ATMP and does not precipitate on moving from alkaline to neutrality. It could replace ATMP in every application. However, PBTC is more expensive, so that the best solution is to split the application.

- Additives based on ATMP are suitable in the majority of the rinses.
- HEDP or PBTC are required to control hardness only in those few cases of low pH.
- Phosphono-polycarboxylates can replace phosphonates when phosphorus is limited.

The sequestrant efficiency depends on pH. Aiming at establishing the right concentration of sequestrant, the whole range of mildly alkaline pH is tested. The result enables an operational graph to be developed from which a suitable concentration of sequestrant can be immediately found. Figure 6.44 explains the concept, and the operational Figure 6.45 gives the result of the test and enables the sequestrant concentration to be derived only from the pH of the first rinse. In this example, a 19 dF hardness is controlled by an additive based on PBTC.

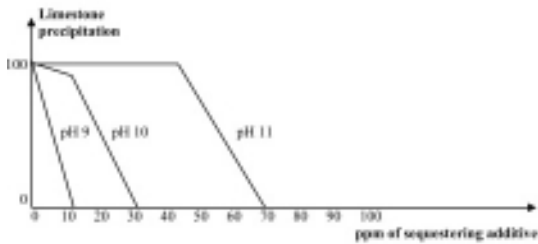


Figure 6.44 Laboratory test for scale prevention.

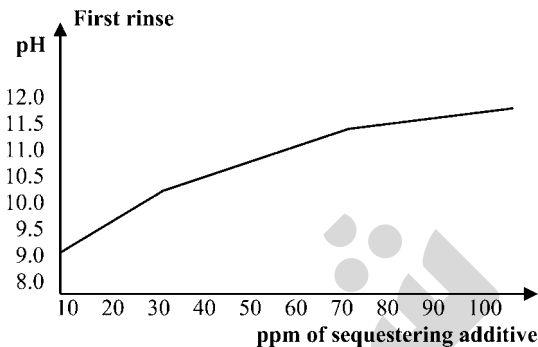
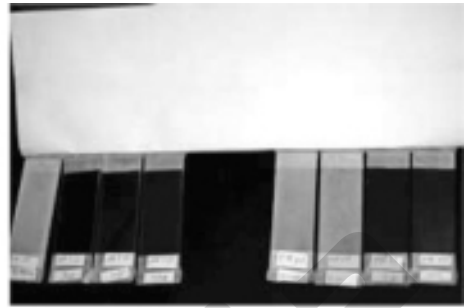


Figure 6.45 Operational graph derived from laboratory test.

6.3.3

Inlet Position

Optimum prevention of scale is frequently achieved by a suitable inlet position of the sequestering additive into the rinse zone. As the water speed increases the deposition rate, the pumps and spray nozzles are the most critical points to protect. Therefore, the correct infeed position is the pipeline before the recycling pump. At this point, the pump and spray nozzles are provided with fresh sequestrant. This approach is recommended in the presence of high hardness. A further benefit in controlling very hard water is achieved by splitting the sequestrant concentration. Roughly 70% should be added to the first rinse and 30% to the second. The feed position is immaterial under non-stressed conditions.

In order to control the cost of treatment, the main object should be to keep the spray nozzles running rather than completely preventing deposits. Periodic descaling maintenance will remove any possible deposits.

When an acid is added to reduce alkalinity, corrosion must be considered. Acid cannot be directly added to the recycle pipeline; the addition must be to the middle of the rinse tanks. This allows the pH to remain above 7 when the acid enters.

6.4

Environmental Impact from Labels

The environmental impact of ceramic labels is well understood, since the most powerful sequestrants (e.g., EDTA) extract and solubilize the heavy metals which they contain. The tendency to save water (minimizing the volume of entering water per bottle) can enable traces of heavy metals (e.g., lead, cadmium and chromium) to remain inside the cleaned bottles at a concentration above the permitted limit (see Subsection 6.2.4). The mandatory limit of heavy metals in beverages is $\leq 10 \mu\text{g}$. A specific technology based on organic acids (e.g., tartaric and citric) and stoichiometric amino-carboxylic sequestrants was developed as a rinse aid. Being the technology based on stoichiometric sequestrants (EDTA), an effective removal of heavy metals needs soft water to be entering the bottlewasher.

Paper labels are believed to be free of environmental impact. However, aluminium, zinc, and copper are often incorporated in them. Aluminium provides labels with silver color and a gold color is produced with brass (copper and zinc).

Rinse removes metals from the bottles, but these metals are continuously disposed of. Thus, the most important chemical treatment of the sewage should be to precipitate these out so as to prevent them from entering the environment. However, such chemical treatment in the bottling industry is uncommon and, even worse, analysts are not aware of the presence of heavy metals. Thus, heavy metals are not analyzed for, survive the treatment processes, and can reach the environment. For environmental safety reasons, bottlers are recommended to move away from metallic colors to organic ones even though these labels may be a little more expensive or a little less attractive.

6.5

Outcoming Bottles

Two points are emphasized:

- Inert components such as clay, quartz, multimetal silicates, sulfates and hydrocarbons constitute the mud and soil of road haulage. Such material does not react to chemicals, whether they are caustics or acids, even if bottles undergo repeated cycles of washing. Washing does not thoroughly remove them but only reduces the amount of contamination.
- The microbial charge is invisible but still present [37].

What happens inside a bottlewasher is visible on the outgoing bottles. It is possible to locate the exact position of the problem by looking at the bottles. Thus, if the bottles

- show an external homogeneous coating of water
- do not react with phenolphthalein
- dry without leaving whitish streaks
- do not have white rings or spots or traces of glue
- do not carry a rust ring
- do not contain inner soil
- leave behind no more than 2 or 3 drops of water on draining
- do not effervesce when just filled
- do not show permanent bubbles on the top (flat water)
- do not contain micro-bodies a few days after filling
- have a potable interior

they are correctly washed and rinsed.

Possible results of inadequate rinsing are discussed below.

6.5.1

Non-homogeneous Coating of Water on the Bottles

Hydrophobic glass, which breaks the film of water, is an indication of two possible problems:

- Insufficient control of hardness in the rinse section. Before being evident, the nucleation of limestone deposition appears as hydrophobic behavior. Check the concentration of the sequestering additive or the good operation of the softener.
- Cleaning of new bottles. A protective hydrophobic layer coats the new bottles (tin and titanium oxides, polyethylene oxide monostearate, polyethylene wax, fatty acid, or graphite). The first cycle of cleaning does not entirely remove it. The residual layer causes the hydrophobic behavior to increase. As bottles are only externally coated, behavior does not affect the result of cleaning.

6.5.2

Bottles React with Phenolphthalein

This indicates inadequate rinsing due to

- Clogging of some spray nozzles. This is one of the most frequent causes.
- Caustic baths too concentrated in alkalinity. Either lower the alkalinity or increase the volume of the entering water or add an acid to the rinse or, sometimes, reduce the machine speed.

6.5.3

Bottles Dry Leaving Whitish Streaks or Foggy Glass

- Insufficient rinse. Bottles react with phenolphthalein.
- Insufficient control of the hardness in the rinse zone. A foggy glass represents the second step of the initial evidence of limestone.
- Dusty bottles could be associated with gypsum, aluminate, or excess of mud in the caustic baths. The problem is usually located in the pre-rinse, which should prevent this occurrence (Section 6.3.1). Undispersed salts become visible on the bottle as a dusty layer or whitish streaks. In order to prevent the already clean bottle from soil redeposition, the pre-rinse cannot be performed without sequestrants and dispersants. Thus, verify that
 - sequestrant concentration in rinse is appropriate
 - pre-rinse is carefully treated
 - caustic baths are not over-concentrated
 - label structure is suitable for the caustic cleaning (pulping)
 - filters are efficient and spray nozzles open.

The appearance of whitish streaks and foggy glass differs from the deposition occurring after a prolonged stoppage of the machine.

6.5.4

Homogeneous White Scale Covers Bottles

This event occurs in the rinse section and is due to the absence of hardness control. A homogeneous whitish scale is the third step of the growth of limestone. Actually, limestone deposition starts as hydrophobic glass (nucleation); the glass then becomes foggy and the scale ends as a homogeneous white deposit. All of this depends on the sequestrant-hardness ratio.

6.5.5

External Non-homogeneous Deposit on the Bottle

Flashes of white spots and rings originate in the caustic section. This is due to the combination of dissolved-dispersed materials and physical-mechanical parameters of the bottlewasher. Salts and inert matter accumulated in the alkaline baths increase the viscosity of the solution, slowing down the draining of the bottles traversing the modules. If left to dry (long stoppage of the machine), the inert matter is unlikely to be re-solubilized. The event becomes more serious in the presence of silicates, aluminate, and gypsum. It is recommended to use silicate-free detergents and good dispersants to prevent leaching.

Each type of detergent generates its own balance between solubilized, dispersed, and suspended soil. The change in the type of detergent sets up a new equilibrium. It follows that the initial period of running could create cleaning problems.

Oliver [38] classifies the chemical composition of the gray film as kaolin (paper), silicates (glass), water constituents, and organic matter (glue). Deposition can be decreased with strong sequestrants (e.g., EDTA, NTA, and high concentrations of phosphonates), and prevented with additives based on tripolyphosphate and phosphoric acid (hydrotropes for defoamers). The efficiency of phosphate in dispersing dirt allows the bottles to remain clean in the course of long stoppages (anti-redeposition).

A concomitant cause of deposits comes from physical and mechanical setup of the machine. High temperatures ($>80^{\circ}\text{C}$) increases label pulping and lead to more rapid drying. Moreover, increasing the distance from one module to the next boosts the formation of deposits on the bottle. In the most critical cases, the addition of sprays at the transition zone helps to solve the problem.

Orange-brownish spots or rings at the bottle neck are indicative of incomplete dissolution of rust. If the number of rusted bottles increases, the addition of specific ancillary additives based on EDTA, TEA, and gluconate enhances rust dissolution. The problem is partially solved by providing the machine with an acidic step. The problem is completely solved by improving the quality of the caps.

6.5.6

Bottles Contain Residues

Calcium carbonate crystals visible inside the bottles identify limestone precipitation. An open bottle in which hard water stands for a long time is subject to limestone deposition. Alkalinity does not dissolve limestone. Hence, limestone must be solubilized in an acidic module after the caustic one.

Soft drinks, beer, wine, and fruit juices provide nutriment for several organisms (fly, larvae, molds). Their metabolism and growth lead to contamination hard to remove. The addition of strong sequestering additives to the caustic solution is mandatory in order to clean in depth and prevent a considerable number of rejected bottles. The hot dry season supports the growth of organisms. Thus, bottles recovered after a dry season need more care than those recovered after a humid and cold one.

Label fibers and flocs, visible in the bottle after filling, reveal either label pulping (fibers) or inadequate cleaning (mold).

6.5.7

Bottles Drain Leaving More than 2 Drops of Water

The more water remaining in the bottle, the more the microbiological risk increases. Bottles containing more than 2 or 3 drops of water after draining run into the microbial risk. The excess of water results from

- Washer speed faster than the time allowed for the bottles to drain.
- Low temperature, which leads to a thicker layer of water and slower evaporation.

- Type and concentration of sequestrant in the rinse. Although the main purpose of the sequestrant is the prevention of the deposition of limestone, sequestrants also help water to drain down and bottles to shine. It is thereby recommended to add a few ppm of sequestrant even if the rinse water is softened.

A suitable speed of the bottlewasher, a good temperature gradient, and an accurate concentration of sequestrant help in minimizing residual water and microbial risk.

6.5.8

Bottles Sparkling when Just Filled

Organic soil and crystals make a solution of carbon dioxide unstable. Organics left behind after cleaning, limestone in the rinse, and foam in the bottlewasher have to be investigated. Surfactants disturb the solubility of carbon dioxide in beverages. As foam is rather difficult to rinse off the inside of the bottle, even traces of defoamer destabilize the dissolved carbon dioxide. Traces of surfactant are also evident from persistent bubbles on the top of non-carbonated water. Surfactant carryover endangers the longevity of the froth on beer.

More effective defoamers and increase in temperature solve the problem.

6.5.9

Just-Filled Bottles Contain Micro-Bodies (or Some Time After Filling)

Organic soil in the form of layers, molds, and cellulose fibers are not thoroughly cleaned or rinsed off. Being micro-bodies, they pass the initial controls, even the electronic eye. Afterward, the dissolved carbon dioxide detaches them from the glass, and, when removed, they are visible in the bottle as moving flocs. Optimization of the overall process and great care in the removal of mold and labels are mandatory.

6.6

Microbiological Condition of a Bottlewasher

The microbiology of a running bottlewasher is complex. The important features are listed below.

- A bottlewasher sterilizes bottles, but is itself a polluted machine.
- Caustic baths are not sterile (the first one, at least). When running, they kill bacteria, yeasts, and molds, but spores take a long time to kill. The microbiological analysis on a running alkaline bath detects microbes developed from spores, but if the solution is allowed to stand for a short time no microbes will grow (no soiled bottles are added).

- Rinse and headspace prove to be the most critical zones where the microbial charge settles and grows freely. Warm temperatures, moisture, and moderate pH promote the growth.
- Bottles leaving the caustic sections are sterile. As they pass through the rinse section, the bottles are flushed with water carrying a dispersed microbial charge. The potable water of the final rinse performs the task of removing this charge. As microorganisms are temporarily in a planktonic condition (not yet attached to the surface), the rinse obeys statistical rules. This means that the removal of the microorganisms requires a volume of water proportional to. As the volume of the rinsing water per bottle is fixed, the concentration of the microorganisms must be kept below the level which allows them to be rinsed off. If microorganisms increase, either the volume of water must be increased or the microorganisms must be reduced. Thus, a disinfectant is added to the second rinse. Usually the ratio between the volume of water and the logarithmic concentration of the microorganisms is in the range 0.3–0.5 liters per one-liter bottle in the presence of $\leq 3 \log/100 \text{ mL}$.
- The headspace of the bottlewasher is the main source of microbial pollution. The head surface needs disinfection every day and cleaning every week, at least.
- If microbial pollution is detected in the washed bottles, various tests should be carried out in order to determine its exact origin:
 - Check the microbial charge in the final rinse water.
 - Check the microbial charge in the bottles before their discharge.
 - Check the microbial charge in the bottles just discharged.
 - Check alkalinity, temperature, and time of contact in the caustic zones (sterilization parameters).

The above investigation will detect the cause and indicate the most suitable preventive action (sterilization parameters, biocide, and bottlewasher head).

The treatment of one-way bottles is by rinse and disinfection in a very short time. Different types of equipment are available, from the simplest (water spray only) to very complex automatic aseptic fillers providing cleaning, sterilization, and filling in a single unit (CAF technology, see Section 6.9 below). Figure 6.46 shows examples.

The handling of the bottles and water used in the process can be equally responsible for microbial pollution. An example of contamination of a bottle with monocellular algae from biofilm in the pipeline carrying spring water is shown in Figure 6.47.

Unpredictable pollution endangers consumer safety and the reputation of the bottling company. Every step in bottling needs extreme care in the processes of cleaning and disinfection.

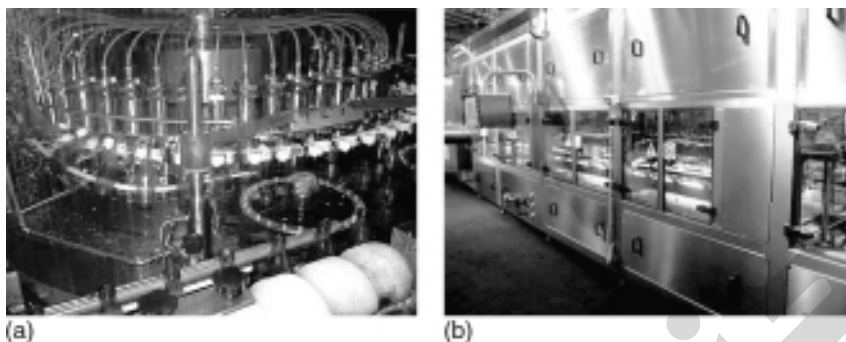


Figure 6.46 (a) Simple equipment to rinse one-way bottles and (b) example of cold aseptic filling unit.

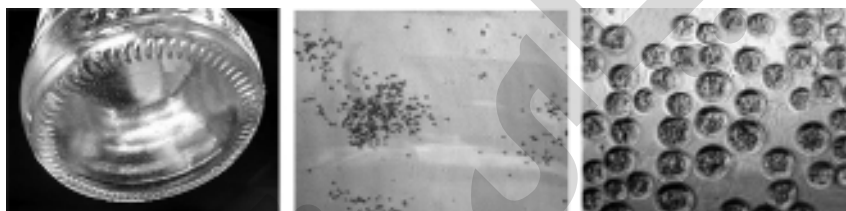


Figure 6.47 Noncarbonated water 4 months after filling.

6.7

What Can or Cannot Be Cleaned

The types of contamination of returnable bottles are well known and are listed below.

- old labels
- old labels with mold
- sand and dust from atmospheric events
- sand and dust from extraordinary events
 - (e.g., desert sand and dust)
- mud from transportation
- cement and wall paint
- organic layer and mold
- insects, larvae, and fly eggs.

What kind of soil is removable in alkaline wash?

What kind of soil is removable coupling alkaline and acidic wash?

What kind of soil is impossible to remove through the chemical process?

The answer to the questions depends on detergents, cleaning procedures, and chemistry of the contamination.

6.7.1

Removable Organic Soils

Molds, insects, larvae, fly eggs, labels, molds on label, glue, and the dried organic layer from a beverage in principle constitute varieties of organic contamination which can be washed away with appropriate chemicals and procedures. Figure 6.48 shows examples of removable contamination.

This type of contamination can be successfully washed away using additives based on EDTA, NTA, GLDA, MGDA, and IDS, or with gluconate, phosphonate, and tripolyphosphate. Hydrogen peroxide added to the recycling pumps enhances the removal. Examples of procedures for mold removal are given in Table 6.7.

MGDA, GLDA, and IDS can replace NTA. The pressure of the spray is crucial to cleaning. The mechanical force supplements the chemical action and is often the key factor. Hence, the bottlewasher pressure should be as high as possible.

Table 6.7 Examples of procedures successfully applied in mold removal.

Alkalinity	2%	2%	2%	2%
Temperature	80°C	80°C	80°C	80°C
Time of soaking contact	8–12 min	8–12 min	8–12 min	8–12 min
Primary additive based on	EDTA 0.4%v/v	NTA 0.4%v/v	NTA 0.4%v/v	NTA 0.6%v/v
Secondary additive based on	EDTA 0.2%v/v	EDTA 0.4%v/v	Gluconate 0.4%v/v	
Pressure of spray in bottle	1.8–2.1 atm	1.8–2.1 atm	1.8–2.1 atm	1.8–2.1 atm



Figure 6.48 Examples of removable contaminations.

6.7.2

Inorganic Soil Removable with Acids

Carbonate, silicate, environmental dust, transportation dust, and sand constitute the various types of inorganic soil. Inorganic soils are inert to alkalinity and cannot be removed in the caustic modules. Carbonate (limestone) reacts with acids and is chemically dissolved, while the remainder are inert to acids. Mechanical action (spray pressure) reduces but does not thoroughly remove such contamination. As manual cleaning is obviously not applicable, what cannot be chemically attacked cannot be practically washed away. Figure 6.49 shows examples of inert contamination which leaves bottles dirty even after several cycles of cleaning.

Cement, mud, excessive dust, and sand are not removed even in a bottlewasher including an acidic step. Acidic cleaning acts only for a few moments (when the carbonate component is dissolved and carbon dioxide is released). Bottles containing these inorganic soils must be disposed of.

6.8

Concepts of Problem Solving in Cleaning Bottles

Whatever bottles may be made from (glass or plastic), cleaning them requires a knowledge of the basic problems of a bottlewasher. The following concepts and basic information about the plant should underlie the management skill needed for cleaning and disinfection:

6.8.1

Glass Bottles

- gradient of temperature not exceeding 30°C from one section to the next, especially in the cold season, so as to prevent breaking of glass



Figure 6.49 Examples of inert nonremovable contamination.

- correct ratio between alkalinity, temperature, and time of contact with the caustic solution, so as to provide sterility (Section 6.2)
- presence or absence of molds inside bottles, so as to select a suitable additive for cleaning (look at the type of beverage)
- quality of labels, so as to select an additive with enhanced removal efficiency
- aluminium on labels/glass, so as to decide on an additive with a high content of gluconate
- level of foam, so as to select an additive with high or low content of defoamer (nonionic surfactants management)
- pulping and fibers carry-over, so as to decide for an epycresis step
- type of treatment available for the waste solutions (environmental care), so as to be able to select either a complete additive or two additives one of which free of defoamer (separate addition)
- long dwell times of bottles inside the caustic section (even one night), so as to be able to select an additive to prevent dusty and white deposits on glass
- water hardness, so as to decide how to manage the rinse section
- disinfectant addition to the rinse, so as to keep the microbial charge below the concentration which allows the entering water to remove the planktonic microbial charge (Section 6.6)
- percentage of scaled-up insides and/or rusted necks of bottles, so as to decide on the acidic step
- preserve the bottle shine with specific additives in order to obtain bottles looking like new for a longer time (reducing scuffing)

6.8.2

Plastic Bottles (PET, PEN)

- temperature not exceeding 62°C, so as to prevent deformation
- alkalinity not exceeding 1.5%, so as to reduce haze
- presence or absence of molds inside the bottles, so as to select a suitable additive for cleaning
- selection of an additive formulated with a suitable nonionic defoamer/wetter, so as to decrease haze and prevent stress cracking (Section 6.2.6)
- level of foam, so as to select an additive with high or low content of defoamer (nonionic surfactants management)
- type of treatment available for the waste solution, so as to select either an additive complete with defoamer or two additives one of which free of defoamer (separate addition)

- water hardness, so as to decide how to manage the rinse section
- disinfectant addition to the rinse, so as to keep the microbial charge below the concentration which allows the entering water to remove the planktonic microbial charge (Section 6.6)
- select a suitable lubricant for tracks in order to prevent stress cracking (low foam and specific nonionic surfactants)
- always ask for an approved additive.

6.8.3

Plastic Bottles (PC-HOD)

- Temperature not exceeding 60 °C, so as to prevent deformation.
- Alkalinity not exceeding 0.5%, so as to slow down haze formation.
- Presence or absence of molds/algae inside the containers, so as to remove soiled containers from the normal cleaning process. The short time of contact with the cleaning section does not allow the cleaning to be as rigorous as that needed when molds and algae are present.
- Dispose of or soak the containers soiled with mold/algae.
- Use detergents free of surfactants in order to allow the container to be thoroughly rinsed. The rinse section does not have enough time to remove surfactants.
- Avoid detergents and disinfectants based on chlorine so as to prevent stress cracking and haze.
- Disinfect with peracetic acid, hydrogen peroxide in citric acid, and chlorine dioxide.
- Select a suitable lubricant for tracks so as to prevent stress cracking (low foam and specific nonionic surfactants).
- Always ask for an approved detergent.

The above concepts and a reliable expert supplier of detergents and disinfectants are the key factors to a successful operation embodying safety, efficiency and productivity.

6.9

Cold Aseptic Filling (CAF)

One of the primary aims of a packaging system is to protect the product from microbial spoilage and chemical deterioration during its distribution and storage. As a result of the development of microbiologically sensitive products and the tendency to move to smaller, lighter-weight packaging, cold aseptic filling technol-

ogy (CAF) increasingly becomes important. All the original equipment manufacturers (OEMs) are offering or developing CAF systems not only for dairy but also for the beverage industry. Most OEMs are looking for a partner that is able to offer hygiene technology and expertise for CAF, including equipment, engineering, chemistry, performance monitoring, validation, and ongoing service support. Various routes are available for the filling and packaging process of beverages:

- cold filling in combination with tunnel pasteurisation
- hot filling
- cold filling with preservatives (with and without flash pasteurisation).

The CAF system has the targets of stability and control of the production and filling process combined with microbiological integrity of products to achieve extended or permanent shelf life without loss in flavor quality.

Because of their formulation and their chemical and physical properties, non-alcoholic beverages such as mineral waters, lemonades, soft drinks, fresh fruit juices, tea products, and milk mix products are selective media that only allow certain microorganisms to grow and multiply. Because of their chemical and physical properties (low pH, low content of nutrients, and lack of oxygen and content of preserving substances) most beverages are to an extent protected against microbiological spoilage. However, milk mix products, fresh fruit and uncarbonated vegetable juices having a pH higher than 5 lack such protecting properties. Even bacterial spore formers are able to grow. Milk mix products and fruit and vegetable juices can therefore be some of the most sensitive nonalcoholic beverages. The production and filling processes for these beverages offer the biggest challenge to microbiological safety and equipment hygiene. The filling has to be done in a way that prevents microbiological contamination of both beverage and container during the process. Filling and closing are therefore carried out in a sterile environment.

6.9.1

CAF Technology

In contrast to so-called optimized hygiene, half aseptic, and ultraclean filling lines, typical aseptic filling lines are totally enclosed in a clean room area separated off from the rest of the bottling hall by glass partitions. The enclosure has a ceiling containing air filters to deliver certain air qualities that are required for class 1000 or class 100 clean rooms. In the case of a filling 'bloc', bottle sterilizing and rinsing equipment, filler and capper are enclosed in one unit. Sterile air is continuously pumped into the area so that there is a constant pressure differential between the inside and the outside. This prevents unclean air from entering the enclosed area, as illustrated in Figure 6.50.

A typical state-of-the-art installation is characterized as follows: PET bottles are fed from the blow-molding machine or bottle store into the aseptic area by air conveyors using sterile air, and passed via an airlock inside the clean room. Inside the airlock the transport air is removed to avoid any unmonitored air flow into the clean area. From this point the bottles are handled by the neck only. In the

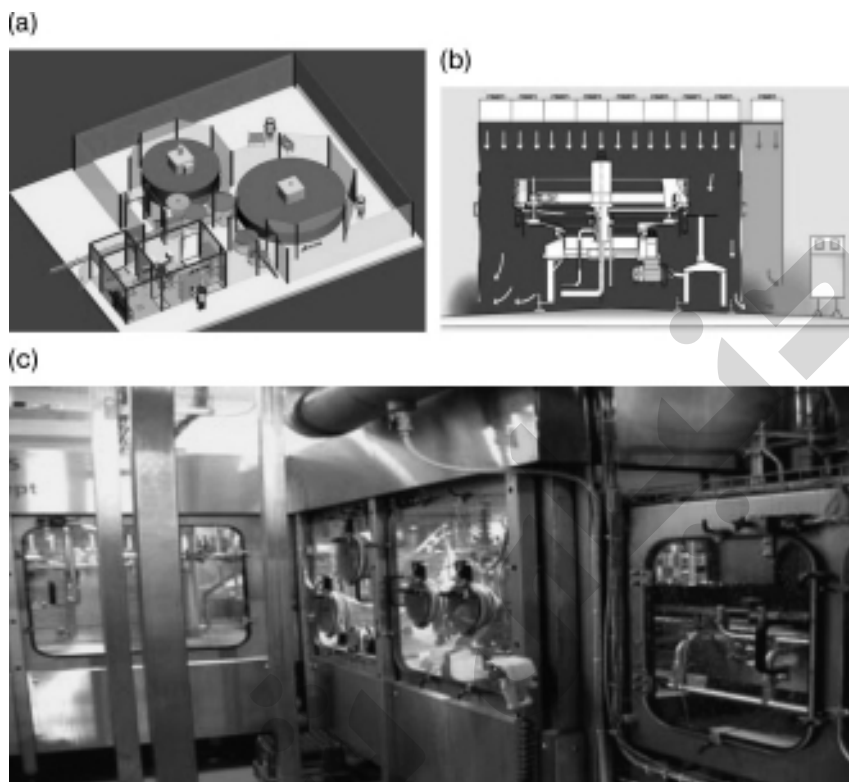


Figure 6.50 (a) KHS technology, (b) Krones laminar flow on filler and (c) Krones bloc.

aseptic area, bottles are first sterilized in an injector, which is usually enclosed in a class 1000 environment. The bottles are passed to a rinser, where destroyed microorganisms are removed. Here, the inverted bottles are submitted to a number of intermittent rinses with sterile air and sterile water, which also removes any traces of disinfectant. The bottle neck is rinsed with sterile water before filling. After rinsing, the bottles are filled in controlled clean conditions and closed with a sterilized cap before re-emerging into the normal environment of the bottling hall via a second airlock. The rinser, filler, and capper units are usually housed in a class 100 clean room cabinet. Operators only get access to the class 100 area by using gloves that are fastened to the enclosure.

Total concept aseptic filling lines include a central sterile water generator and a product sterilization unit (flash pasteurizer, UHT, filtration). Equipment of aseptic filling lines should be designed according to hygienic design criteria. This means that it is designed with cleanliness in mind. Care is taken to avoid the creation of corners and small cavities where contamination could accumulate. Where possible, flat surfaces are designed with a slope to facilitate run-off of spills or cleaning fluids. Specific resins and stainless steel with low surface roughness are used throughout, unless this is prevented by technical requirements. The

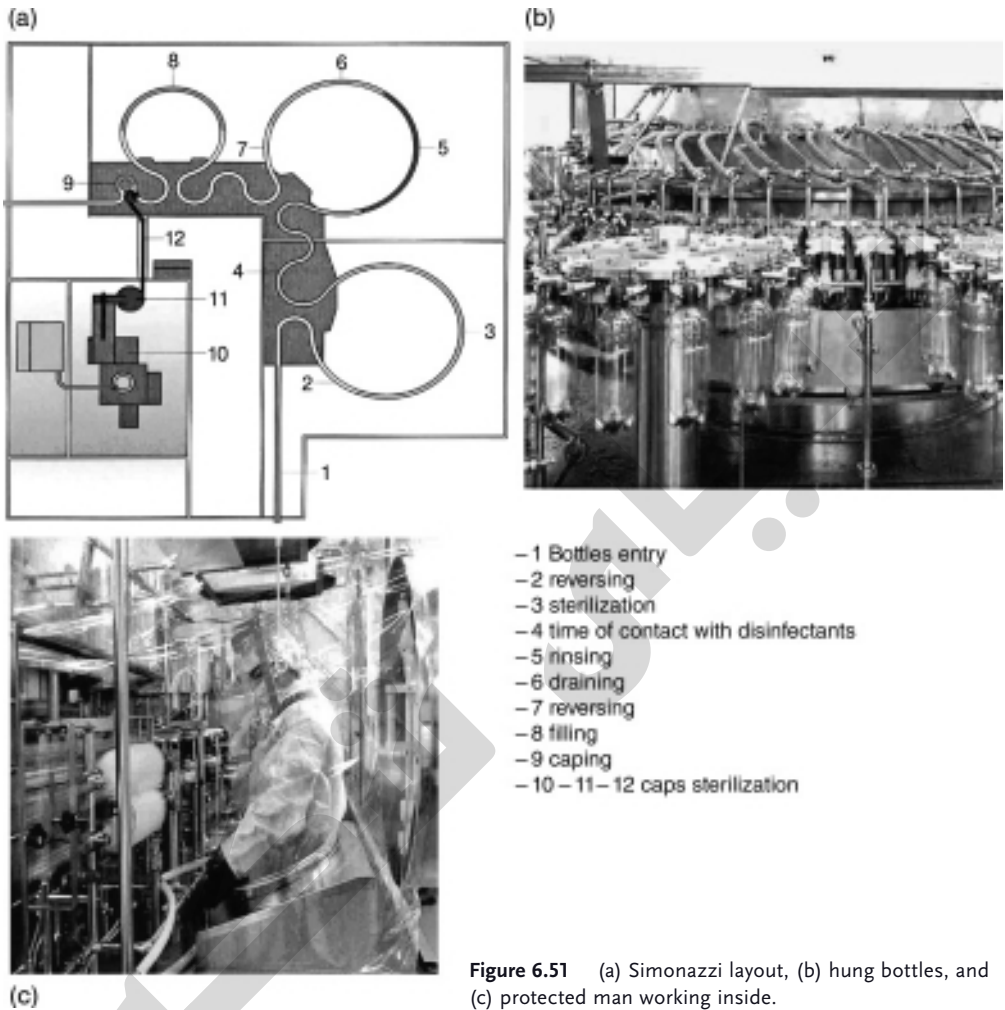


Figure 6.51 (a) Simonazzi layout, (b) hung bottles, and (c) protected man working inside.

floor of the clean room or clean cabinet slopes downwards from the center for easy cleaning and the machinery is mounted well above floor level. CIP (cleaning in place) and SIP (sanitation in place) are standard in aseptic filling installations. In addition to heat treatment, chemicals such as peracetic acid (PAA) are suitable for disinfection (Figure 6.51).

6.9.2

Microbiological Sensitiveness

Microorganisms that occur in beverage producing and filling plants can be divided into 3 types: hygiene indicators, product-spoiling microorganisms, and pathogens. The production and filling process of beverages is the biggest

challenge to microbiological safety and equipment hygiene. It is difficult to find any regulation or recommendation that exactly defines a standard for asepsis. Tests have to be carried out using different microorganisms, for instance:

- *Bacillus subtilis* for package treatment with H_2O_2 .
- *Bacillus stearothermophilus* for package treatment with steam and cold water
- *Bacillus subtilis* var. *niger* for package treatment with dry heat.

No unsterility in 100 000 bottles is one of the targets. A disinfectant for the bottle treatment in cold aseptic filling machines has to fulfil the following requirements:

- strong and fast acting
- excellent wetting of the inner surface of plastic bottles (up to 2 L)
- a five to seven log reduction within 10 seconds against spores of bacterial spore formers (e.g., *Bacillus subtilis*) or molds (e.g., *Aspergillus niger*, *Chaetoniium globosum*)
- excellent rinsability (peroxide residues in the bottles less than 0.5 ppm).

OEMs are meeting the requirements mentioned above using peracetic acid (PAA) for the bottle disinfection. Depending on the functionality of disinfecting equipment, PAA concentrations from 1500 ppm up to even 4000 ppm are necessary to reach 10^5 to 10^7 reductions within 10 seconds at 50–60 °C. Surfactant concentrations from 200 to 1200 ppm are added to the PAA to achieve better wetting of the inner and outer surface of bottle.

The hygiene plan includes all cleaning and sanitizing measures and products for a CAF line. The plan should explain in a clear and simple way *who* should do *what*, *when*, *in which way*, *how often*, and for *how long*. The hygiene plan also includes cleaning method cards for each individual plant objective. OEMs guarantee their customers a specified performance (e.g., no unsterility in 100 000 filled bottles). This leads to the use of high ratios of PAA to wetting agent

6.9.3

Cleaning Programs

Each plant objective can require different cleaning methods. Because of their different composition, their specific chemical and physical properties, and their specific microbiological sensitivity, different beverages require different cleaning programs. Therefore, the first step in creating a hygiene plan is to divide the beverages filled at the customer site into risk groups. Tables 6.8 and 6.9 give further information on risk groups.

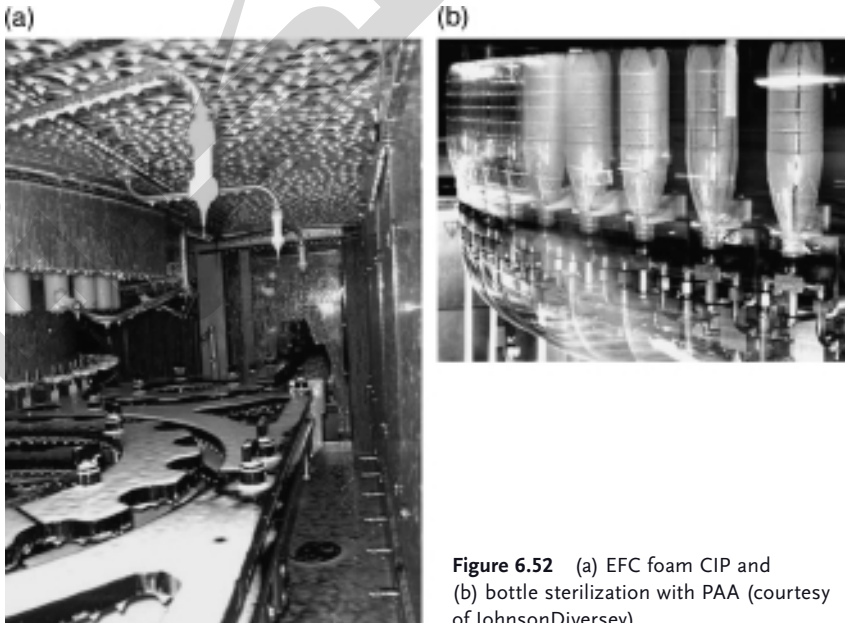
Two basic programs are given according to the requirements of external and internal cleaning. The external filler cleaning (EFC) programs include all cleaning and disinfecting steps for injector, filler, capper, submersion bath, and conveyors. An EFC program (Figure 6.52) always comprises the following steps:

Table 6.8 Beverages in risk groups.

Product characteristic	Risk
CO ₂ content	Microbiological sensitivity
pH	Microbiological sensitivity
Content of nutrient	Microbiological sensitivity
Intensity of flavor/color	Flavor/color carryover
Product residues	Deposits

Table 6.9 Applied ratio of PAA to wetting agent.

Risk group	Bottle disinfection (injector) ppm PAA/ppm wetting agent	Cap disinfection (submersion bath) ppm PAA
Juices	1000/200	800
	2000/800	1000
Juices with intense flavor/color	2000/400	1000
	2000/800	1300
Low-acid tea products	4000/800	1000
	2000/1000	1800
Low-acid milk-based products	4000/800	1500
	3000/1200	1800

**Figure 6.52** (a) EFC foam CIP and (b) bottle sterilization with PAA (courtesy of JohnsonDiversey).

- pre-rinse
- alkaline and/or acidic cleaning (foam/gel detergents)
- intermediate rinse
- disinfection (peracetic acid)
- final rinse.

If beverages mainly having inorganic components are bottled (e.g., mineral water), acidic cleaning is required on a regular basis. If organic soil is present, an alkaline step is necessary. If product residues can build up deposits or coloring, alkaline cleaning with an oxidant (chlorine or hydrogen peroxide) is applied.

The internal cleaning programs set a complete CIP/SIP operation for tanks, pipelines, and filler as follows:

- pre-rinse
- alkaline and/or acidic cleaning
- intermediate rinse
- disinfection (hot water or PAA)
- final rinse (Figure 6.52).

The CIP/SIP program is carried out at least once a day before or after production and in the case of a product change.

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مکتبہ

7

Lubrication

Any moving thing experiences a force, known as friction, which opposes the motion. Steady movement calls for energy. When a compound able to decrease this opposing force is interposed between two surfaces in contact, those surfaces are lubricated. Thus, lubrication is the act of striving to lower friction and energy in order to keep the surfaces in motion.

Friction, lubricity, energy, durability, sensitiveness to cationic and anionic hardness, pH, foam depression, stainless steel and plastic conveyors, stress cracking, speed, spray time (on and off), black soil, paint fading, corrosion, and biofouling are key factors in the lubrication process. All of these are discussed in the present chapter.

7.1

Theory of Lubrication

Competent investigations into the mechanisms of lubrication started halfway through the twentieth century concurrently with the industrial revolution. There are two main types of lubrication:

- **Hydrodynamic lubrication:** The lubricating film is macroscopic. The dynamic friction depends on the hydrodynamic properties of the interposed layer, especially viscosity, and is independent of the nature of the lubricated surfaces.
- **Boundary lubrication:** The lubricating film is made up of a few molecular layers. Surfaces assume an important role in producing friction as well as the nature of the film and its ability to coat an area. Boundary lubrication is the method used in the food sector.

The theory gives an insight into friction and the chemical means of reducing it.

7.1.1

Friction

Two different types of friction are described [1]:

- **Static friction:** between resting surfaces
- **Dynamic friction:** between two surfaces in motion.

The dynamic friction is the most important and depends on:

- speed of surfaces
- actual contact area
- surfaces hardness
- surfaces finish
- surface oxidation
- humidity
- perpendicular force
- types of material in contact
- surface temperature
- shape of the surfaces in contact
- environment of the surfaces

Surfaces are not smooth, and only their prominences come in contact. The actual area of contact is calculated to be approximately 0.01% of the total, directly depending on the perpendicular force acting on it. Contacts are the only cause of friction (Amontons's laws) as shown in the Figure 7.1 [2]:

High pressures are generated at the contact points. Pressure promotes plastic deformation and local rise in temperature, which welds the prominences together. The applied energy (engine) breaks the welds and thermally generates metal oxides. Analysis of the black deposits which form on tracks and are scraped off after welding reveals the same metals as those in stainless steel (Fe, Ni, Cr). The welding of prominences causes friction. Amontons's law describe the relationship between the energy promoting motion and the contact friction as a function of the applied weight (Figure 7.2).

However, this is an oversimplification. Other factors must be involved as well as those that feature in the above equation. These are

- a constant (α) representing the tangential strength of the drag which affects the friction, widening the welding area
- a coefficient (c) connecting the resistance to the shearing stress (s) for each surface in contact

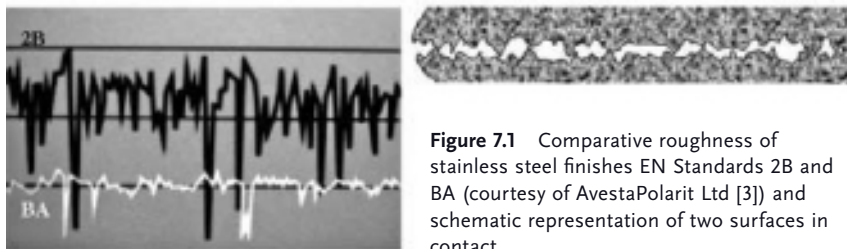


Figure 7.1 Comparative roughness of stainless steel finishes EN Standards 2B and BA (courtesy of AvestaPolarit Ltd [3]) and schematic representation of two surfaces in contact.

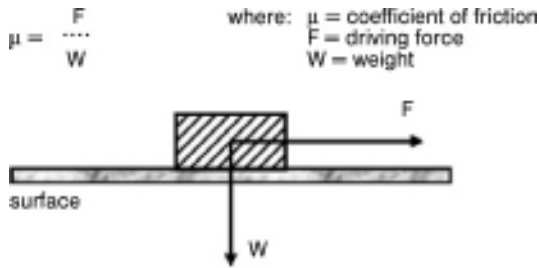


Figure 7.2 Calculation of coefficient of friction.

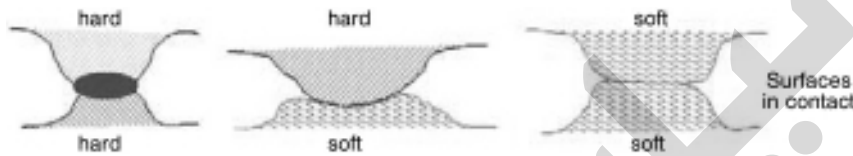


Figure 7.3 The effect of surface hardness on friction.

The complexity of the coefficient of friction could be more accurately expressed by incorporating the following expressions [2]:

$$\frac{c}{[\alpha(1-c^2)]^{1/2}}$$

K.c.s

plastic deformations where c is within the range 0–1

reversible elastic deformations (K = material constant)

However, since the Amontons's empirical law incorporates each individual micro-effect (α , c , s), the macro-ratio (F/W) is considered to be a simplification suitable for describing lubrication in food processes. Every calculation and conclusion in this section makes use of it.

The macro-effects of friction are summarized in the following statements [2]:

- **First law:** friction is independent of the apparent area of contact. Friction does not depend on the geometric area but rather on the real area of contact.
- **Second law:** friction is directly proportional to the force perpendicularly applied. Force increases the number of asperities coming into contact. For this reason, filled containers show higher friction than empty ones.
- **Third law (Coulomb's law):** the kinetic friction is independent of the relative speed of drag. The law is verified for common surfaces at relatively low speed. Section 7.1.3 proves the validity of this law for lubrication in food conveyances.

Surface hardness (Figure 7.3) is one of the most important factors influencing friction.

The drag of hard surfaces welds the peaks and makes the temperature rise by several hundreds of degrees (°C) at the micro-points of contact. Motion breaks the welding and gives rise to black oxides on conveyors. Plastic surfaces undergo

softer elastic deformations and do not produce black deposits. The soft friction caused many to think that plastic tracks in contact with plastic containers do not need lubrication. In practice, even if the coefficient of friction on plastics proves to be lower than steel/glass coefficient, the shelf life of tracks shortens and the energy of motion increases in the absence of lubricant.

7.1.2

Lubricity

When a mobile layer lies between two surfaces and keeps them apart, the surfaces are dynamically lubricated. The energetic level of a surface accounts for a few classes of molecules suitable to lubricate. A permanent electric field deriving from free external valences is diffused on the outside of a solid surface. The electric field is responsible for chemical reactions and physical absorption of substances in contact with the surface. As a consequence, all the polarized molecules can react, but the priority will be for those having a strong permanent dipole. When one of the poles is in acidic form, not only physical absorption but also a chemical reaction occurs on the metal surfaces. As surfaces slide better on a mobile layer, the second pole must be shaped like a flexible long chain. Then, the dipole is necessary but not sufficient for good lubricity (Figure 7.4).

X-rays and electronic diffraction enabled Trillat [1] to demonstrate the theory and prove that the long-chain fatty acids give the best lubricity since they exactly correspond to the ideal physico-chemical dipole. Other classes of molecules having strong dipole and a long chain, such as nitrogenous fatty compounds, can give good lubricity as well.

According to Lagmuir and Woog [1], lubricity depends on the dipole strength, how the molecules coat the area and on their melting point. How different molecular structures can cover an area is freely represented in Figure 7.5.

The nitrogen group forms a strong dipole, but it cannot chemically react with the surface. Its adhesion is only attained by adsorption and proves to be weaker than of the carboxyl group. The lower the chemical adsorption, the lower is the durability. Durability describes the efficiency in maintaining the dynamic

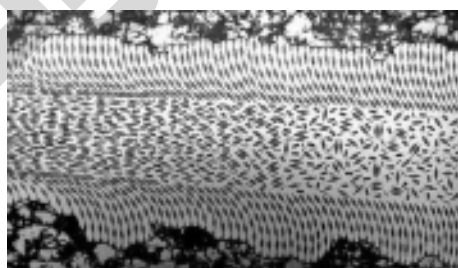


Figure 7.4 Schematic representation of surfaces sliding on a soap-based lubricant (courtesy of Recine [1]).

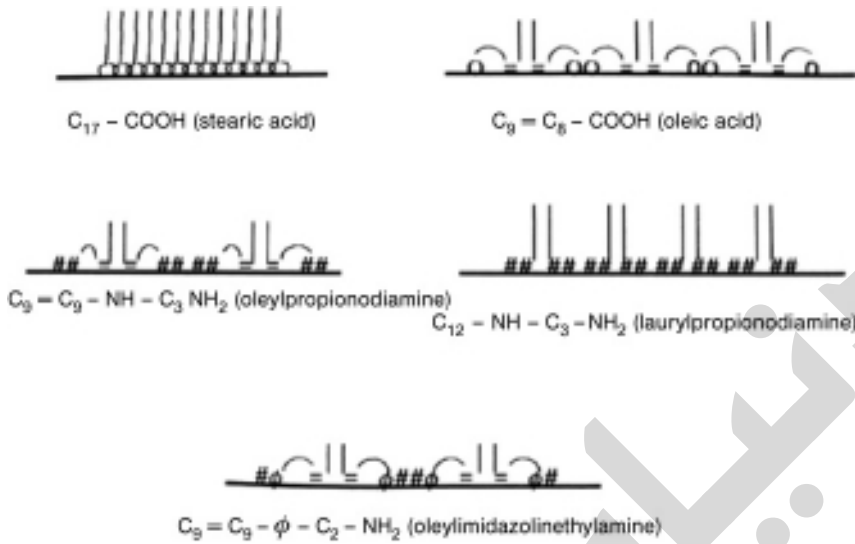


Figure 7.5 Schematic representation of lubricants, where: — represents a long chain; O a carboxylic group; ϕ an imidazole ring; = a double bond; # a nitrogen group.

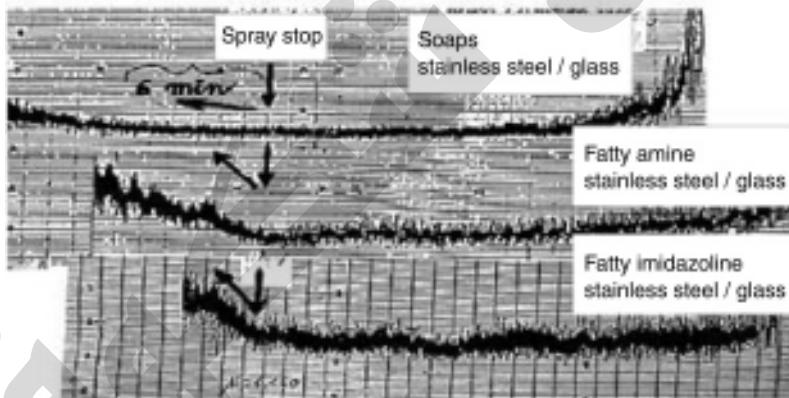


Figure 7.6 Differences in durability for soap, fatty amine, and fatty imidazoline.

lubricity constant when the addition of the lubricant solution ceases. In other words, durability represents the resistance of lubricating molecules to being scraped off the surface. Figure 7.6 shows differences in durability for soap, fatty amine, and fatty imidazoline. The differences are exactly those expected from theory.

Fatty amines and, even worse, fatty imidazolines show negligible durability, while that of soap exceeds 6 minutes. Steric hindrance of the amino group, the imidazole ring, and double bonds in the fatty chain reduce the number of

molecules per unit area. It follows that the more the compound deviates from the ideal structure of stearic acid, the worse is the lubricity. However, although stearic acid possesses the ideal structure, it has far from an ideal lubricity. Stearic acid is a solid substance at room temperature, and the flexibility of its chain perpendicular to the surface is less than that of the oleic chain. The latter is balanced by the shorter chain (double bond), and is liquid at room temperature. Moreover, oleic diamine gives three points of absorption ($C_9=C_9\cdots N\cdots N$) and reaches the steady condition before lauric diamine which has only two points ($C_{12}-N\cdots N$). However, in a laboratory test (Figure 7.7), the latter lubricates just a little better at the steady condition (less friction).

This difference derives from applying a simple test of lubricity which is explained by only a fragment of the lubrication theory. In practice, the overall performance expected from a lubricant shows oleic diamine to be more efficient in persistence and reproducibility.

Natural esters (e.g., lanolin) and every fatty long chain containing electron-attracting groups (e.g., acylated fatty acids) have a strong dipole. Nevertheless, although those chemicals provide acceptable lubricity, they behave like mineral oils and fats (hydrodynamic lubrication). Such insoluble hydrophobic matter gives cleaning problems. It is adsorbed and remains on the surface, incorporates oxides (formed by friction) and dust, soon makes a black oily deposit grow on the track, and dirties the bottom of containers. Figure 7.8 shows this after lubrication with a blend of fatty diamine and acyl- C_{16} -acid.

Water-soluble molecules leaving a clean track are the reference materials when assessing a lubricant (wet lubrication). Compounds similar in shape to the ideal structure of soaps were investigated in order to obtain lubricity and insensitivity to the hard water. Replacement of the carboxylic group with sulfonic, phosphonic, sulfate, and phosphoric groups yields lubricating molecules but never ones comparable with soaps:

- $\text{~~~~~} \text{SO}_3^-$ alkylsulfonates
- $\text{~~~~~} \text{PO}_3^-$ alkylphosphonates

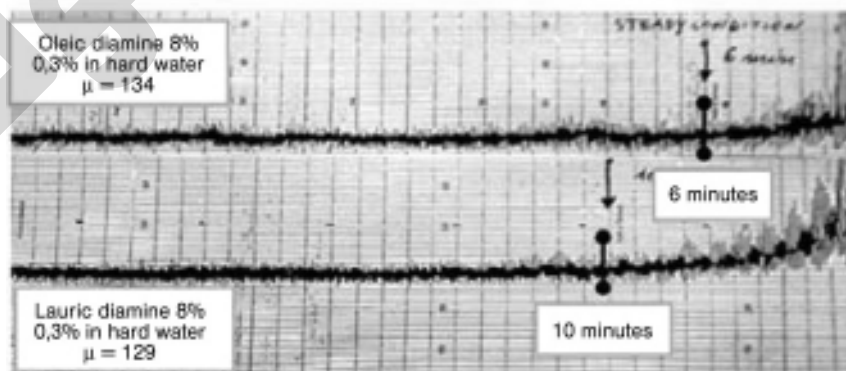


Figure 7.7 Attainment of the steady condition for oleic and lauric diamines.



Figure 7.8 Oily deposit containing black oxides.

- $\text{C}_{14}\text{--C}_{18}\text{OSO}_3^-$ alkylsulfates
- $\text{C}_{14}\text{--C}_{18}\text{OPO}_3^{2-}$ alkylphosphates

Although α -olefin sulfonate (AOS) ($\text{C}_{14}\text{--C}_{18}\text{--SO}_3\text{Na}$) received United States patents for its use as lubricant alone and together with soaps, interest was soon lost because of a coefficient of friction higher than that of carboxylate, too much foam, and persistent sensitiveness to the cationic hardness. It is not worth changing from soaps to new molecules less effective and having the same troubles. The only practical application involves AOS with soaps even if it is added as surfactant rather than lubricant. However, alkyl(ether)phosphates synergize lubrication by fatty diamines [4]. The decrease in friction is accomplished through a sort of plasticizing activity. They perform by enhancing the spreading of the fatty diamines and keeping the area thickly covered for longer.

A totally different type of lubrication arose from the concept that two surfaces can be lubricated by sliding on a mobile solid. Droplets of PTFE (Teflon) were reputed to be suitable to fill depressions and keep two surfaces apart but sliding. The concept was the starting point of the dry-lubrication technology which soon afterwards evolved in a different direction (Section 7.7).

The type of absorption and the way of coating an area determine lubricity and durability, in other words, define the quality of a lubricant. When lubricity fails, containers fall down and the energy needed to move the conveyor increases, as does the temperature of the motor. The thermal protection can stop an electric motor and conveyor (decrease in productivity). Friction makes the tracks jump and damages gear-wheels. Figure 7.9 shows the moment of jumping.

7.1.3

Variables of Lubrication

The variables of lubrication can be investigated on pilot plants, an example of which is schematized in Figure 7.10.

The pilot track consists of chains on which containers are linked to a load cell connected to a recorder through a transducer. The conveyor is restored to the

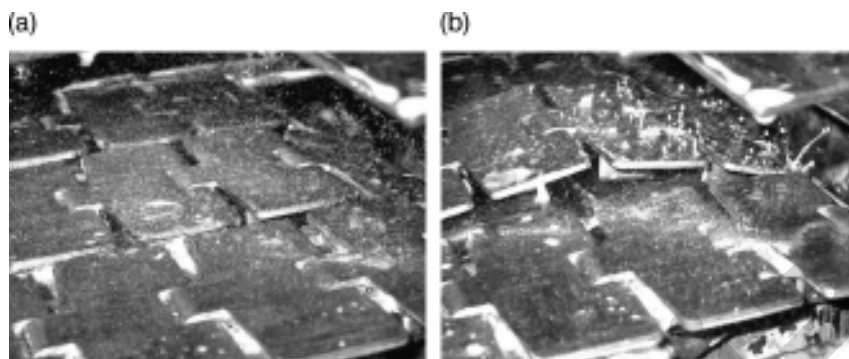


Figure 7.9 (a) Tracks running regularly. (b) Poor lubricity makes the same tracks jump.

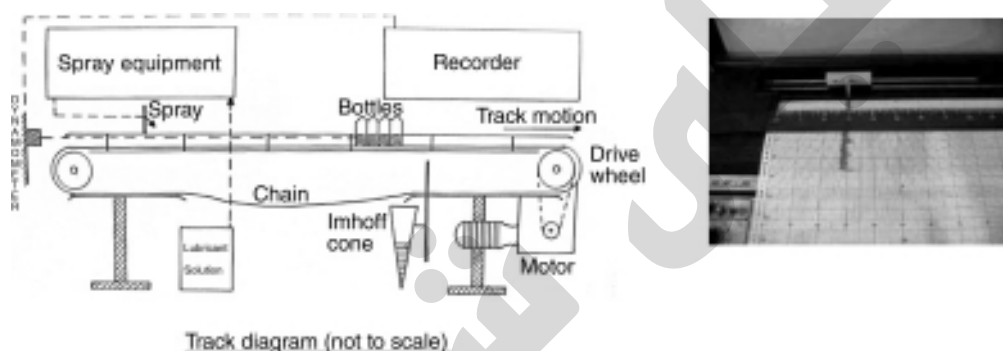


Figure 7.10 Type of pilot plant.

standard condition after each test by a thorough removal of the previous lubricant (cleaning). Hence, a pilot track should be as simple as possible while being efficient and reproducible.

The most significant variables are the lubricant, the track, and friction.

7.1.3.1 Quantity of Solution on the Track

Good practice suggests setting the concentration as low as possible and spraying a volume of solution as high as possible, depending on the various classes of lubricants. In this way, lubricity is optimized, foam is controlled, and cleaning achieved. The water hardness affects the quality of lubrication. When soft water is available, the concentration in use is quite arbitrary, even for soaps. Then, applying a suitable lubricant, the success of the lubrication mostly depends on setting up the delivery plant (volume of solution) rather than the lubricant itself.

7.1.3.2 Quantity of Lubricant on the Track

While the volume of the solution is first aimed at enhancing cleaning, a suitable concentration of the lubricating molecules makes lubricity more easily and rapidly

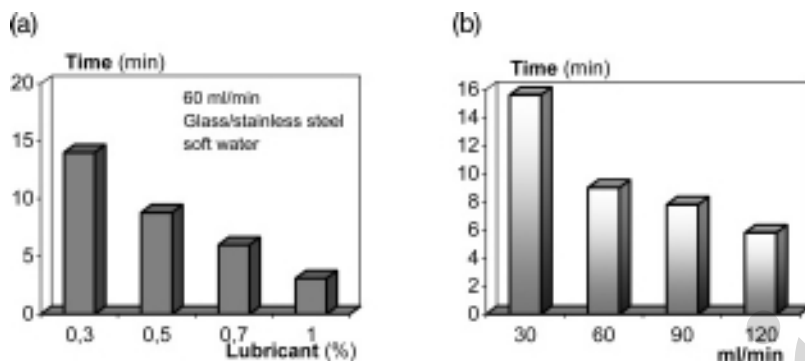


Figure 7.11 Time to reach the steady condition as a function of (a) the lubricant concentration, and (b) the volume of solution.

achieved, and maintains a steady condition. Each molecular structure gives its own lubricity, which is independent of the concentration in use. However, a good lubrication also depends on a surface entirely covered and free of foam. After coating the surface, the lubricating molecules must be enough to compensate for the carryover. Both conditions are achieved by either concentrating the solution or spraying longer. Concentration and time of spray (on) are complementary. The type of track (length, curve, and slope) could require several spray points to ensure the right concentration per area. Thus, inspection and assessment of the layout of the conveyor are useful to identify the most suitable lubricant, divide the plant into opportune zones, and decide the correct 'on' and 'off' periods in each case. In any case, 'on' should be a track revolution long, at least. Figure 7.11 shows the time required to reach steady conditions as a function of either different concentrations of soap or different volumes of solution.

Concentration of the lubricant and on-off timing are equivalent basic factors in adjusting lubricity. However, it is always opportune to remember the fundamental rule which recommends spraying the highest volume of solution at the lowest concentration, depending on the type of lubricant.

7.1.3.3 Speed of the Track

Two distinct issues depend on the speed of the track:

- what happens to the lubricity
- what happens to the statics of containers.

Speed does not affect friction (or to a negligible extent) according to Coulomb's law, and Figure 7.12 illustrates the results of an experiment to demonstrate this.

The experiment shows that the change of speed from 17 to 60 cm s⁻¹ does not affect lubricity either with soaps or with fatty diamines. The coefficient of friction of soaps changes from 0.120 to 0.121 on glass/stainless steel and from 0.083 to 0.080 on plastic. Fatty diamine performs similarly (namely from 0.128 to 0.132 and from 0.088 to 0.080 respectively). Thus, friction does not change with varying

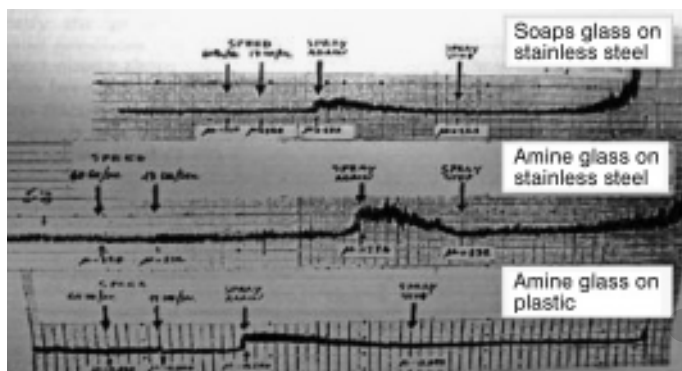


Figure 7.12 The speed of the track does not change the coefficient of friction.

speed. On the contrary, the statics of containers (e.g., slim packs) is destabilized by changes in velocity. During start-up, stopping, curves, slopes, and change of track, the friction stays the same, but frequent falls are caused if the lubricity is not at its maximum. Therefore, when problems of speed are discussed, they normally involve inertia, collision, center of gravity, and centrifugal force rather than friction. As a matter of fact, each lubricating molecule is characterized by its own absolute lubricity. A lubricating molecule having been decided upon, co-formulants affect it, usually adversely, and form a product which has its own relative lubricity. Each lubricant satisfies a target established when the formulation is decided. Thus, instead of judging a lubricant to be good or poor, it would be better to consider whether it is suitable or unsuitable for the application.

7.1.3.4 Temperature of the Track

It is known that some bottlings involve filling the containers with hot beverage (stock pasteurization). The track locally increases in temperature. According to the theory of lubrication, the more the mobility of the lubricating layer increases (rise in temperature), the more the lubricity enhances as well. The theory is correct if the surface remains wet. Usually, extending the 'on' and shortening the 'off' prevents drying.

7.1.3.5 Friction and Micro-friction

When graphs of lubrication are compared, two types of friction stand out. The first derives from the Amontons's law and concerns the lubricity, usually expressed as the coefficient of friction (μ). It represents the macro-friction, which is useful to identify large differences between lubricants. However, when good lubricants are compared, friction (μ) is no longer sufficient to discriminate between the good and the best. Here, evaluation of the extent of the fluctuations along the entire graph is helpful. These fluctuations show friction at every point of contact, in other words it defines the micro-friction. The same value of the coefficient of friction (μ) can conceal evident instability in lubricity, which only appears by

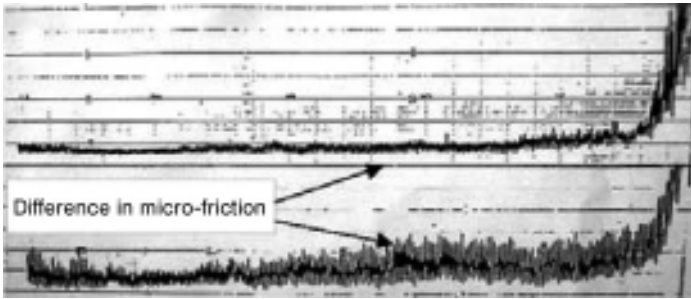


Figure 7.13 Friction and micro-friction.

analyzing the shape of the micro-friction graph at every instant, as shown in Figure 7.13.

A lubricant having lower micro-friction fluctuations ensures satisfactory lubricity especially in critical zones of the plant (inclined conveyor, canalization of bottles, sharp bends). Micro-friction is also directly linked to noise [5]. Lubrication aims at facilitating the movements of tracks and containers. The more the efficient the lubricity, the less is the force of traction and the less is the amount of noise from the bottles. The noise level (decibels) decreases and the health of personnel benefits [6].

7.1.3.6 Dry Tracks

The loss of lubricity has a dramatic effect on dry stainless steel, while plastics still have a reasonably low level of friction. This lower friction has led to the concept of self-lubrication of plastic tracks. However, rapid (a few weeks) and severe abrasion becomes evident on polyacetalic (POM), Teflon (PTFE) and polybutyleneterephthalate (PBT) tracks when they run dry or are wetted with water alone, as indicated in Figure 7.14.

As plastic materials reduce friction, vast amounts of investigation into new plastics and new shapes have been carried out. Nevertheless, when two surfaces slide in contact, they are in any case undergoing friction, which eventually damages them. The best policy is therefore unchanged, namely to spray a lubricant able to prevent damage, and to provide bacteriostatic action and good cleaning.

7.1.3.7 Bottles, Cans, and Composite Containers (Cartons)

Size, shape of bottom, and type of container affect lubricity. Comparing soap and fatty diamine:

- An aluminium container (can) gives higher friction than glass.
- Glass performs better than PET on stainless steel.
- A rounded base causes higher friction than a flat one.
- A carton is the most difficult container to lubricate.



Figure 7.14 Tracks are always damaged in the absence of lubricant.

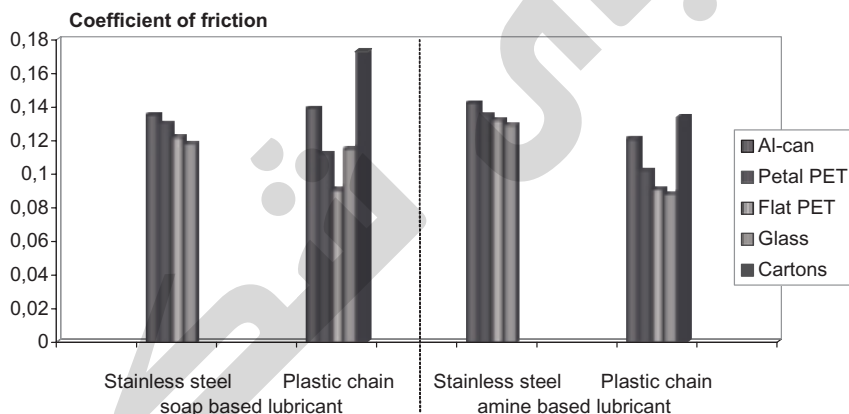


Figure 7.15 Coefficients of friction in wet lubrication.

- Small and slim bottles critically depend on steady running of the track. Their instability depends on the ratio between radius and height of its center of gravity [r/h_c] and even on the shape of their bases.

The behavior is illustrated in Figure 7.15.

Silicone, which not shown in the graph, proves to be the best lubricant for plastic on plastic, its coefficient of friction always being less than 0.1 (Section 7.6).

Friction also changes according to the shape of the base of the bottle. Besides the difference in lubricity from rounded and flat PET, the shape of small glass bottles (e.g., bottles for fruit juices) affects the friction. Even if the friction is constant, the micro-friction can become worse, as shown in Figure 7.16.

Bottles A and B (200mL), which differ only in the shape of their bases (Figure 7.16), have the same friction but different micro-friction. Bottle B was rejected because of instability problems on the tracks.

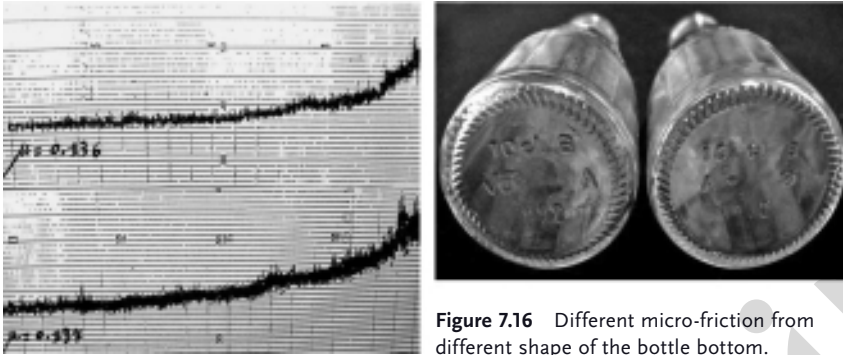


Figure 7.16 Different micro-friction from different shape of the bottle bottom.

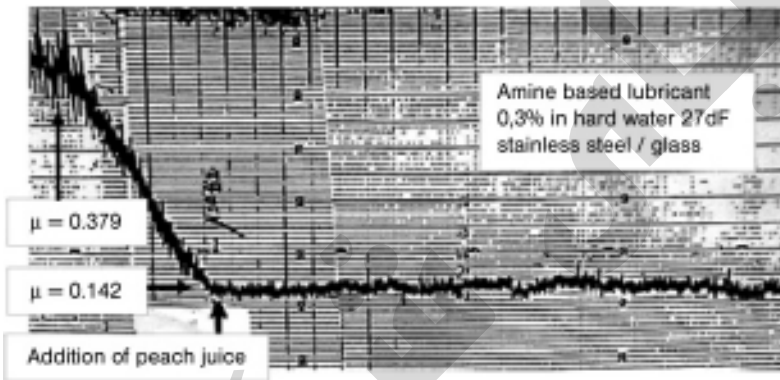


Figure 7.17 Rapid change of friction related to decrease in pH.

7.1.3.8 Type of Beverage

Spillage affects lubricity. Their slightly acidic pH makes soft drinks, beer, wine, and fruit juice safe and agreeable but spillage causes the pH on the track to decrease and friction to increase. The best lubricity for soaps is achieved in mildly alkaline pH, mildly acidic pH for fatty amines. Change in pH affects lubricity immediately, as Figure 7.17 shows.

The buffering power of the lubricant should prevent this loss in lubricity, but this depends on the type of lubricant and its volume sprayed on the track. Alkaline pH and higher concentration in use give soaps a much higher buffering power than that of amines. Soaps have a pH of 9.5–10, fatty amines 6–7. Soap is therefore able to quickly restore the lubricity after spillage. The two graphs in Figure 7.18 show the difference between fatty diamines and soaps with regard to restoring lubricity.

The rise in friction of the aminic lubricants (from 0.131 to 0.223) caused by acid spillage is dramatic in comparison with soap, which maintains its lubricity. For this reason, the vinegar and pickled preserves industry usually still lubricates with soap.

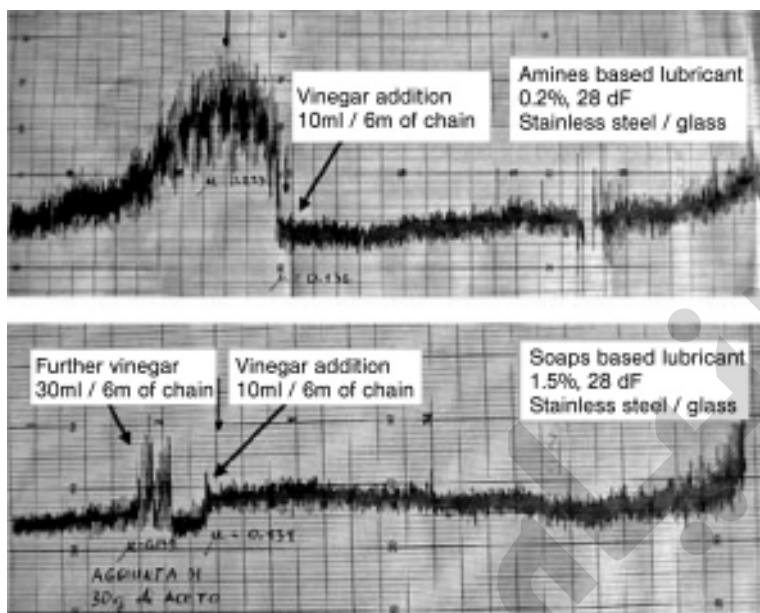


Figure 7.18 Difference in restoring lubricity between fatty diamines and soaps.

Spillage soils tracks, stimulates infection, and generates unpleasant odors, beverages being the main source of organic matter supporting the growth of microorganisms.

7.2

Soap-Based Lubrication

The carboxylic group at the end of a long hydrocarbon chain is extremely reactive with metals. While the reaction with the track metals is the basis for durability, the polyvalent metals dissolved in the water insolubilize and precipitate metal soaps. Calcium soap is one of the worst contaminants. Calcium soaps break down foam but clog pipelines and nozzles, causing unexpected stops in manufacturing. Consequently, in order to neutralize the negative influence of the water hardness, a suitable sequestrant is formulated together with soaps. As described in Sections 1.3.3 and 3.4.5, EDTA is the only sequestrant able to compete with soaps for calcium. EDTA is a stoichiometric sequestrant, so that the more the hardness increases, the more the concentration of EDTA must be increased. Moreover, alkali soaps (K, Na) are foaming and cleaning salts. Thus, it would be better to lubricate in softened water with as low as possible concentration of lubricant. This is not always possible or desired. Plotting all of this in graphical form (Figure 7.19) immediately reveals the difference in behavior.

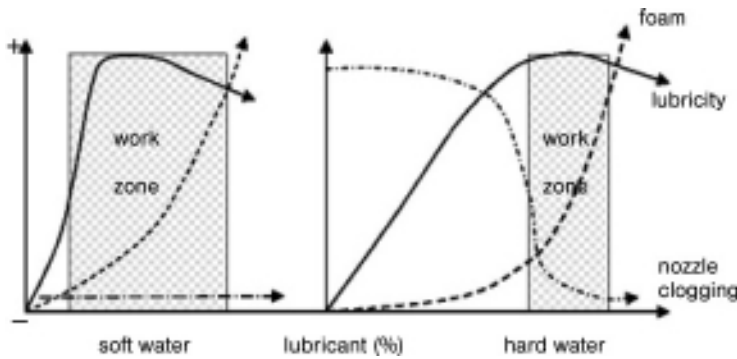


Figure 7.19 Soft water makes lubrication easier.

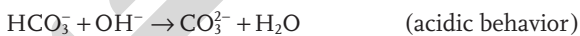
Several variables are involved in soap lubrication and all need attention to reduce friction, keep tracks clean, nozzles performing, and foam minimized:

- buffering power and alkalinity donors
- type of fatty acid, its saponification and concentration
- sequestrants
- keeping tracks clean
- fluidification and antigelling
- stress cracking.

7.2.1

Buffering Power and Alkalinity Donors

Bicarbonate is usually the main anion present in water and, as described in Section 1.2.1, it shows amphoteric behavior. Bicarbonate behaves as an acid and a base, reacting with both hydroxyl and hydrogen ions:



The coefficient of friction is at a minimum when the pH is in the range 9–10 (Figure 7.20).

Bicarbonate disturbs mildly alkaline solutions by lowering the pH. When this occurs, soap reverts to the acidic form, lubricity decreases, and the solution becomes cloudy.

As KOH and monoethanolamine (MEA) improve stability and lubricity in comparison with NaOH alone, KOH and MEA are usually selected as alkalinity donors for saponification. However, they play a different role in the lubricant. While KOH only performs as alkalinizer, alkanolamines contribute to the buffering. When 14% of fatty acids (stearic:oleic:lauric = 40:57:3) are neutralized to pH 10.5 in deionized water and titrated down to 8 with HCl 1N, the result is as given in Table 7.1.

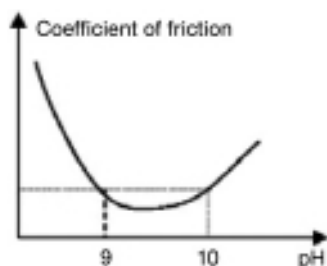


Figure 7.20 Lubricity is adversely affected by both low and high pH. The steady condition is attained by buffering the pH within the range 9–10.

Table 7.1 Titration of a buffered lubricant.

% of reactant to reach pH 10.5	mL of HCl 1N to go back to pH 8
KOH = 3.40	KOH = 8.5
MEA = 8.75	MEA = 96.5

Table 7.2 EDTA improves the buffering of the lubricant.

% of reactant to reach pH 10.5	mL of HCl 1N to go back to pH 8
KOH = 4.17	KOH = 21.0
MEA = 10.73	MEA = 115.5

The addition of EDTA 1.5% to the above formula improves the buffering (Table 7.2).

The different buffering power from MEA and KOH as well as the intense influence of bicarbonate in the solutions in use are apparent in Table 7.3.

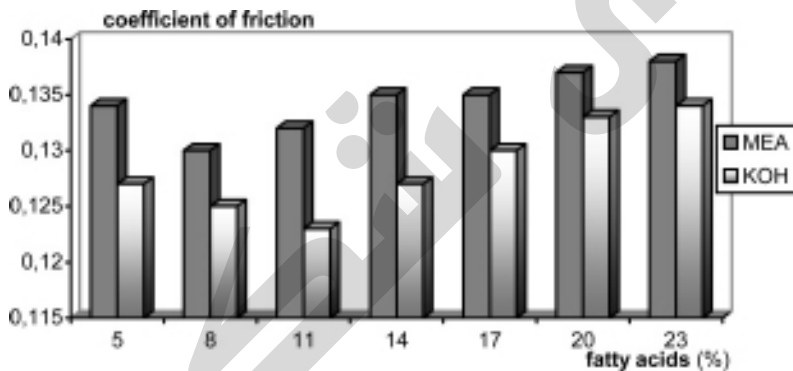
Thus, the soap-EDTA-MEA buffer is necessary to maintain a steady pH. When MEA is absent, destabilization and precipitation of saturated soaps occur at low temperatures. However, MEA is also an emulsifier, even cleaning off the lubricant, and reduces lubricity. Thus, MEA is added in small amounts just to get a sufficient buffering, and hence stability, while KOH supplies the remaining alkalinity. Figure 7.21 shows the difference in lubricity.

The graph also reveals an optimal concentration of fatty acids to obtain the lowest friction. Soap (8–12%) is usually enough to lubricate in very hard water, while 5–8% soap is included in lubricants devoted to soft water. Since the complete neutralization of soaps is accomplished above pH 8.2 (phenolphthalein), lower pH values are unacceptable (loss of lubricity). In practice, lubricity is lost both by lack of saponification below pH 9 and too much alkalinity above pH 10. Low lubricity also promotes the formation of black deposits. Thus, a suitable pH enhances cleaning as well.

Table 7.3 Buffers from KOH and MEA.

Lubricant pH	In-use concentration (%)	KOH alkalinizer		MEA alkalinizer	
		pH tap water ^{a)}	pH deionized water	pH tap water ^{a)}	pH deionized water
9.5	1.0	8.40	10.13	9.00	9.70
	0.5	7.74	9.95	8.62	9.55
	0.1	7.70	8.86	8.10	9.00
10.0	1.0	8.68	10.27	9.40	10.00
	0.5	7.77	10.00	9.20	9.83
	0.1	7.73	9.00	8.55	9.20
10.5	1.0	9.10	10.28	9.85	10.30
	0.5	7.98	10.03	9.67	10.18
	0.1	7.79	9.00	9.05	9.86

a) Tap water = 27 dF.

**Figure 7.21** Lubricant: fatty acids + EDTA 1.5% alkalinized with KOH and MEA.

7.2.2

Types of Fatty Acids and their Concentration

The previous graph also shows that excess of lubricant increases friction and reduces the quality of lubrication. Excess means foam. Foam is one of the parameters that identify a wrong concentration. While, in the absence of foam, high friction is a signal of insufficient concentration of lubricant, in the presence of foam poor lubricity indicates an overconcentration. Foam lowers the quantity of lubricant in contact with the surface and performs a sort of suction effect, which increases the energy of motion. Moreover, too much foam wets the containers and causes paint to fade, ink to be removed, less adhesion in labeling, and penetration of humidity to into the package.

Calcium soap makes lubricity worse but is effective as a defoamer even in very low concentrations. Consequently, it is good practice to keep traces of calcium soap in solution to depress the foam on the track. Fatty acids are compared below:

- Stearic acid gives the best packing per area and causes the longest chain length to protrude out of the surface. Being solid at room temperature, it cannot be used alone as primary fatty acid.
- Oleic acid provides the best balance, although the double bond distorts its chain length.
- Lauric is an ancillary acid. It shows poor lubricity but promotes the solubilization of saturated fatty acids (formula stabilizer) and is a good regulator of viscosity and the best cleaner. Figure 7.22 shows coefficients of friction of blends of fatty acids.

After 21 minutes from starting, friction coefficients are respectively 0.13, 0.11, and 0.10. However, it is evident that micro-friction and durability dramatically change with time as a function of the blends. Oleic acid together with a small quantity of lauric acid represents the best choice as regards both lubricity and cleaning.

The cost of the formulation should also be optimized. A balance between theoretical and commercial requirements is the best solution. In this regard, suppliers make cheaper blends of fatty acids available, such as distilled (resin-free) tall oil. Instead of the pure but expensive oleic acid, commercial blends of oleic, linoleic, and a few saturated stearic, palmitic and lauric acids, are considered to be a good balance from the point of view of cost-effectiveness. Furthermore, a few saturated fatty acids enhance durability in comparison with formulations based only on unsaturated ones.

As already discussed, lubricity depends on the number of lubricating molecules per area. This number is derived from both the concentration of fatty acids (type of lubricant) and the sprayed volume of solution. Therefore, the steady condition is achieved by carefully deciding on the delivery plant (zoning and on-off), choice of the lubricant, and proper concentration in use. From all of this, only two categories of lubricants are strictly necessary to satisfy every application:

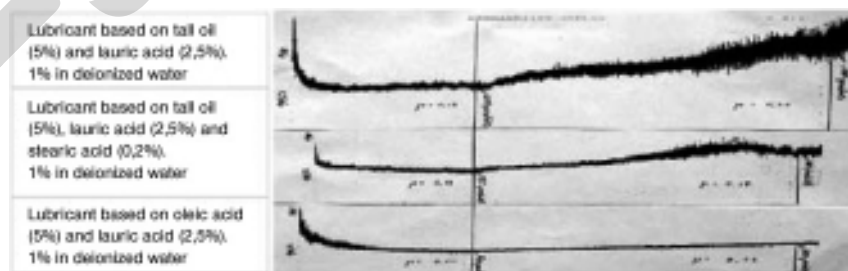


Figure 7.22 Friction of blends of fatty acids.

- fatty acids ~6%, so as to have a cheap product suitable for soft water and hardness below 15 dF.
- fatty acids ~12%, so as to be able to use hard water and decrease as much as possible the concentration in soft water (lower cost in use).

In order to run steadily, the set-up of the lines (zoning and on-off) is as important as the choice of the lubricant.

7.2.3

Sequestrants

The competition between sequestrants and precipitants (Section 1.1.3.2) justifies EDTA as the sole useful sequesterant. So far, investigations have found no sequesterant to compete with EDTA. Theory and competition are well synthesized in the Cutler and Davis representation [7] (Figure 7.23).

The stability constant is such that any sequestering agent shown on this figure is able to keep in solution or dissolve only the chemicals located higher on the scale. The inductive effect of the long hydrocarbon chain on the carboxylic group makes fatty acid one of the strongest competitors for metals. The inductive effect of the chain is evident in the graph showing the positions of the different fatty acids. Thus, it is extremely hard to succeed in pulling calcium out of soaps having more than 12 carbons (Figure 7.24). This is only feasible by means of EDTA.

EDTA is also a seizing-up agent which increases friction. If we accept 0.13 as the limit of the coefficient of friction for good lubricity, the EDTA concentration

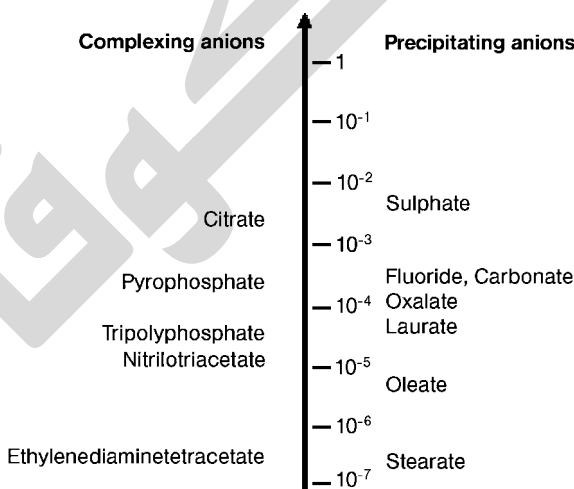


Figure 7.23 Competition between sequestrants and precipitants. Concentrations of free calcium ion (in mol L⁻¹) are shown.



Figure 7.24 Calcium soap precipitation due to sub-stoichiometric ratio between EDTA and water hardness.

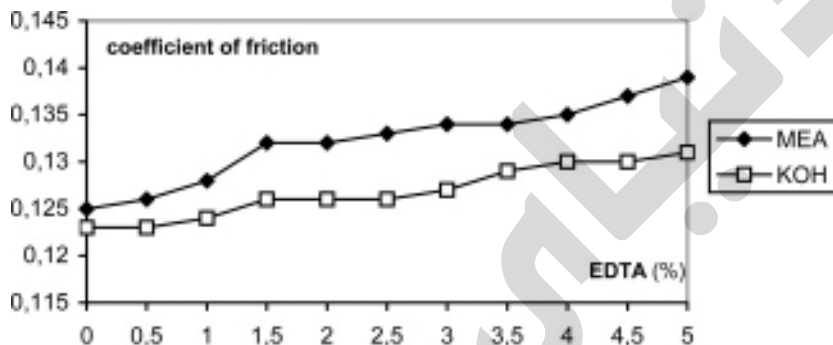


Figure 7.25 Lubricant: fatty acids 14%, C₁₃–C₁₅ 9EO 2%, hexylene glycol 10% and EDTA neutralized alternatively with MEA and KOH.

in the formulation cannot be increased without limit. Acidic EDTA 6% should be considered the extreme limit and the ratio 1:3 for EDTA:soap should be taken as the optimum, as Figure 7.25 demonstrates.

Besides showing EDTA to be a friction maker, Figure 7.25 once more confirms that the friction is higher when MEA is the main alkalinizer. Every chemical providing cleaning properties affects the lubricity just as it also cleans off the lubricating molecules. Surfactants behave in a similar way.

Sodium is another component which affects friction, solution, and also the stability of the formula. Sodium soaps, being solid at room temperature, lead to higher cloud points and depress the mobility of the track. Thus, a lubricant is optimized if KOH is preferred, EDTA is included in the acidic form, a small amount of MEA is present, and surfactants are reduced to a minimum ($\leq 3\%$).

7.2.4

Keeping Tracks Clean

Theoretically speaking, surfactants are not strictly necessary in a soap-based lubricant to get clean tracks. Cleaning is attained with good blend of fatty acids, correct concentration in use, and shrewd arrangement of the delivery plant. Experience demonstrates that rate of soiling and accumulation of dark deposits

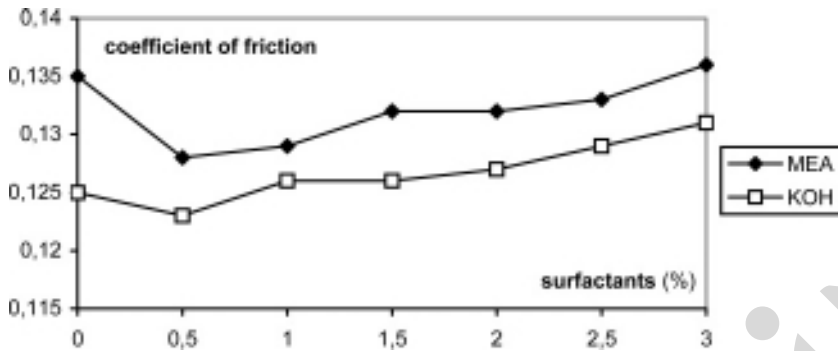


Figure 7.26 Lubricant: fatty acids 14%, EDTA 2%, hexylene glycol 10%, alcohol $C_{13}C_{15}9EO$, neutralized alternatively with MEA and KOH.

significantly decrease as a function of the lubricating power (μ and durability). The presence in a lubricant of a few percent of saturated C_{12} and C_{16} fatty acids improves the self-cleaning capacity and detergency. Furthermore, the more a high volume of solution is sprayed, the more the soil drips down and is cleaned off. Thus, the best balance derives from decreasing the in-use concentration as far as possible and increasing the spray time.

However, a small quantity of nonionic and anionic surfactants synergizes cleaning and enhances detergency. Moreover, in the presence of very hard water surfactants prevent soaps from gelling on the spray nozzles and blocking them when they are not in use. Nevertheless, as already mentioned, surfactants are cleaning agents, and as their concentration increases, the durability decreases. Surfactants promote the removal of both soil and lubricant from the track. Although the loss in lubricity is evident from Figure 7.26, surfactants provide a curve with a minimum of friction.

Taking 0.13μ as the lower limit for good lubricity, surfactants should not exceed 3% in a lubricant. Nonionic and cationic surfactants can cause paint fading on both cans and cartons in contact with the lubricant solution. Different concentrations of nonionic surfactant give fading, as shown in Figure 7.27. In such cases, cleaning can be also obtained with more mild chemicals than surfactants such as glycol derivatives.

Another aspect of cleaning concerns the removal of colored deposits from food and beverages. Fruit and tomato juices are examples of foods leaving the plastic tracks colored. Cleaning is easily accomplished through glycol ethers and alcohols. Such solvents can replace surfactants and yield more eco-friendly lubricants.

7.2.5

Fluidifying and Antigelling

The reaction between fatty acids and alkali (Na, K and alkanolamines) gives products increasingly viscous as a function of their concentration. As lubricants



Figure 7.27 Paint fading by excess of surfactants.

are delivered through automatic equipment, viscosity must not exceed the limit of pumping. Thereby, lubricants include fluidifiers able to keep the viscosity unchanged for all the seasons of the year (from 0 to +40 °C at least). Short alcohols (e.g., isopropyl) and glycols (e.g., hexylene and propylene) together with short-chain fatty acids prove to be good fluidifiers and dispersants. Dispersion prevents lump formation and increases the saponification rate in manufacturing. Moreover, they prevent solutions from freezing inside the pipelines during the cold season.

7.2.6

Foam Control

Foam increases friction, discolors paint, spreads microbial contamination, and leads to soiled and slippery floors. The foam formation depends on soaps and surfactants. Concentrating to improve lubricity often leads to an excess of foam.

As lubrication takes place at room temperature, no defoamer is effective except silicone. Unfortunately, silicone is unstable in the product and accelerates the



Figure 7.28 The right concentration contains traces of calcium soap (last but one).

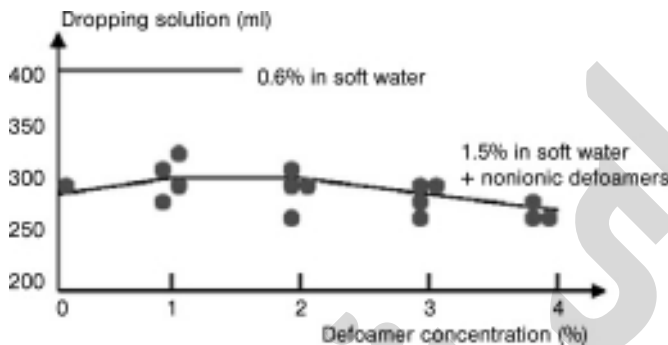


Figure 7.29 Ineffectiveness of nonionic defoamers. Solution collected from the track within 30 minutes of running.

blockage of nozzles. As a consequence, foam control has to be achieved by using the correct concentration, which should be lowest in soft and even hard water where traces of calcium soap help to depress the foam (limit of EDTA stoichiometry), as illustrated in Figure 7.28.

The volume of solution draining from the track is inversely proportional to the amount of foam growing on it. Thus, it is possible to assess the foaming property just by collecting the drained-off solution. Figure 7.29 shows the ineffectiveness of the usual nonionic defoamers in depressing foam.

A slight opalescence of the solution indicates the presence of calcium soaps. A trace of calcium soap does not disturb lubricity, does not precipitate, and is recommended as the best way to reduce foam and enhance the economy of the plant.

7.3

Amine-Based Lubricants

As high concentration in use, sensitiveness to hard water, foam, and precipitation of calcium soaps characterize lubrication with soaps, research has been carried out aimed at finding a solution to these problems. The nitrogen group in a fatty

chain gives a structure capable of providing lubrication. Fatty amines, being insensitive to cationic hardness, can be used at very low concentrations ($<0.3\%$) and also have bacteriostatic properties. However, they do not solve foam problems, do not lubricate like soaps on stainless steel, and prove less durable. As a consequence, more black soil is generated on the tracks. Moreover, fatty polyamines prove to be more harmful to health when an aerosol is formed at spray points [8].

If a lubricating molecule is drawn schematically, a soap could be represented as a nail driven into the surface (chemical reaction) whereas a fatty polyamine could be described as attaching itself by suction (physical absorption). Equally, whereas the moving surface slides over a stable flexible layer of soaps, it moves over a confused layer of amines rolling like wheels. Thus, the adhesion of fatty amines differs from that of soaps. They are more readily removable than soaps when spraying ceases. For this reason, amine-based lubrication shows lower durability (Section 7.1.2) and higher friction on stainless steel. In spite of all of this, insensitiveness to hard water (cations) and biocidal activity mean that these synthetic lubricants are preferred to soaps.

7.3.1

Types of Lubricating Molecules

Early in the 1980s, the investigation of new molecules was directed toward nitrogen compounds because they resulted in the more promising molecules. However, as the toxicity of the fatty amines is greater than that of soaps, one of the first synthetic lubricants was based on long-chain quaternary ammonium. Further investigations established the fatty diamines as providing the most suitable balance for industrial lubrication. *N*-oleyl-1,3-diaminopropane and *N*-lauryl-1,3-diaminopropane were selected for their lubricity and the tertiary lauryldimethylamine for its defoaming ability. Alkyldiamines exhibit small but interesting differences in lubricity. Figure 7.30 shows their distinctive behavior.

According to the theory, oleic diamine first reaches a steady condition because of three points of absorption ($C_9=C_{10}\cdots N\cdots N$) and lauric diamine packs the surface

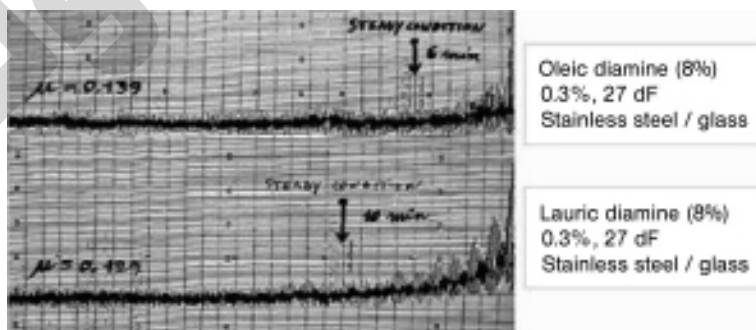


Figure 7.30 Attaining the steady condition.

more closely, with two points of absorption and a longer chain (C_{12} instead of C_9). According to the theory, lauric diamine takes more time to reach the steady condition but gives a little lower friction when investigated in strict laboratory conditions. In practice, considering the overall performance expected from a lubricant, oleic diamine is superior in persistence and reproducibility.

Lauryldimethylamine (LDMA) has defoaming properties. It does not lubricate and, even worse, reduces the average lubricity of the usual fatty diamines. Therefore, LDMA is included in formulations only because of its defoaming properties. The defoaming capacity is inversely proportional to its state of neutralization. When fully neutralized, LDMA actually generates foam, as shown in Figure 7.31:

As the control of the inorganic anionic interference (bicarbonate) is effective at an acidic pH, LDMA does not guarantee a reproducible depression of foam. Being also a friction promoter, LDMA is not included in lubricant formulations intended for very demanding applications.

The basic lubricity of fatty polyamines can be improved by adding synergistic molecules [4]. In particular, TBEP (tributoxyethylphosphate) [4] and DMAD (oleic/linoleic dimethylamide) are members of this group of promoters, the structures of which are given in Figure 7.32.

Although they provide flexible long chains, the absorption of the second pole is insufficient to decrease friction and maintain durability. Nevertheless, when TBEP and DMAD are blended with fatty diamines, lubricity improves as if they

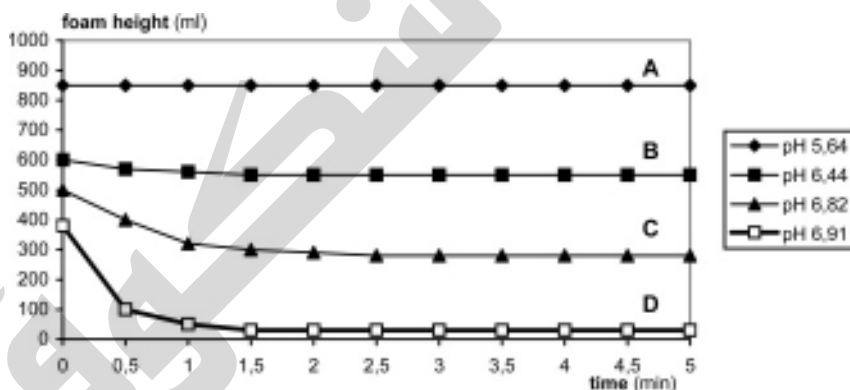


Figure 7.31 Effect of LDMA on foam; procedure: reverse Ross Miles; condition: lubricant 0.5%; pH adjusted with acetic acid; 27 dF hard water.

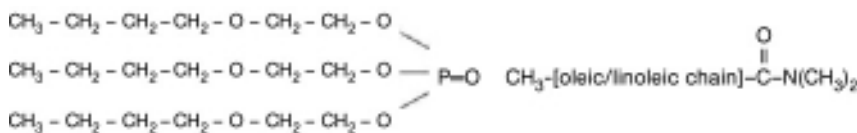


Figure 7.32 Tributoxyethylphosphate and unsaturated long-chain dimethylamide.

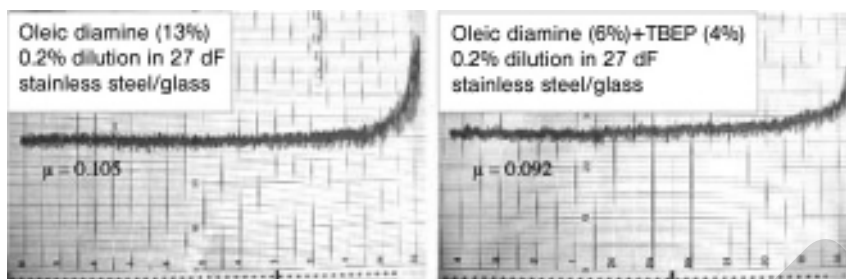


Figure 7.33 TBEP synergizes the lubricity of fatty diamines.

form a substrate which allows the surfaces to slide better. They behave like plasticizers and enhance spreading and joining. The lubricity curves are shown in Figure 7.33, where oleic diamine 6% blended with TBEP 4% gives a coefficient of friction (μ) lower than that due to oleic diamine 13% alone.

7.3.2

Anionic Interference

Fatty amines are cationic and react with the anionic charges to give salts whose stability follows the rule of the solubility product. As they are, fatty diamines possess weak solubility, and their alkaline hydrolysis precipitates calcium carbonate from the bicarbonate in the water. They are therefore neutralized with acetic acid to $< \text{pH } 7$. Neutrality provides the best operating conditions and the best biocidal activity. If the water is sulfate- and phosphate-free, the turbidity of the solution shows a linear relationship to pH in both soft and hard water. Turbidity results from an incomplete neutralization of the fatty diamines.

Thus, insensitiveness to hardness only applies to cations. The anionic components of raw waters react with fatty amines and give insoluble salts. Sulfate, phosphate, silicate, bicarbonate, and colloids (humic and fulvic acids) are anions of reference:

- **Phosphate** should be absent in raw waters and its influence is usually negligible. The presence of phosphate means polluted water. Sometimes, a few ppm of phosphate can be found where water is softened with STP or treatment with vitreous phosphate.
- **Silicate** is never excessive in normal waters and its influence is quite insignificant. It can influence the solubility of polyamines if the concentration exceeds 20 ppm.
- **Sulfate** represents the most important interference because the solubility of its salts at both alkaline and acidic pH is negligible, as illustrated in Figure 7.34.

The sulfate concentration does not affect the lubricity, but does affect the time interval between cleans. Maintenance (cleaning of pipelines and filters) is usually

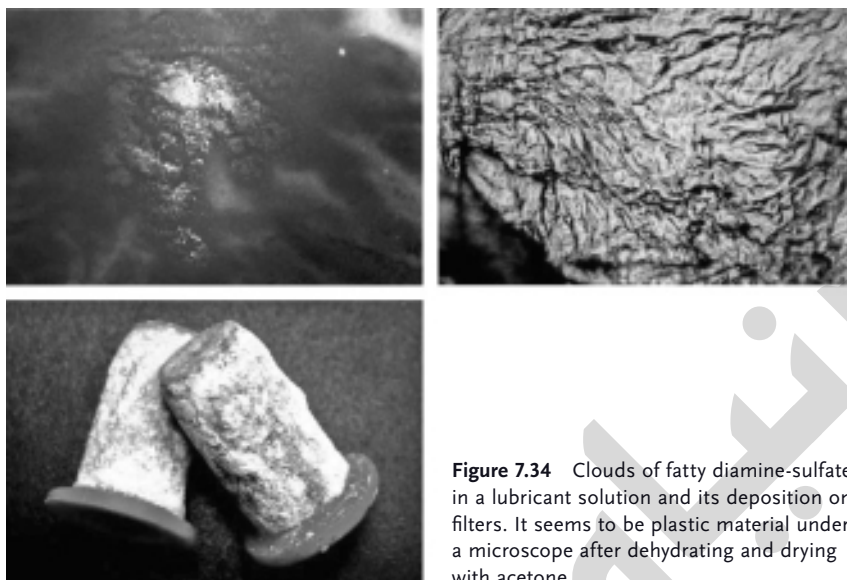


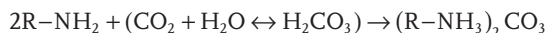
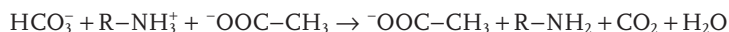
Figure 7.34 Clouds of fatty diamine-sulfate in a lubricant solution and its deposition on filters. It seems to be plastic material under a microscope after dehydrating and drying with acetone.

planned for once or twice a year, usually before and after the busy season. In order to maintain this interval, the sulfate in raw water should not exceed 50 ppm. The higher the concentration, the shorter the interval becomes. When the concentration exceeds 300 ppm, maintenance is required roughly once a month. This makes lubrication practically impossible without using lubricants capable of keeping the amine sulfate salt soluble.

- **Bicarbonate** is the main constituent of normal waters. As described in Section 1.2.1, it shows amphoteric behavior, behaving both as acid and base. Bicarbonate reacts with the hydroxy and hydrogen ions in the following way:



The basic behavior increases pH and gives free fatty diamines and fatty diamine carbonate. The reaction generates cloudy solutions and promotes the coagulation of the salts into macroscopic agglomerates:



The pH varies only when the bicarbonate exceeds the stoichiometric amount of buffer between acetic acid and fatty amine. This happens when a low concentration of lubricant is diluted in very hard water. Fatty diamines give the typical double buffer with acetic acid, as shown in Figure 7.35.

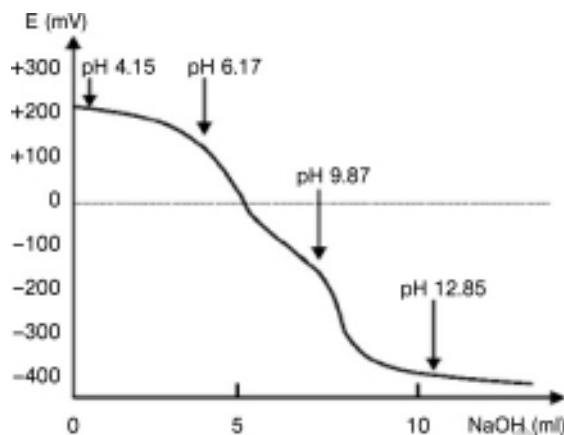


Figure 7.35 5 mL of lubricant (oleic-diamine 10% neutralized with acetic acid at pH 4 in soft water) is diluted in deionized water and titrated with NaOH 0.1N.

- pH 5–6 acetic acid alkyldiamine acetate sodium acetate
- pH 9–10 alkyldiamine alkyldiamine acetate sodium acetate

The potentiometric titration reveals the buffer points (Figure 7.35).

Operation at a pH below 7 makes fatty diamines insensitive to bicarbonates.

- **Humic and fulvic acids** do not strongly tend to precipitate fatty diamines. They do neutralize the cationic charge but would insolubilize even in the absence of fatty diamines. Thus, humic and fulvic acids, when present (e.g., in water from strata close to rivers and marshes), need to be treated irrespective of whether they are in contact with cationic compounds or not (sand or micro-filters, crossflow filtration). The prevention of sulfate insolubilization also controls traces of humic and fulvic acids.

Summing up:

- Sulfate and phosphate cause problems directly proportional to their concentration.
- Bicarbonate interference is prevented by maintaining an acidic pH in operation.
- Silicate interference is usually negligible.
- Humic and fulvic acids (>3 mg/L O₂ from Kübel test) form deposits even in the absence of fatty diamines.

7.3.3

Sequestrants

As polyvalent cations do not affect the lubrication by fatty diamines, sequestrants might be considered pointless. Nevertheless, the inorganic anions disturb the cationic charge and lead to a sort of reverse destabilization in comparison with

the usual concept of sequestration. So far, sequestrants have been regarded as anionic chemicals able to keep other anions soluble. The concept of sequestrants in cationic systems means chemicals able to compete with the fatty diamines for anions and keep their salts soluble or dispersed. Owing to the ionic strength of the fatty diamines, prevention of precipitation of salts must be regarded as a delay of insolubilization and agglomeration rather than indefinite solubilization by complexation. As sulfate is the main chemical of insolubilization, the investigation is carried out on this component of water. Figure 7.36 (a) shows the quantitative influence of sulfate on clouding the lubricant solution. UV-Vis spectrophotometry at 450nm shows the precipitation of salts (turbidity), and the photograph [Figure 7.36 (b)] shows the appearance of the turbidity.

The insolubilization of the fatty diamine sulfate is insufficient to lead one to expect rapid fouling of pipelines and nozzles. There is a boundary point between dispersed and coagulated salts. Only if salts coagulate does a sticky deposition occur within a few days. The change in behavior is illustrated in Figure 7.37.

Dispersion does not mean prevention of deposition but slower growth of the deposit. Thus, keeping the solution clear is always the best approach.

Different fatty diamines react with sulfate in different ways with respect to both intensity and time. Figure 7.38 shows the tolerance of C_{12} -diamine, C_{18} -diamines and C_{12} -dimethylamine.

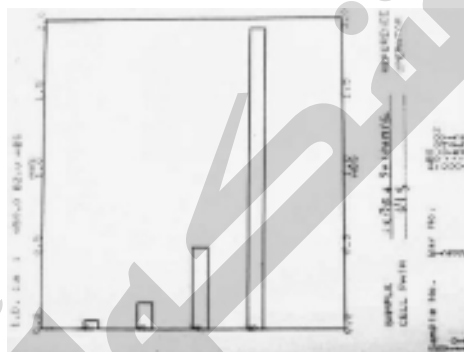


Figure 7.36 Oleic diamine 200ppm in water. Concentrations of sodium sulfate up to 1000ppm. PH 6.8 with acetic acid. The picture relates turbidity to absorption.



Figure 7.37 Dispersed and coagulated oleic diamine-sulfate salt.

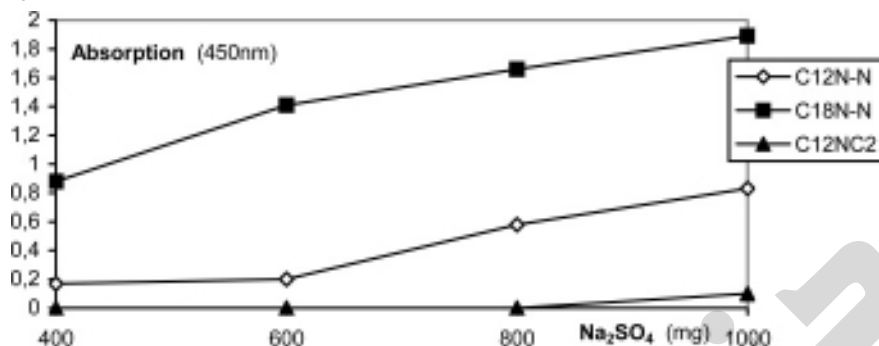


Figure 7.38 Effect of sodium sulfate on fatty amines. Turbidity from fatty amine (200ppm) determined after 30 min. in 27F tap water solution.

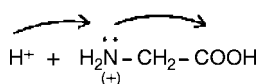


Figure 7.39 Stabilization of the cationic charge.

The most used fatty diamine [oleic diamine ($\text{C}_{18}\text{N-N}$)] is also the most sensitive to sulfate. Lauric diamine ($\text{C}_{12}\text{N-N}$) shows more tolerance. Lauryldimethylamine ($\text{C}_{12}\text{N}(\text{CH}_3)_2$) is practically insensitive.

7.3.3.1 Glycine

Besides providing amphoteric surfactants that perform as dispersant emulsifiers, glycine is a molecule able to provide both anions and cations. As well as amine-based lubrication, the glycine structure exploits its positive charge in competing with fatty amines for anions. A stronger inductive displacement of the nitrogen lone pair enhances the strength of its cationic charge compared to long-chain fatty diamines. The acidic medium further stabilizes the positive charge (Figure 7.39).

The strong charge and the ability to form soluble salts make glycine actually delay the insolubilization and coagulation of the salt, as Figure 7.40 shows.

Glycine behaves as a stoichiometric agent, so that the more the glycine concentration increases, the more the turbidity decreases. Figure 7.40 shows that absence of turbidity just corresponds to a 1 : 1 ratio. This means that the lubricant concentration either increases as a function of the concentration of sulfates or the glycine concentration in the formulation should be so high as to enable any unpredictable concentration to be controlled. In both cases, the resulting lubricant is not cheap in application. Moreover, as polyamines compete for the same anions, glycine loses the competition in time, roughly within 60 min in the presence of sulfate >200ppm. Opalescence soon appears again, as shown in Figure 7.41.

Although plants rapidly exploit the freshly made solution, the stoichiometric reaction and the relatively expensive application mean that glycine is only useful when the inorganic interference is moderate.

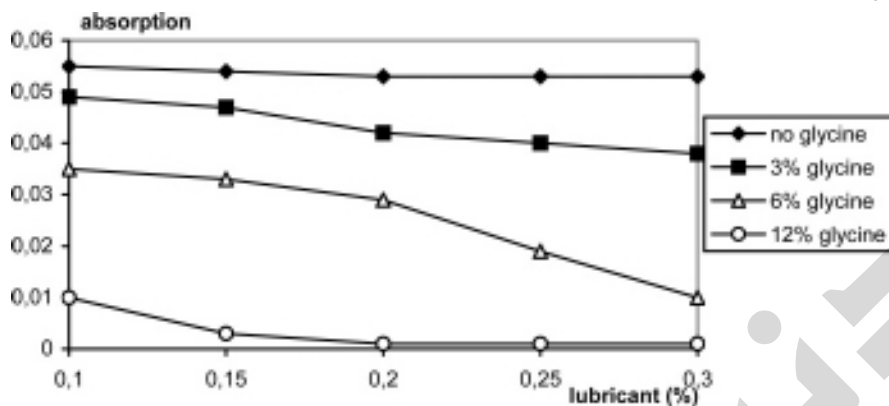


Figure 7.40 Effect of glycine on long-chain fatty diamines. Condition: wavelength 450 nm, absorption 2 h after preparation. Lubricant: oleic diamine 13% and acetic acid to pH 5.2. Lubricant diluted in 27 dF hard water containing sodium sulfate 250 ppm.

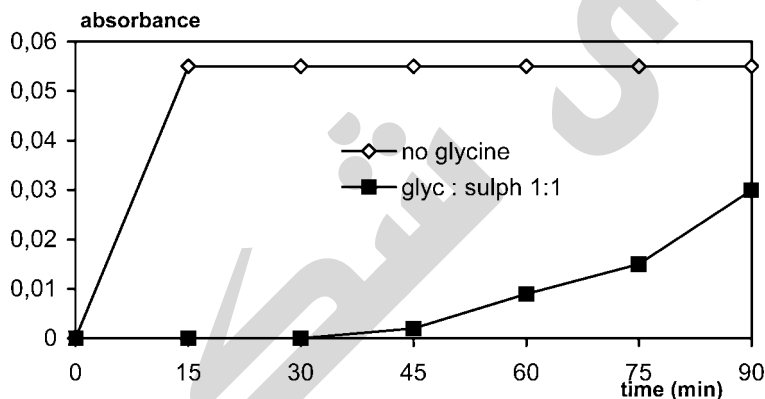


Figure 7.41 Appearance of turbidity after time. Conditions: 0.2% solution in hard water (27 dF) + 500 ppm of sulfate. Lubricant: oleic diamine 13% neutralized at pH 5.2 with acetic acid. Glycine 1:1 with sulfate.

7.3.3.2 Lauryldimethylamine [CH_3 (lauryl) $\text{CH}_2\text{-N}(\text{CH}_3)_2$] (LDMA)

Lauryldimethylamine successfully prevents sulfate salts from precipitating. LDMA has already been described as a foam controller (see Section 7.3.5). The more the concentration increases, the more the insolubilization of fatty diamine-sulfate salts is delayed. Rather than being a sulfate conditioner, the tertiary amine seems to behave as a temporary hydrotrope for the polyamine-sulfate salt.

The Figure 7.42 shows fixed concentrations of LDMA in a 1% lubricant solution and sulfates varying from 100 to 800 mg L^{-1} .

The sulfate control is temporary. The transparency of the solution is retained as a function of the LDMA concentration and for how long the contrary action of

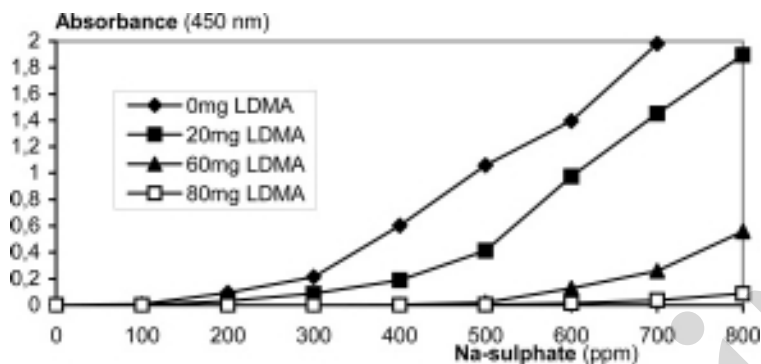


Figure 7.42 Sulfate control depends on the LDMA concentration.

the ionic strength of the fatty diamines is counterbalanced. The transparency is maintained for 20–40 min after preparation as a function of the type of fatty diamine. Opalescence slowly appears and remains dispersed for a long time. Delay and dispersion prevent precipitation in the delivery plant.

Lauryldimethylamine is a foam depressant. When co-formulated with fatty diamines, it provides sulfate control, low foam and acceptable cost-in-use. However, LDMA is also a friction promoter. Increase of LDMA reduces the lubricity. Lubricants based on LDMA cannot be used when a robust lubricity is required. It is the best alternative to silicone on plastic C Raine.

7.3.3.3 Fatty Alcohol Ethoxy Carboxylate (FAEC)

The prevention of precipitation from sulfate-amine and phosphate-amine is accomplished through emulsifying and dispersing carboxylate condensed surfactants. A typical molecule is represented below:



The combination of anionic (carboxylation) and nonionic (ethoxylation) hydrophilic strength keeps the fatty diamine salt soluble. FAEC behaves as an effective hydrotrope. Figure 7.43 shows the effectiveness of FAEC in preventing turbidity: FAEC moves the absorption to zero (limpidity)

FAEC maintains clear solutions for an indefinite time when properly concentrated. Lubricity is not disturbed. Figure 7.44 demonstrates its effectiveness in 0.2% oleic diamine solution with sodium sulfate from 100 to 1000 ppm.

The absence of FAEC generates an immediate cloudiness. Being conscious that surfactants are sometime undesirable because of environmental problems, it follows that an ideal solution to the sulfate control problem does not exist. Adaptation of different chemicals to the practice is advisable, bearing in mind that periodic maintenance of the equipment (cleaning) is part of the lubrication process.

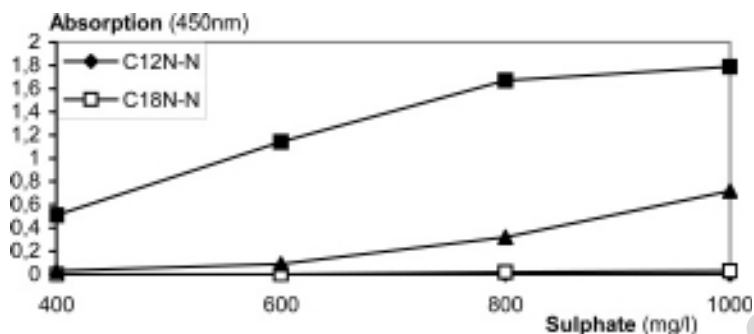


Figure 7.43 Effect of FAEC in preventing turbidity.



Figure 7.44 Test of FAEC efficacy in preventing turbidity.

7.3.4

Cleaning and Microbial Control

When a mobile layer is placed between two surfaces to keep them sliding, the surfaces are lubricated. Surface roughness and protuberances, however, come into contact and produce friction. Friction welds, scrapes granules of surface off and forms metal oxides responsible for the black contamination on and beneath the tracks. Fatty diamines generate higher friction and produce more voluminous black deposit than soaps. Contamination is cleaned off by using the lowest

possible concentration and spraying the highest volume of solution, as mentioned in Section 7.1.3. Nonionic and amphoteric surfactants help the lubricant to keep the tracks clean and disperse slime. As physical adsorption gives lubrication less sensitive to the presence of surfactants than soaps, surfactants are fundamental to cleaning when amine-based lubrication is used.

Their insensitivity to cationic hardness and their biocidal activity have led to fatty diamines being the most important group of lubricants in the food industry. Their stability in water and disinfecting power improve when fatty diamines are neutralized to a pH less than 7. Figure 7.45 shows the biocidal effect of oleic and lauric diamines.

Lauric diamine at 8% performs even better than oleic diamine/triamine at 13%. This result shows that the C₁₂-chain is the ideal length for killing microorganisms. However, alkylpolyamines have slow biocidal activity because of a partial positive charge. This slowness gives longer stability in soil and enhanced bacteriostatic activity. Thus, open surfaces (tracks) are protected longer. A comparison of the durability of various disinfectants on open surfaces is diagrammatically represented in Figure 7.46.

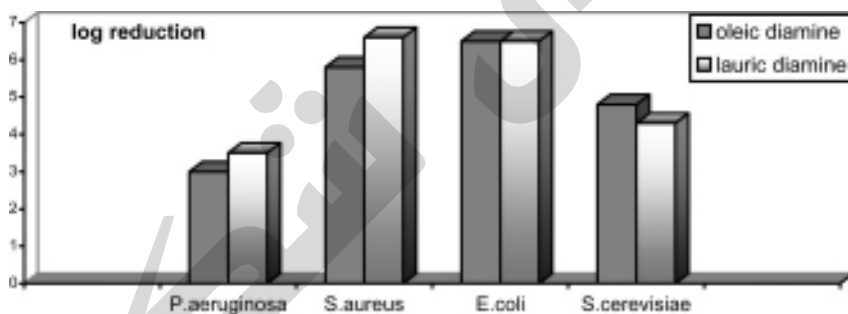


Figure 7.45 Biocidal effect of lauric and oleic diamines. Condition: European Suspension Test: 0.3% w/w, 5 min at 20°C. Lubricant: oleic diamine 10% + lauric triamine 3% + acetic acid; lauric diamine 8% + acetic acid.

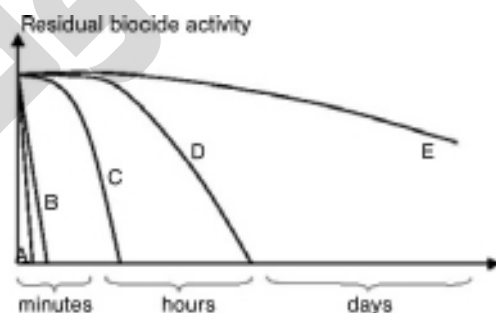


Figure 7.46 Durability of various disinfectants. A = peroxides; B = halogens; C = monomer QAC; D = polymeric QAC; E = alkylpolyamines and amphoteric alkylpolyamines.

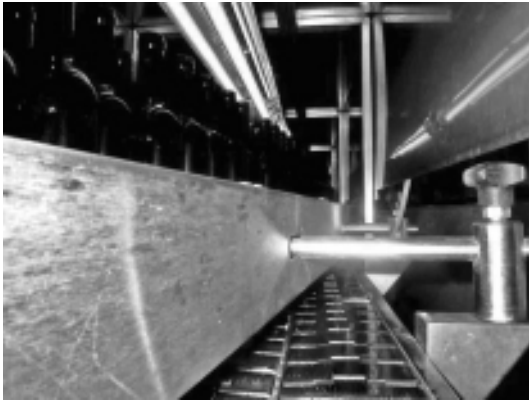


Figure 7.47 UV-lamps microbiologically protect the environment around a conveyor running in stainless steel reflecting tunnel.

Track disinfection involves the concept of infinite time of contact. When running, conveyors are regularly covered with the lubricant solution. Fatty diamines have all the necessary time to express their biocidal activity and control the growth of the microorganisms after the end of the bottling process. As described in Section 7.3.5, the microbial control required is bacteriostaticity. The complete eradication of microorganisms is quite impossible because of the relatively low concentration and being in open space. Moreover, it is known that the cationic charge has more difficulty in killing Gram-negative microorganisms (e.g., *Pseudomonas*). Thus, fatty diamine-based lubricants select a typical biofouling which grows inside pipelines and on tracks. Additional disinfectants are periodically required such as chlorine dioxide, high concentrations of QACs, and isothiazolone (see Section 7.3.5).

Some manufacturers protect the beverage during its entire journey through the plant in a sterile de-oxygenated environment by providing a pressurized atmosphere of nitrogen or carbon dioxide. Containers, in contrast, are often biologically unprotected from warehouse or bottlewasher to filling area. In order to guarantee a sterile atmosphere and prevent recontamination, UV lamps can be installed along the path, as shown in Figure 7.47.

7.3.5

Biofouling in the Delivery Plant

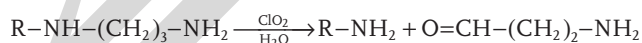
Although use of the appropriate chemicals prevents fatty diamines from reacting with sulfate, phosphate, carbonate, or silicate, nevertheless a deposit frequently occurs in pipelines and spray filters. Deposition originates from biofouling. Biofouling follows a definite sequence. Nothing happens, even for months, but after a slight deposit appears, it grows exponentially and obstructs the sprays within a

few weeks or even a few days. The deposit looks like a gelatinous slime, as shown in Figure 7.48.

The protonated fatty diamine is a cationic agent, whose concentration in the solution is in the range 100–300 ppm on average. However, this does not succeed in eradicating bacteria such as *Pseudomonas*, whose resistance to cationic biocides (QACs, amphoterics, and polyamines) is well known, this microorganism having been comprehensively investigated because of its rapidly produced filaments and bulky slime.

Chlorinated alkaline detergents perform the periodical cleaning of the delivery plant. Chlorine adds disinfection to cleaning and the plant remains clean even for months. During this period, the cationic biocide-resistant microorganisms are gradually selected. The time delay before further growth depends on the microbiological quality of the raw water diluting the lubricant and niches of biofouling still alive in the pipelines after cleaning. The metabolism of the microorganisms excretes glyco-proteic-alginic substances in which they protect themselves (see Chapter 14). When established, the microorganisms and their slime grow exponentially until the delivery plant is obstructed.

Good quality of water and absence of residual biofouling after cleaning are crucial factors to smooth running for a long time. The delivery plant is therefore periodically treated with chlorine dioxide, peracids, isothiazolone, bromine, and high concentrations of quaternary ammonium compounds (daily or once a week). Boosting the basic biocidal activity of the lubricant with such disinfectants is possible provided that certain dangers are guarded against such as the risk of foam (QAC), decrease in lubricity by breaking the lubricant chain (chlorine dioxide), loss of biocidal action (isothiazolone), environmental risk, and metal spots on stainless steel tracks and cans (heavy metals). The following equation shows how chlorine dioxide can break the lubricant chain:



Fatty diamine-based lubricants, however, are protected by biocides directly co-formulated or added to the solution. In particular, isothiazolone and QACs are

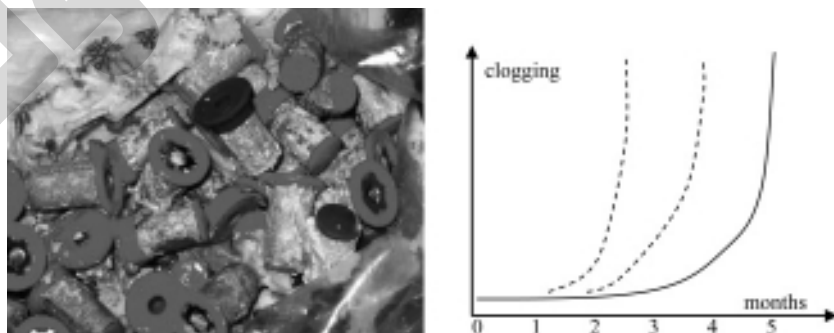


Figure 7.48 Biofouling on filters and growth rates.

suitable to be included in the lubricant. Chlorine dioxide is the biocide of choice to treat the water diluting the lubricant.

7.3.6

Chlorine Dioxide in Preventing Biofouling

Biofilm-producing microorganisms are believed to provide a matrix resisting mechanical and chemical treatments. They may also form anaerobic and acidic micro-environments by reducing the oxygen concentration and producing acid [9]. These niches afford a convenient environment for facultative or obligate anaerobic and acid-tolerant spoiling bacteria. Once established in the biofilm, the potential beverage-spoiling microorganisms can infect the product during the bottling process via aerosols [9]. The high risk area is reputed to be the filler line, where the hygiene status should be tackled with special attention. As well as the filler line, the lubrication system is crucial for safe beverages. Fatty amines and imidazolines have a biostatic rather than a completely biocidal effect on the products. Options to increase the biocidal efficiency and reduce the cost of cleaning are either to formulate a lubricant including a disinfectant of reinforcement (e.g., isothiazolone, QAC) or blend the lubricant solution with a separate biocide such as chlorine dioxide (ClO_2).

Although laboratory tests demonstrate that most of the amine-based lubricants inactivate more than 60% of chlorine dioxide within two minutes [10], the benefits of chlorine dioxide addition are visible even after a few days of treatment. Figure 7.49 [10] shows the percentage recovery of chlorine dioxide in the presence of 0.3% solution of lubricant after 2 min of contact time.

Chlorine dioxide (4–7 ppm) is added to the lubricant solution to counterbalance its inactivation, the level having fallen to 1–2 ppm residue at least a few minutes after the addition. As an alternative option, more compatible lubricants can be used to reduce the degradation of the molecule (see Section 7.3.5). In both cases the following benefits are achieved [10, 11]:

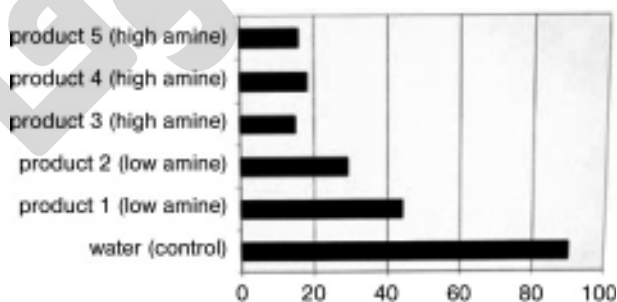


Figure 7.49 Percentage recovery of chlorine dioxide in the presence of 0.3% solution of lubricant after 2 min of contact time (courtesy of von Rège [10]).

- decrease in the number of total cell counts in all areas
- improvement in the self-cleaning process of conveyors
- visual appearance much better than when periodical conventional cleaning is practiced
- installation of an automatic conveyor-CIP for cleaning not needed
- lower frequency of chain cleaning procedure
- no negative influence on operators' health, environment, waste water, and materials.

Chlorine dioxide technology is based on handling two products: lubricant and ClO_2 . This complex process can be simplified if a biocide is included in the formulation of the lubricant. Reinforcement of a lubricant with isothiazolone or QAC is as effective as separately adding chlorine dioxide.

7.3.7

Foam Control

When soap is the lubricant, traces of calcium soap in solutions provide foam control in hard water. The decrease in concentration associated with suitable adjustment of 'on' and 'off' attains the same goal in soft water.

When alkylpolyamine is the lubricant, the only opportunity to depress foam generation consists in decreasing its concentration. As described in Sections 7.3.1 and 7.3.3, lauryldimethylamine in the lubricant can reduce the foam. However, LDMA is known as a friction maker. Hence, the success in reducing foam mostly depends on setting the delivery plant rather than on the lubricant. As already mentioned, the best practice consists in lowering the lubricant concentration and spraying a higher volume of solution. In this way, foam is acceptable, and lubricity and cleaning improved.

An acceptable level of foam should be preferred to its thorough elimination. Foam becomes troublesome when it grows in static form like stalagmites. It is often sufficient if the foam is made to flow like a liquid by the use of flow agents (e.g., nonionic defoamers), as Figure 7.50 shows.

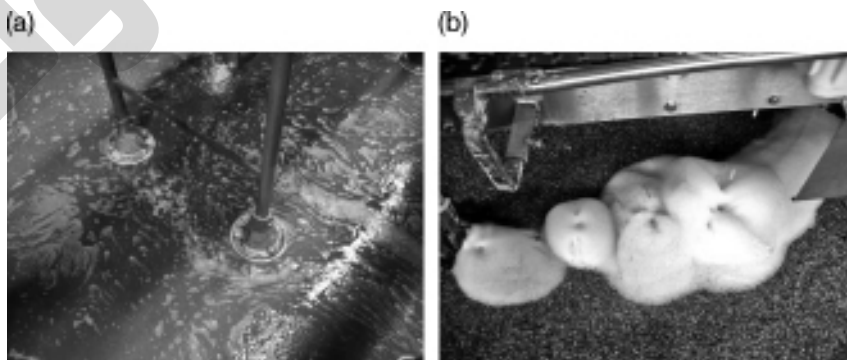


Figure 7.50 Foam (a) flowing like a liquid and (b) solid like a stalagmite.



Figure 7.51 Progressive foam control.

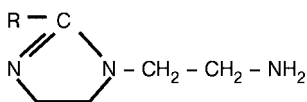


Figure 7.52 Structural formula of aminoethylalkylimidazoline.

As well as using nonionic defoamers, there are other ways of helping to diminish foam. Antifoaming chemicals can be added such as organic and phosphoric esters, glycol and glycol ethers, fatty dimethyl amides, and dispersed silicone. Even fatty acids (e.g., oleic acid) can be stabilized together with fatty diamines by means of suitable hydrotropes in order to enhance lubricity and act as defoamers, as illustrated in Figure 7.51.

7.4

Imidazoline-Based Lubrication

Fatty imidazoline compounds form a further group of synthetic lubricants (Figure 7.52), where

- fatty means R-chain $\geq \text{C}_{12}$
- the imidazole ring contains a secondary shorter chain ending with an amine group.

Fatty imidazolines have properties comparable to those of fatty diamines. They are insensitive to cationic hardness (Section 7.3.2), can be used at very low concentrations, and provide comparable biocidal activity, as shown in Figure 7.53.

However, according to the theory of lubrication, fatty imidazolines do not coat surfaces as effectively because of the steric hindrance of the ring. Thus, they take more time to reach steady conditions than fatty diamines and their lubricity is inferior. Figure 7.54 shows inferior performance with respect to friction, micro-friction, and time to reach steady conditions (> 20 min).

The differences are remarkable on steel/glass and decrease on steel/plastic and plastic/plastic. Fatty imidazolines have no durability, as do fatty diamines (Section 7.1.2). Fatty imidazolines are foaming agents and sensitive to inorganic anions.

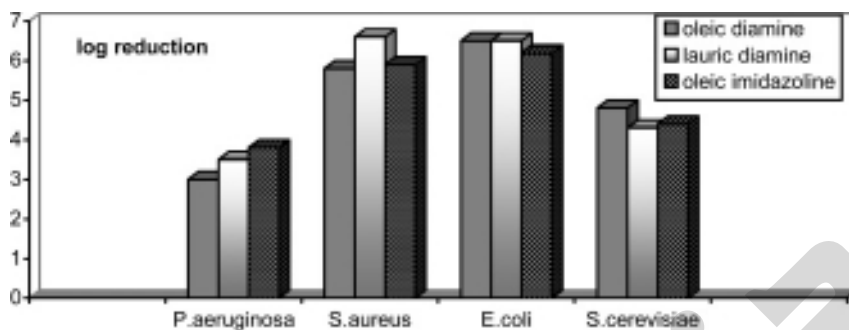


Figure 7.53 Biocidal effect of fatty imidazolines. European Suspension Test: 0.3%w/w, 5 min, 20°C.

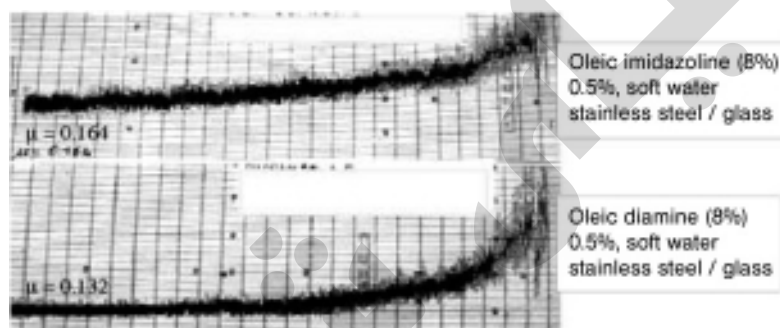


Figure 7.54 The difference in lubricity between oleic imidazoline and diamine.

Thus, concentration, pH in use, biofouling prevention and ‘on-off’ arrangements are set according to what described for fatty diamines.

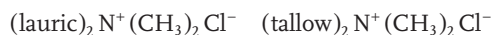
In contrast, toxicology favors fatty imidazolines (2000 mg/kg LD_{50rat} vs 500).

7.5

Lubrication Based on Fatty Quaternary Ammonium Compounds (FQACs)

The investigation of synthetic lubricants dates back to the early 1980s with pilot experiments on several categories of chemicals aimed at finding any chemical suitable to replace soaps. Lubricity, insensitivity to water hardness, and low toxicity were parameters asked of the new molecules. Nitrogen compounds promised to satisfy all of them. As toxicity was one of the most considered parameters in the early application, fatty quaternary ammonium compounds (FQAC) were first applied in the field, although fatty diamines provided better lubricity.

In compliance with the theory of lubrication, QACs carry two fatty chains which offer the flexible layer to the moving surfaces. Di-lauric and di-tallow chains give the best result:



The steric hindrance of four groups per nitrogen is considerable and, moreover, the methyl groups contribute absolutely nothing to the lubrication. Consequently, the coating is less compact, absorption is weak and desorption is facilitated. Even if acidified below pH 7, the solubility of FQACs in water remains incomplete because of a permanent molecular repellency. Comparing the coefficient of friction of soaps, fatty diamines, FQACs, and silicone, there are notable differences in lubricity on stainless steel/glass and plastic material. While silicone does not perform on stainless steel/glass at all, FQACs retain a trace of lubricity from nitrogen adsorption. Table 7.4 summarizes and compares average coefficients of friction obtained from different categories of lubricants.

The result is in accordance with the theory, which provides for different ways to lower the coefficient of friction:

- Metal surfaces chemically react with the carboxylic group.
- Metal-free surfaces (plastic) are unable to provide anything to chemically react with the carboxylic group (soap)
- The negative permanent electric field associated with metals allows the positive charge (nitrogen) to be only physically absorbed.
- Being made of soft and hydrophobic material, plastic chains and plastic containers offer less resistance to motion.

Thus,

- Soaps are the best lubricants for stainless steel/glass.
- Fatty diamines and imidazolines perform equally on steel, glass, and plastic.
- Silicone does not lubricate stainless steel, but it proves to be the best lubricant for plastic/plastic surfaces.

Table 7.4 Coefficients of friction obtained with various lubricants. Conditions: lubricants in a typical formulation and concentration in soft water: Soap 10% diluted to 0.6%, nitrogen compounds 8% to 0.3%, silicone 10% emulsion to 0.3%, FQAC 8% to 1%.

Lubricant	Coefficient of friction			
	S. steel/glass	S. steel/PET	POM/glass	POM/PET
Soaps	0.121	0.110	0.088	0.091
Oleic diamine	0.132	0.119	0.109	0.110
Oleic imidazoline	0.164	0.136	0.121	0.124
D-lauric QAC	0.221	0.154	0.133	0.121
Silicone	0.404	0.212	0.136	0.090
D-lauric QAC + Silicone	0.229	0.147	0.122	0.108

- FQACs are effective on plastics. The lauric chain interacts with the positive charge less than the tallow chain because of the lower inductive effect. Thus, di-lauric QAC lubricates a little better than di-tallow.
- Silicone can synergize with FQACs when co-formulated. By adding two silicone compounds (lubricating and defoaming), lubricity is enhanced and foam depressed.
- LDMA gives better lubricity on plastic than oleic and lauric polyamines.

7.6

Silicone-Based Lubricant

Interest in lubricants based on silicone has kept up with the increasingly widespread use of plastic chains and containers. Silicone proves to be the most suitable lubricant for plastic materials. Neither fatty amines nor soaps nor FQACs are able to lower the coefficient of friction and micro-friction in a similar way. The stickiness of silicone makes it suitable for dry technology as well (see Section 7.7). Figure 7.55 compares the lubricity of silicone with that of two other lubricants for cartons on polyacetalic belts.

Cartons, being large and non-rigid composite containers, need efficient lubricity to prevent falls at start-up, stops, on slopes, and during change in direction.

Silicone does not lubricate stainless steel tracks (see Figure 7.56).

Lubricity becomes increasingly unacceptable for values of μ above 0.130. Thus, lubrication on stainless steel is unacceptable.

The greasiness and viscosity of silicone readily leads to absorption of spillage and airborne contamination, so that frequent cleaning of the conveyor is required.

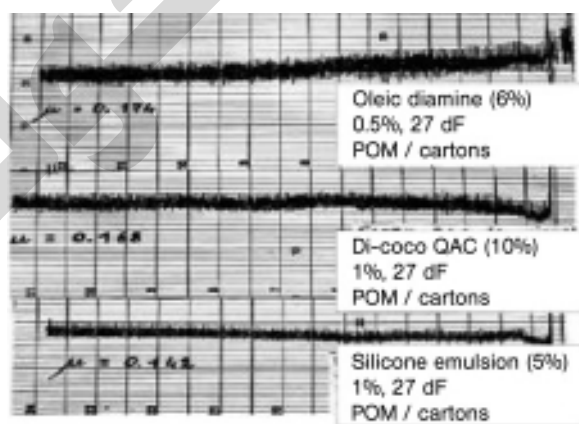


Figure 7.55 Comparison of three classes of lubricants.

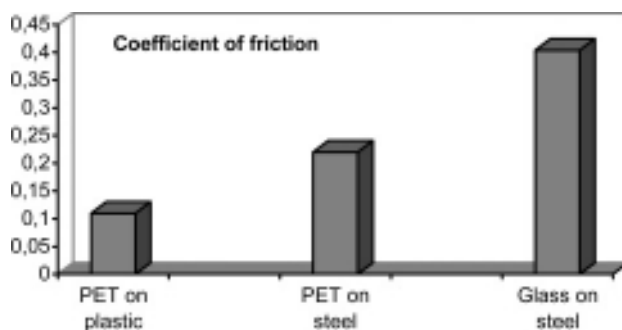


Figure 7.56 Effect of silicone on coefficient of friction for different materials.

Table 7.5 Coefficients of friction of siliconic lubricants containing biocides.

Biocide	μ
Silicone (blank)	0.104
Isothiazolone ^{a)}	0.104
Polymeric QAC	0.115
Bromonitropropanediol	0.118
Biguanide	0.123
Fattytriamine	0.134

a) Kathon WT. Kathon® is a Rohm and Haas trademark.

Table 7.6 Microorganisms on chain in mineral water bottling.

Total bacterial count	5×10^2
Total coliforms	0
<i>Escherichia coli</i>	0
<i>Enterobacteriaceae</i>	0

Users demand bactericidal activity, and the nonionic nature of silicone readily tolerates disinfectants. However, the lubricity of silicone is affected when it is mixed with nonlubricating molecules. Table 7.5 shows the effect of added biocides on the coefficient of friction of silicone.

Isothiazolone does not affect the coefficient of friction and provides the lubricant with an effective biocidal property. The lubricating solution covers the conveyor belts for several hours a day. Thus, the concept of infinite time of contact sets bacteriostatic conditions. The microbiological analysis (Table 7.6) of a track used in mineral water bottling bears out the theory.

The result is remarkable in spite of the low concentration of biocide and the fact that this open plant is exposed to continuous movements of people, motors, and machines.

7.7

Dry Lubrication

The term 'dry lubrication' means that a thin film of neat lubricant is discontinuously spread on the conveyor chains (no pre-dilution in water). Silicone-based lubricants were first used for this purpose. A few drops are placed on the plastic chain at intervals varying from 10 min to 1 h.

As crests and depressions responsible for friction persist even on smooth surfaces, the concept of keeping two surfaces separated by interposing a mobile solid was believed a good approach to dry technology. The solid has to be small enough to fill depressions, resistant to prevent contact of crests, and elastic enough to allow regular sliding. Small PTFE balls were first proposed. Polytetrafluoroethylene microballs, dispersed in an oily fluid, were periodically laid on the chain to enable the surfaces to slide smoothly. A schematic view is given in Figure 7.57.

Teflon (PTFE) is a polymer whose physical and chemical resistance is well known, as well as its use in several industrial applications (e.g., gaskets, chains, worktables, sliding supports, and as an additive in resinous and polymeric coatings for food contact surfaces). It can also be atomized into very small particles (Figure 7.58), improperly called nanoballs, suitable to fill depressions, keep surfaces separated, and reduce friction.



Figure 7.57 Representation of lubrication by PTFE.

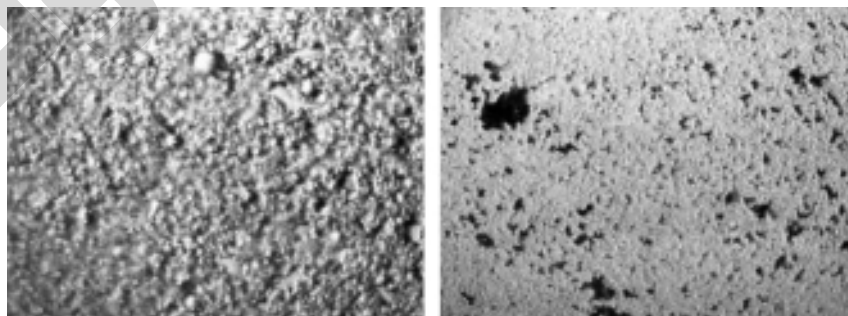


Figure 7.58 Dry lubricant: two photomicrographs of PTFE microballs on a surface.

However,

- Lubrication in the food industry requires not only lubricity but also clean tracks in order to have clean containers and a low microbial charge.
- Airborne and spilled soil should be prevented from being collected and accumulated on the track.
- PTFE is a solid with a density of $\sim 3.1 \text{ g mL}^{-1}$, and needs to be stabilized in a liquid formula. Such stability requires co-formulants selected from viscous chemicals (e.g., glycols, glycerol, silicone, and glycerides). Triglycerides from seeds (i.e., vegetable oils) have been adopted because of their outstanding lubricity on stainless steel/glass.
- As PTFE is a solid, the lubricant cannot be diluted in water. If diluted, PTFE microballs lose their stability because of gravity, separate, and clog nozzles.

For the reasons mentioned, the lubricant is put down neat. Special equipment is used to provide very small volumes at regular intervals. Brushes frequently assist this equipment to spread the lubricant on the chain, though, as brushes gather dirt, they can be replaced with lubricant-spraying micro-injectors. Figure 7.59 shows a typical spreading operation by brushes.

Viscous lubricants need modified of delivery equipment.

Although less pressure is used than in earlier proposed equipment, a pressure of several bars is still required to enable a viscous liquid to be delivered, and the equipment and pipelines must be pressure-proof. However, in line with the trend to formulate non-viscous lubricants, even traditional delivery plants have become suitable for the newly developed lubricants. Wet and dry treatments are compared below:

- Wet conventional systems lose 90% of the lubricating solution (on the floor or in draining pipeline), whereas dry lubrication reverses this ratio.
- The overall volumes of lubricant differ significantly. The dry lubricant is added at the rate of a few mL every 20 or more minutes. This low consumption of chemicals means a considerable cost saving.

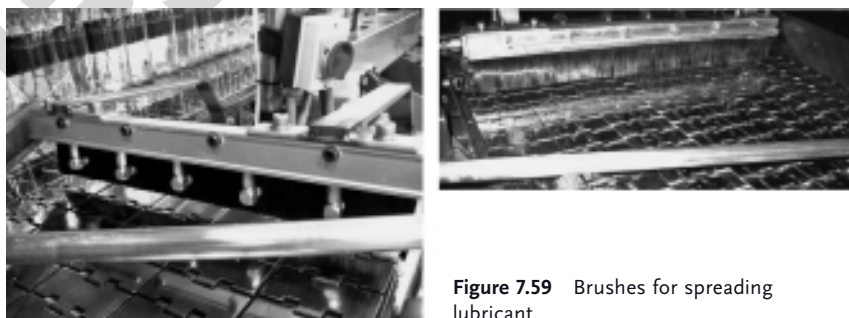


Figure 7.59 Brushes for spreading lubricant.

- As non-aqueous systems do not drain away and do not allow slime to form, floors remain clean and the environment maintains a tidy appearance.
- Lubricity is excellent with dry technology. The coefficient of friction (μ) is one of the lowest on both steel/glass and plastic/plastic.

However, the theory of PTFE lubrication has proved to be suspect. The practical evidence is that the lubricity does not change when PTFE microballs are removed from the formula, and decrease in the coefficient of friction actually derives from the co-formulants such as triglycerides, oil from α -olefin polymerization, glycerol, polyglycols, silicone, and fatty acids rather than from PTFE microballs. PTFE has no practical effect on the lubricant performance. As a consequence, PTFE remains a 'magic buzz word' to denote a type of lubrication rather than being an effective friction reducer. Figure 7.60 compares lubricants, the formulae of which only differ in the presence or absence of the PTFE component. They prove that there is no benefit from having PTFE microballs in a formula.

The coefficients of friction (μ) are absolutely comparable with and without PTFE. Looking at the performance of the co-formulants, the theory of lubrication is confirmed once again. Triglycerides, structurally similar to soap, perform like soaps and attain good lubrication in all conditions. Glycols and glycerol do not have a chemical structure suitable to reduce friction, so they can be used either with silicone on plastic or with fatty acids (and triglycerides) to lubricate plastic and stainless steel/glass (Figure 7.61).

Glycerol does not lubricate hard surfaces (Figure 7.61) ($\mu = 0.335$ vs $\mu = 0.098$ from vegetable oil). Nevertheless, dry glycerol is suitable for lubrication on plastic materials where friction is not so severe. Thus, the dry technology does not add

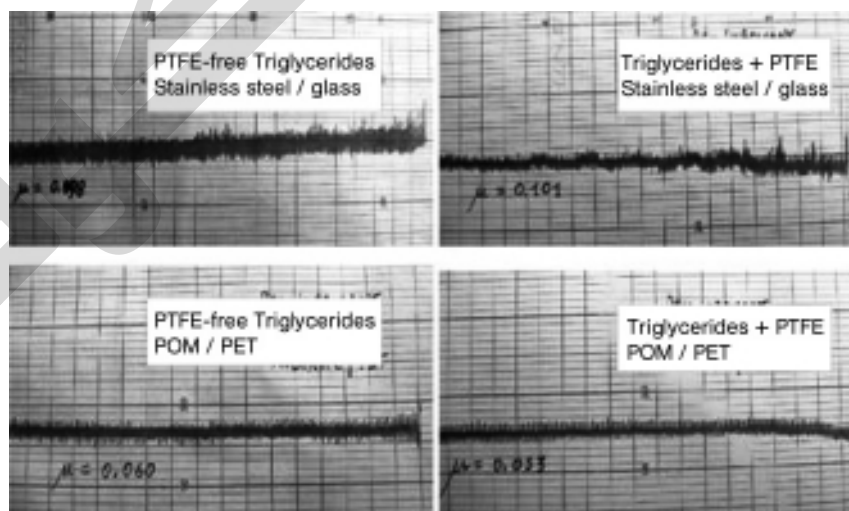


Figure 7.60 Dry lubrication does not need PTFE.

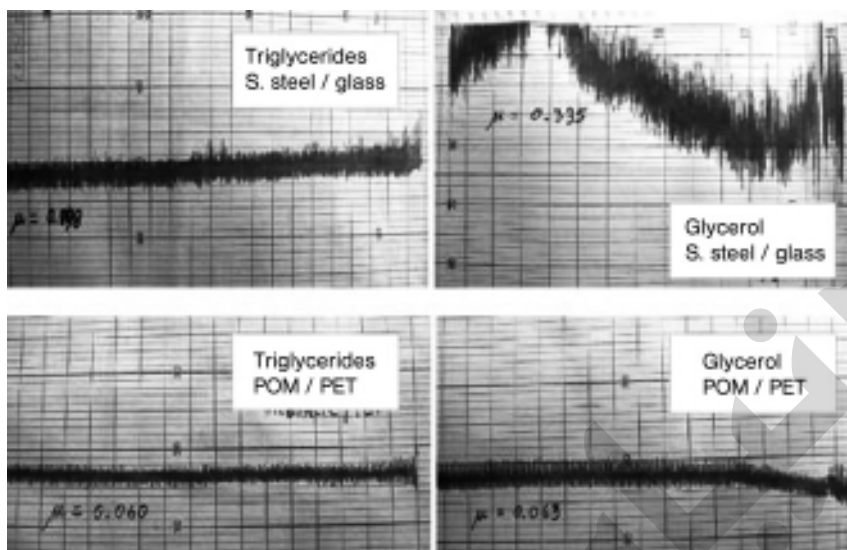


Figure 7.61 The theory does not change in dry lubrication.

anything new to the conventional theory of lubricity. Vegetable oils and fatty acids for stainless steel/glass, glycols, polyglycols and silicone for plastic/plastic perform as expected from the theory. Conventional soap-based lubricants could be applied as dry lubricants if they were free of water and tracks were free of aqueous spillage. Since water causes sticky foam on chains, water and spillage in practice make them unsuitable for a satisfactory application.

On the other hand, non-neutralized fatty acids are selected and co-formulated with polyglycols, triglycerides, and silicone to provide lubricants with excellent lubricity on stainless steel.

As a very small volume is sprayed onto the chain, the lubricant has difficulty in reaching the chain-guide and track-guide structure. The back chain and guide undergo high friction and fretting corrosion. A few nozzles spraying on the back chain underneath the track are needed to lubricate these critical areas in order to prevent damage. Figure 7.62 show a back chain with damage due to scraping caused by the absence of lubricant and debris resulting from fretting corrosion.

Therefore, as ever, good lubrication mostly derives from planning of the delivery plant.

Although the lubricity on stainless steel/glass can be excellent, in practice the dry lubrication of these materials needs care due to a rapid accumulation of black sticky soil which contaminates the container. The following steps constitute the soiling process:

- Friction causes microscopic areas of high temperature at the contact points of the crests.
- Temperature welds the crests together.

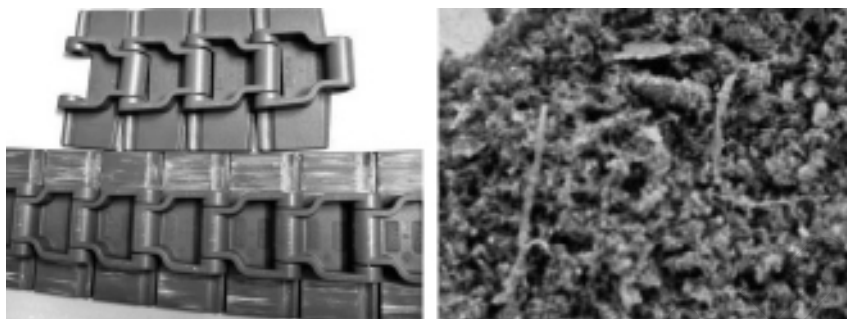


Figure 7.62 Damage caused by lack of lubrication of PBT back chain.

- Traction force breaks welds and generates black oxides.
- Black oxides remain on the chain absorbed into the viscous layer of the lubricant.
- Black contamination sticks on the bottom of containers.
- Soiled bottles stain tablecloths and the company loses its reputation.

A few hours of running are quite enough to make the black contamination grow and dirty the track and the containers sliding on it. This does not occur on plastic. Hence, the dry technology suits plastic-on-plastic and also mixed systems where at least one surface is plastic. Conversely, glass-on-steel needs the dry lubrication to be linked to a planned procedure for cleaning tracks. Thus, a cleaner compatible with the lubrication process is included in a procedure which provides for repeated cleaning at regular intervals (of a few hours) during running. This allows tracks and containers to be kept clean without affecting productivity. The cleaner can be even a lubricant based on fatty diamine rich in surfactants. Surfactants clean and fatty diamine goes on lubricating. The cleaning product is diluted in water to clean successfully. Thus, the lubrication stops being dry just for the time needed to clean.

7.8 Stress Cracking

The convenience and remarkable versatility of plastic bottles were the reasons for their penetration into every sector of the beverage business. The success of drinks packed in plastic also led to the rapid implementation of synthetic chains. Polyethylene terephthalate (PET), polycarbonate (PC), polyethylene naphthalate (PEN), acetalic copolymers (POM), polybutylene terephthalate (PBT), and polytetrafluoroethylene (PTFE) represent the majority of the current plastic containers and chains. Unfortunately, plastics are sensitive to chemicals. When plastics are exposed to specific chemicals, cracks appear at those points where internal tensions are naturally present or induced by pressure (bottles) or traction (chains).

The damage is known as stress cracking, and can be caused by many compounds, including free hydroxylions and amines, acetylated monoglycerides, glycols, glycol ethers, alcohols, ether sulfates, alkanolamines, diethanolamides, ethoxylated surfactants, ethylene alcohols, amine oxides, ethoxylated amides, and acids.

The intensity of the stress cracking depends on

- chemical agents, in direct proportion to their concentration
- applied strength (pressure and traction)
- time of contact.

Examples of stress cracking on PET bottle, polycarbonate and PET coupons are shown in Figure 7.63.

In order to be classified as stress cracking free, a lubricant must pass tests reproducing normal conditions of lubrication and using specifically developed protocols. Examples of methodologies are given below.

Bottle: test method (normal condition)

- Pressurize a number of bottles with carbon dioxide at different pressures (from 0 to 4 bar).
- Prepare solutions of the lubricant at concentrations in the range 0.2–2%.
- Immerse the bottles in the solution to a depth of 5 cm for 5 minutes. A statistic assessment needs at least 5 bottles for each concentration.
- Remove and store the bottles at room temperature for two weeks, monitoring them daily. Note the type and number of cracks.

Bottle: test method (stressed conditions)

- **(stage 1):** Keep 10 bottles soaking in water for 24 h. This is to allow the water content of the polymer/resin to equilibrate.
- **(stage 2):** Fill the bottles with carbonated water (4.2 volumes of carbon dioxide) at a pressure of about 3 bar. Allow bottles 24 h to equilibrate with some shaking.
- **(stage 3):** Immerse the bottles in neat lubricant to a depth of 3 cm. Allow the bottle to drain for approximately 10 seconds.

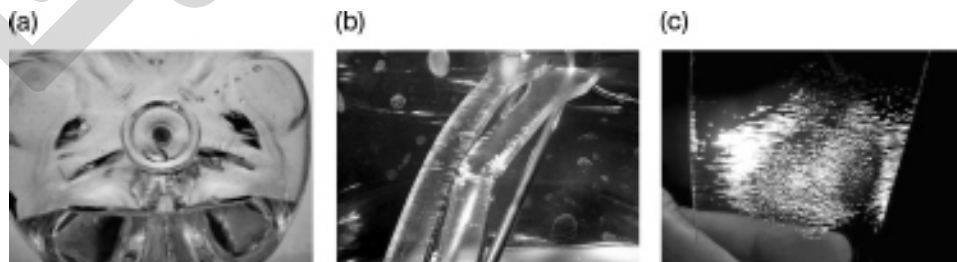


Figure 7.63 Stress cracking of (a) PET bottle, (b) polycarbonate, and (c) PET coupons.

- (stage 4): Store the bottles at 38°C and 80% relative humidity for 1 week.
- (stage 5): Monitor the bottles daily and note the type and number of cracks.
- After 1 week repeat stages 3 to 5.
- Perform 4 cycles, that is, do stages 3 to 5 four times (test lasts 4 weeks).
- No bottles should fail during the 4 week period. Bottle failure occurs when the bottle leaks due to cracking.

Test method for chains

- Bend links up to reach 90% of their length and lock them in this position (bending replaces the traction force).
- Prepare solutions of lubricant (from 0.2 to 2%).
- Keep 2 links per solution soaking for 4 weeks at room temperature with daily inspection.
- Note type and number of cracks.

The Figure 7.64 shows an example of dramatic cracking on acetalic chains in an acidic medium (phosphoric acid).

Tests indicate pressure, traction force, and chemicals as necessary but not alone sufficient to generate stress cracking. Internal tensions, pressure, and traction do not cause stress cracking in the absence of chemical agents. Conversely, when chemical failures are thermodynamically possible, they occur if physical forces accelerate their kinetics. All factors are simultaneously present in the industrial process. Figure 7.65 shows the influence of pressure and EO nonionic surfactants on PET bottles.

No failures are observed in the absence of pressure. Differences in crack severity depend on the concentration of nonionic surfactants.

Acetalic chains (POM) also suffer stress cracking. Tracks need to be periodically cleaned. Cleaning is carried out with foam technology based on alkaline, chlorinated alkaline, and acidic detergents. While alkaline and chlorinated

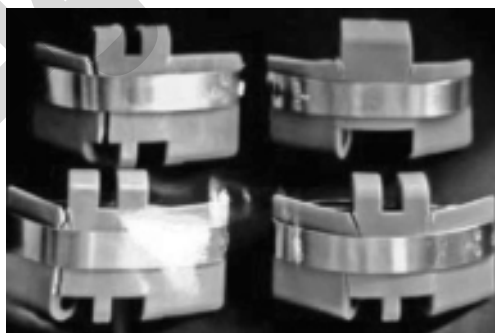


Figure 7.64 Stress cracking on POM chains exposed to acids.

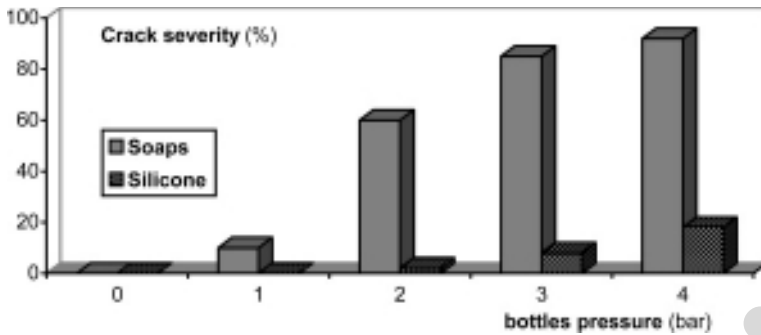


Figure 7.65 Effect of pressure and nonionic surfactants on stress cracking of PET bottles. Lubricants: alcohol $C_{13}C_{15}$ 9EO 1.5% in soap-based lubricant; silicone emulsion 1.5% in

FQAC lubricant. Bottles: PET soaked in 0.5% solution for 5 min. Stress cracking at room temperature after 30 days.



Figure 7.66 Stress cracking of POM chains from acidic cleaning in the field.

products do not affect POM, strong acids (e.g., phosphoric) attack the acetalic bonds and cause the polymer to decompose progressively. The acidic stress cracking is so rapid as to bring about a complete rupture of the chain after a few treatments (traction force at pins), as seen in Figure 7.66.

It follows that acidic treatment of plastic tracks cannot be recommended except as an emergency application.

7.9

Concepts of Problem Solving in Lubrication

Whatever containers are made of (glass, PET, PEN, PC, and cartons), the lubrication of chains and tracks must be performed so as to be compatible with the basic problems of the conveyance lines associated with their layout and type of beverage. In summary, the following principles should govern the management of conveyance lines and delivery equipment.

General points

- All containers can be lubricated with all categories of lubricants except silicone, which does not provide lubrication of glass on stainless steel.
- All the types of bottled beverages can be moved on tracks sliding on all the classes of lubricants.

Detailed points:

- Soaps and amine-based lubricants are preferred on stainless steel chains.
- Soaps and amine-based lubricants can lubricate glass, PET, and PEN.
- Amines and silicone based lubricants are preferred on plastic chains.
- Silicone-based lubricants are preferred for cartons, PET, and PEN on plastic.
- Soaps and amine-based lubricants are preferred for slightly acidic beverages.
- Their more powerful buffering effect makes soaps preferred for strongly acidic beverages such as wine, vinegar, and preserves based on vinegar (Section 7.1.3).
- Dry lubrication is preferred on plastic chains.
- Dry lubrication on stainless steel needs to be coupled with a cleaning system because of the rapid formation of dark contamination on the track and the bottom of the container.
- Dry lubrication needs the addition of lubricant at the bottom of the chains in order to lubricate the guides (correct layout of the delivery plant).
- Periodical cleaning of the conveyor lines is needed whether or not there are high or low levels of biofouling.
- The interval of time from one cleaning to the next can be significantly prolonged if a disinfectant reinforces the lubricant. The disinfectant is included in the lubricant (complete lubricant) or added to the solution in use (e.g., chlorine dioxide).
- The delivery plant may suffer biofouling if an amine-based lubricant is used (survival of Gram-negative microorganisms). The reinforcing disinfectant prevents the biofouling from forming and keeps tracks hygienically safe.
- The concentration of sulfate, phosphate, humic and fulvic acids (anionic hardness of water) affects the solution stability of amine-based lubricants (salt formation and deposition on spray filters). Phosphate, high concentrations of sulfate (>100ppm) and humic/fulvic acids (high results of Kübel test) need specific lubricants.
- Soap-based lubricants are affected by cationic hardness (metals). The higher the hardness, the higher must their concentration be to obtain a clear solution.
- Suitable concentrations of lubricant lead to low levels of foam on tracks. High foam generally means the lubricant concentration is too high.

Skill in the application of lubricants and a reliable supplier are key factors in a successful operation that runs safely, efficiently, and productively.

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دینی جای
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8

CIP (Cleaning in Place)

CIP (Cleaning In Place) is defined as 'The cleaning of complete items of plant or pipeline circuits without dismantling or opening the equipment and with little or no manual involvement on the part of the operator. The process involves the jetting or spraying of surfaces or circulation of cleaning solutions through the plant under conditions of increased turbulence and flow velocity'. (NDA Chemical Safety Code, 1985 [1]).

CIP is a process of cleaning items of plant in a closed-down condition. It involves minimal manual intervention and is automatically controlled. A crude simplification of CIP is shown in Figure 8.1, which represents pipelines connected to a recirculation tank, two pumps, and a user.

According to the definition of soil as any matter undesired in that place, the goal of a CIP aims at removing this matter in a closed system using chemical (detergent), physical (recirculation), and thermal (temperature) means. Shapton defines a clean surface as [2]

- physically clean when free of soil, scale, or residue
- chemically clean when also free of detergent and sanitizer
- microbiologically clean when its microorganisms are reduced to an acceptable level.

In order to attain this goal, the CIP program is divided into a sequence of cleaning and rinsing cycles, and a final sanitizing step if necessary. The combination and repetition of steps yields a large number of different programs. These are standardized in the following general procedure:

- 1) **Pre-washing:** rinse with water to remove gross and loosely attached soil.
- 2) **Alkaline cleaning:** removal of some of the remaining soil, usually involving heat.
- 3) **Rinse:** prevention of interference with the next step.
- 4) **Acid cleaning:** removal of some more of the remaining soil, focusing on inorganic materials.
- 5) **Rinse:** rinse off the acid and the inorganic soil.
- 6) **Disinfection:** reduce any remaining microorganisms to an acceptable level.
- 7) **Final rinse:** removal of the disinfectant to leave only a residue of potable water.

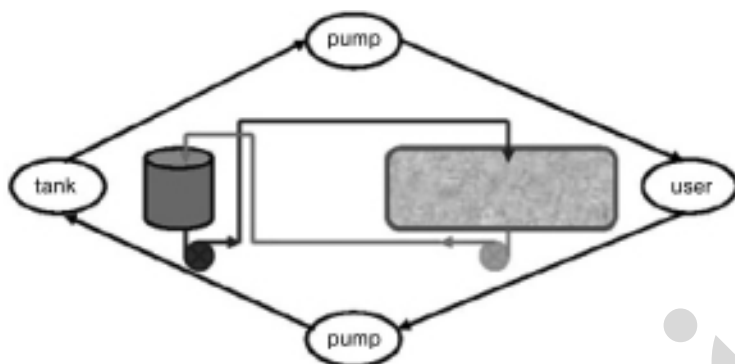


Figure 8.1 Simple scheme of CIP.

Although alkaline cleaning is usually the first step, sometimes acid cleaning comes first, for example, crossflow filtration of whey [nanofiltration (NF), reverse osmosis (RO)] and contamination mainly consisting of starch. The reason for reversing the order of treatment is that there is a risk of precipitation of phosphate if this comes into contact with the caustic solution and also a risk of gelling of starch. If the cleaning step is carried out at a very high temperature or a sanitizing detergent is applied, the final disinfection can be omitted. The one-step alkaline detergents do not need to be followed by a further application of acid. The acid step sometimes replaces the alkaline one, but only if the acid performs as a detergent. Also briefly described there are a number of modifications which can be tailored to each individual requirement.

8.1

CIP Classification

CIPs are divided into classes according to how they manage the exhausted cleaning solutions and the rinse water. Cleaning-in-place is schematically based on three concepts: total loss, partial recovery, and total recovery. The descriptions given below are simplified in order to emphasize the essential features of the system. Hence, the tank devoted to water is indicated as raw water. The sanitizer tank is not mentioned. Chemicals are referred to as caustic, acid, or detergents without mentioning other possible additives.

8.1.1

Total Loss CIP

In this method, used solutions are drained off (Figure 8.2). As no recovery is carried out, total loss CIP is also known as 'single tank' or 'single use' [1].

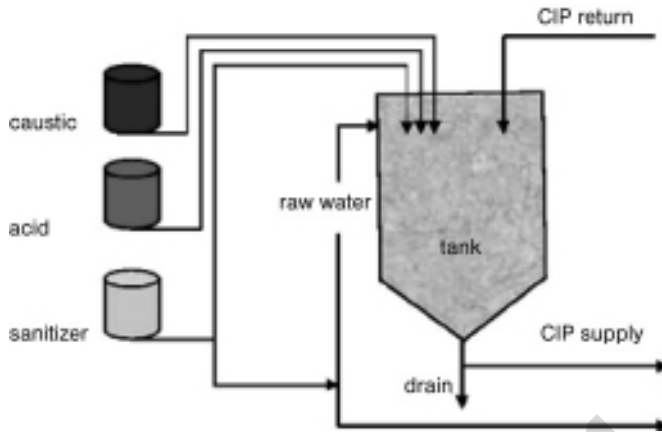


Figure 8.2 Total loss CIP.

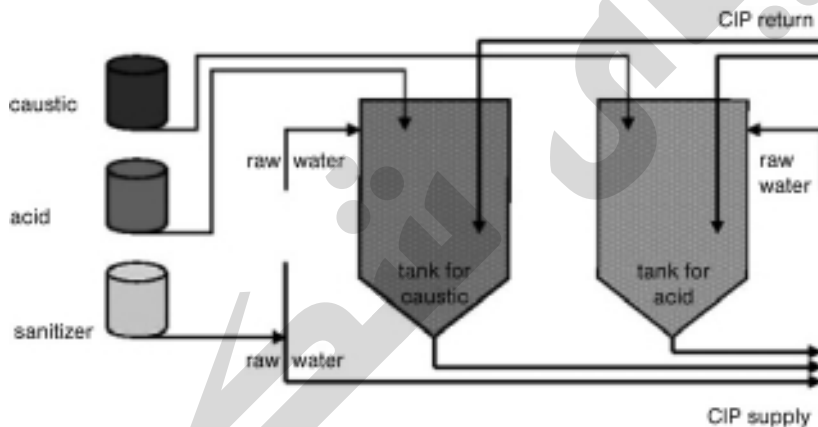


Figure 8.3 Partial recovery CIP.

Detergents and sanitizer are directly added in sequence to a single tank from the bulk product. As well as conductivity control, the concentration can also be determined by a timed pump. A heat exchanger or direct injection of steam raise the temperature.

8.1.2

Partial Recovery CIP

The cleaning solutions are recovered (Figure 8.3). Detergent concentration and volume of solution are automatically restored based on conductivity measurement. A heat exchanger controls the temperature.

Most sanitizing agents rapidly lose activity. Disinfectants should be never recovered unless they are saved to be re-used as water.

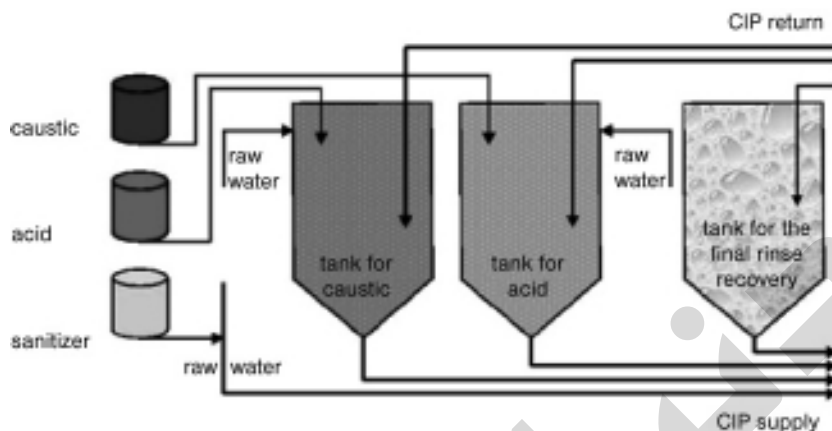


Figure 8.4 Total recovery CIP.

8.1.3

Total Recovery CIP

The total recovery system re-uses the final rinse as pre-wash in the subsequent cleaning. This minimizes the water consumption and makes the pre-wash more effective due to the presence of detergent residues. Concentration and temperature are governed in the same way as in partial recovery CIP (Figure 8.4).

The decision on which to choose depends on the process and local restrictions. If there is a large amount of contamination in the plant, the cleaning solution becomes heavily contaminated, and the risk of redeposition becomes real if the solution is re-used. Then, total loss CIP will be the best decision. However, an increase in the cost of chemicals, a shortage or a charge for water in or water out can direct the option toward partial or total recovery CIP.

What has been discussed is an obvious simplification of the CIP design. An idea of the complexity of a CIP plant (chemicals tanks, balance and utility tanks, process tanks, pumps, pipelines, valves, flow, temperature, conductivity and pressure monitors, heater, recorder and filters) is given in Figure 8.5.

8.2

CIP Parameters

The cleaning process follows a reaction of first order:

$$v = -d[A]/dt = k[A]$$

from which

$$d[A]/[A^0] = -k \, dt$$

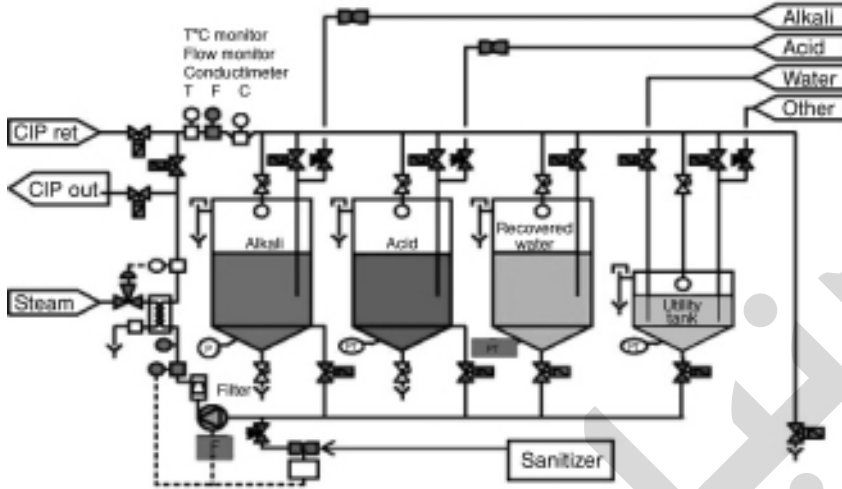


Figure 8.5 A CIP plant (courtesy of JohnsonDiversey).

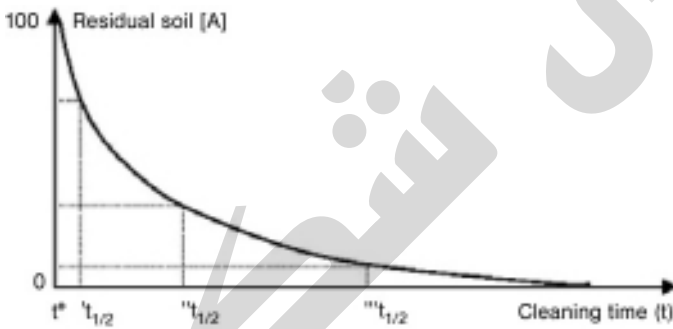


Figure 8.6 Removal rate as a function of time.

where v is the removal rate of the contaminant A. The cleaning process can be better understood if the previous equation is referred to the half-time of the soil removal, that is when the concentration of contaminant A decreases to half of the initial level: $[A] = [A^0]/2$. The previous equation becomes, in logarithm form,

$$\ln[A]/[A^0] = -k t$$

when $[A] = [A^0]/2$

$$\ln 1/2 = -\ln 2 = -k t_{1/2}$$

$$t_{1/2} = \ln 2/k$$

The last equation indicates that the half-time of removal is independent of the initial concentration of soil. Thereby, the removal rate decreases as the amount of soil decreases, as Figure 8.6 shows.

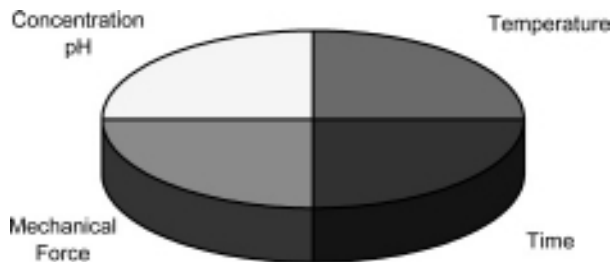


Figure 8.7 Synergistically linked parameters in the CIP process.

Four parameters, temperature, time, chemicals, and mechanical action (flow velocity and kinetic energy) are synergistically linked (Figure 8.7) to accomplish cleaning in a CIP process.

If a parameter is modified, at least one other must change as well, in order to maintain cleaning efficiency. If temperature, for instance, is lowered, the concentration of the chemicals has to be increased and/or the time of the cleaning process prolonged. Monitoring devices are installed to measure the CIP parameters:

- **Flow velocity:** connected to the mechanical force of a turbulent flux (cleaning of pipelines)
- **Flow rate:** connected to the cleaning of large surfaces (cleaning tanks)
- **Pressure:** connected to the mechanical force of impact and to the volume of solution on the surface (setting of sprayballs)
- **Conductivity:** connected to the detergent concentration
- **Temperature:** connected to the rate of the chemical reactions with soil.

The monitoring devices send the CIP control system a signal indicating the current status. This allows the system to correct unfavorable situations or give an alarm if they cannot be corrected.

Whereas soil and detergent vary as a function of the different industrial processes, three physical parameters are common to every CIP and prove to be as important as the detergent: flow velocity, flow rate, and temperature.

8.2.1

Flow Velocity

The existence of laminar and turbulent flow under the control of the Reynolds number (Re) is discussed in the literature [3, 4]. In a cylindrical tube the flow is laminar when $Re < 2100$, intermediate when $2100 > Re < 4000$ and turbulent when $Re > 4000$. Current investigations show that, if the fluid velocity increases, the thickness of the boundary layer of soil decreases without any relation to the Reynolds number and independently of the pipe diameter, as Timperley shows in Figure 8.8 [5].

This rapidly decreasing thickness reaches a minimum around 1.5 m s^{-1} . It follows that an average velocity of 1.5 m s^{-1} is considered to be the lowest consistent

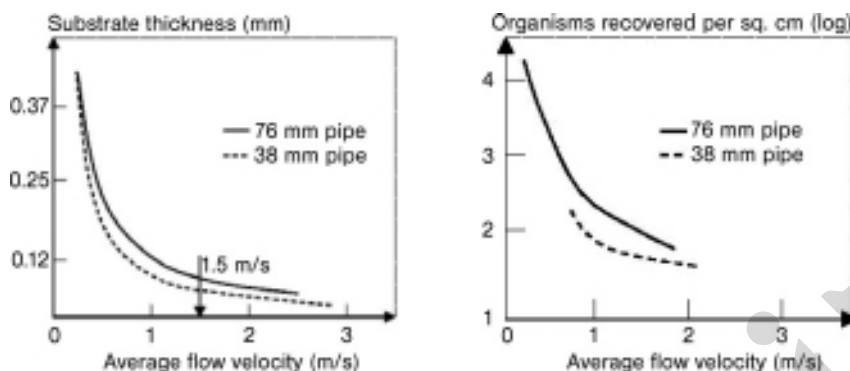


Figure 8.8 The lowest limit of velocity (1.5 m s^{-1}) to clean and disinfect (courtesy of Timperly in Ref. [5]).

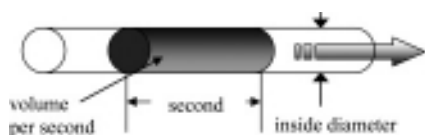


Figure 8.9 Ultrasonic device to detect velocity.

with adequate cleaning and rinse (optimal 2 m s^{-1}). In a similar way, the residual bacteria on the surface are reduced to a minimum when the average velocity is $\geq 1.5 \text{ m s}^{-1}$ [5].

Velocity can be measured by different devices such as a flowmeter and also using ultrasonic waves. Figure 8.9 shows an ultrasonic system applied to a pipeline to check the inner flow velocity.

8.2.2 Flow Rate

What happens inside the pipelines must happen on the tank wall. The tank surface receives a volume of solution as a function of the type of sprayballs and pressure (holes and their positioning). While the mechanical action inside the pipeline is the result of the flow velocity, the force of the impact on the tank wall is due to the pressure and volume of the solution, as represented in Figure 8.10.

The pressure of the solution is monitored in order to ensure that it exceeds 1 bar and that the constantly descending flow on the wall is turbulent (Figure 8.11). Such flow should experimentally be $>27 \text{ L min}^{-1}$ per meter of vessel circumference.

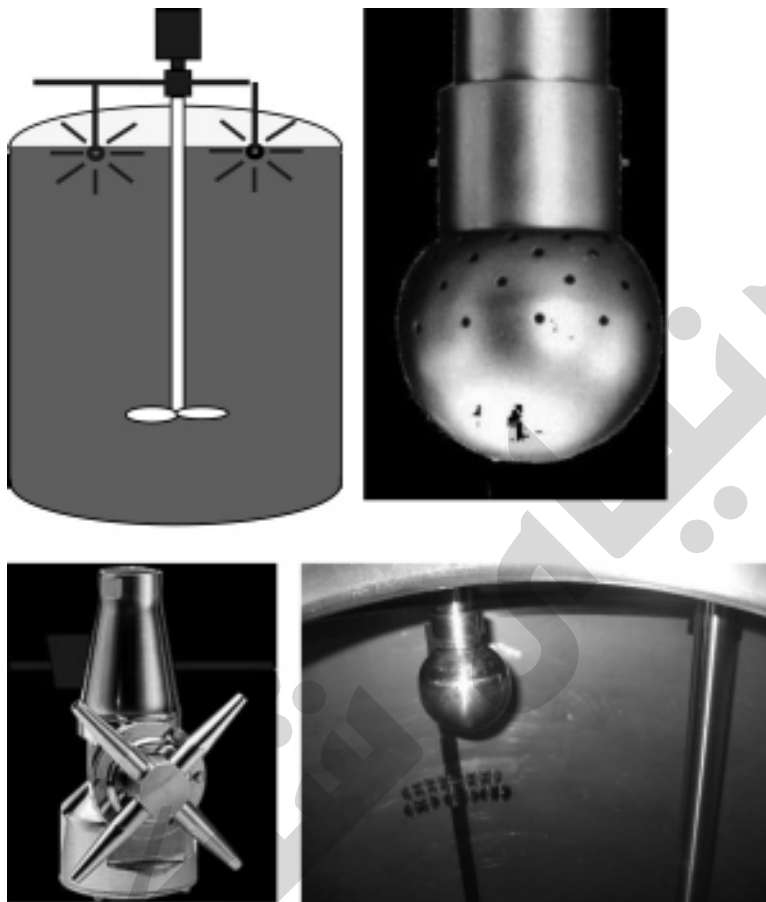


Figure 8.10 Examples of spray devices.

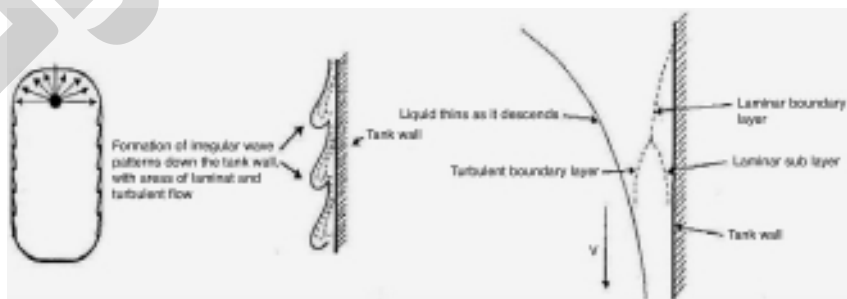


Figure 8.11 Laminar and turbulent flow in CIP (courtesy of Romney in Ref. [6]).



Figure 8.12 Example of dead zone.

The formation of irregular waves on the tank wall indicates the condition of turbulent flow [6].

The following equation describes the flow rate to attain successful cleaning:

$$Q_r = D_t \cdot F_s \cdot \pi$$

Where:

Q_r = flow rate (L min^{-1})

D_t = tank diameter (m)

F_s = soil factor ($\text{L m}^{-1} \text{min}^{-1}$)

π = 3.14

The lowest F_s :

- 27 light soil condition
- 30 medium soil condition
- 32 heavy soil condition
- 35 acidic cleaning.

Dead areas are critical points where soil and microorganisms are safe and protected. These areas cause foods to have unpredictable pollution. Figure 8.12 shows a typical dead area behind a tube.

8.2.3

Temperature

High temperature enhances the effectiveness in cleaning. Temperature is the third crucial parameter in CIP. The removal of soil from a surface involves consecutive physical steps:

- detergent diffusion through the boundary layer
- detergent diffusion through the soil
- reaction between soil and detergent to weaken the structural lattice and forces of adhesion to the surface
- back diffusion of the solubilized contamination.

Table 8.1 Alterations by heating.

Caramelization	Sugar
Polymerization	Fats
Denaturation	Proteins
Precipitation	Mineral salts

High temperature provides beneficial effects at every step:

- Transport phenomena accelerate.
- Chemical reactions speed up. The rate of the chemical reactions approximately doubles with every 10°C rise in temperature.
- Microorganisms are readily killed.

In order to ensure that fats are liquefied and defoamers are effective, a temperature above 40°C is recommended. Liquid is more easily and rapidly washed off than solid. The roll-up mechanism (see Section 5.1.5) relates to oily contamination and cannot be applied to a solid, which is chemically peeled off layer by layer. KOH gives better cleaning results on fats simply because the melting points of its compounds are lower than those of NaOH.

Although temperature provides benefits, it needs careful assessment. Temperature is decided according to the type of contamination. Cleaning contamination from heat exchange equipment (e.g., for pasteurization and sterilization) benefits when carried out at high temperatures (80–90°C), since no further structural modification of the contamination is likely. On the contrary, high temperature on fresh residues (nonthermally treated food) causes proteins to denature and phosphate to deposit, and makes cleaning harder to achieve. Thus, temperatures below 65°C are recommended on fresh contamination. Summing up in Table 8.1, four alterations are observed in consequence of prolonged heating.

Temperature affects the amount of soil deposited and also its composition. Heating accelerates reactions with polyvalent cations. Cations cement the lattice of denatured proteins. Fats are trapped inside larger amounts. The resulting deposit protects itself and offers greater resistance to cleaning in comparison with residues of fresh matter. The thickness of the fouling on heat-exchanging surfaces influences the planned thermal program. The reduction in heat transfer is sensitively dependent on the thickness of the deposit [7].

Every industrial fluid leaves deposits of different types and cohesion, defined as the ‘fouling factor’. It is essential to know the contamination, identify the influential key factors, and ensure a suitable choice of detergents and procedures to perform the cleaning according to the targeted standards.

8.3

Dairy

Milk is a complete food. Mammals feed their young solely on milk in the early stages of their life, so milk provides all the necessary nutrients for healthy growth

Table 8.2 Nutrients in milk that could affect the cleaning process (wt%). Courtesy of Quaglia [8].

Species	Protein	Fat	Calcium	Phosphorus
Cow	3.5	3.6	0.122	0.090
Goat	4.3	4.6	0.143	0.123
Sheep	5.6	6.9	0.175	0.128

and development. The average composition of nutrients that could affect the cleaning process is reported in Table 8.2 [8]:

The milk industry is one of the largest users of CIP technologies and includes some of the most difficult-to-clean processing plant (e.g., pasteurizer, sterilizer, and crossflow filtration). When the raw milk, collected from farms, arrives at the site, it takes different paths according to its final destination, either directly to consumers via heat exchange processes or after being transformed into a huge variety of derivatives (cheese, cream, butter, yogurt. ...). In terms of cleaning, substantial differences exist between treatments involving heat exchange and those that take place at ambient temperature.

8.3.1

Treatment with Heat Exchange

Owing to the method of milking and withdrawal, the biochemical composition, the high water content, and the neutral pH of milk, it is a good substrate for the growth of microorganisms. Although it is secreted free of germs, milk is affected by different sources of microbial pollution [9]:

- **Animal and human source:** coliforms, salmonella, enterococcus, and staphylococcus
- **Water source:** coliforms, pseudomonas, coryneforms, and alkaligenes
- **Feed source:** clostridium, listeria, bacillus, and lactic bacteria
- **Ground source:** clostridium, bacillus, pseudomonas, mycobacterium, yeasts and molds
- **Air source:** streptococcus, micrococcus, coryneforms, bacillus, yeasts and molds
- **Litter source:** clostridium, bacillus, and klebsiella
- **Inner udder source:** streptococcus and corynebacterium
- **Udder skin source:** micrococcus, staphylococcus, enterococcus, and bacillus
- **Milking machine source:** molds, micrococcus, streptococcus, bacillus, and coliforms
- **Faeces source:** coliforms, staphylococcus, listeria, mycobacterium, and salmonella.

The main groups of bacteria are connected to the categories of thermo-tolerant and psychrotrophic bacteria, as shown in Table 8.3 adapted from Cantoni *et al.* [9]:

Table 8.3 Examples of thermotolerant and psychrotrophic microorganisms.

Thermotolerant bacteria		Psychrotrophic bacteria	
Gram positive	Gram negative	Gram positive	Gram negative
Mycobacterium	Alkaligenes	Micrococcus	Pseudomonas
Micrococcus		Bacillus	Alkaligenes
Bacillus spores		Arthrobacter	Chromobacterium
Clostridium spores		Clostridium	Enterobacter
		Corynebacterium	Citrobacter
		Lactobacillus	Escherichia coli
		Mycobacterium	Flavobacterium
		Sarcina	Klebsiella
		Staphylococcus	Serratia
		Streptococcus	

All of these can be further divided into three groups:

- animal pathogens (toxin-producing bacteria)
- deteriorating bacteria (saprophytes)
- fermenting bacteria

In order to prevent diseases (e.g., tuberculosis and typhus), to destroy as many organisms as possible (nonpathogenic organisms and enzymes), and to safeguard production quality, milk is heated to a pre-determined temperature and held there for a certain time before it is cooled again. Temperature and time provide the dairy process with the key to quality, guaranteeing safe human consumption.

The pasteurizer and sterilizer are typical plants involving the application of heat. Their typical residue is commonly known as milkstone. The hot-generated milkstone consists of an amorphous lattice made up of denatured casein, calcium phosphocaseinate, calcium phosphate, and fat (which adds hydrophobic behavior to the deposit).

Milkstone is so resistant as to historically require a cleaning procedure based on robust caustic and acid solutions (3%), high temperature (80°C), and a long contact time (>30 min). As already described in Section 1.4, casein, phosphate, fats, hydrolyzed fatty acids, calcium, and magnesium together form a typical self-protected contamination which is very hard to remove in its entirety. An example is shown in Figure 8.13.

Webb and Johnson [10] report that about 35% of the soluble calcium in milk is found in its ionic state, while 55% is complexed to citrate and 10% to phosphate. It has been known since 1888 that heat can be used to reduce the calcium and phosphate content in milk [11]. Later, several researches described the type of phosphate and its precipitation induced by temperature. Significant loss in soluble calcium and phosphorus occurs in the pasteurization process as a function of



Figure 8.13 Pasteurization plates coated with milkstone and milkstone from a tubular sterilizer.

temperature and the duration of the heating. Evenius and de Vries [12] suggest that precipitation of the hydroxyapatite crystals $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ begins at 60°C and rapidly increases at higher temperatures. Most of the calcium phosphate lost from milk precipitates as milkstone on the heat exchanging surfaces. Calcium phosphate proves to be the main cleaning problem, as it builds a milkstone structure having one of the highest constants of stability. Only a few chemicals, for example, nitric acid and EDTA, succeed in re-solubilizing it.

Caustic soda is an effective cleaner, but each time requires the nitric acid step to remove residual inorganic salts, essentially calcium phosphate and carbonate. Also, caustic soda precipitates limestone if not boosted with sequestrants. Hence, when raw materials are used, the CIP procedure needs two hot cleans and three rinses (5 steps). Although this cleaning procedure is successful, the raw materials (NaOH and HNO_3) cause severe losses in thermal and mechanical energy, rapid damage to gaskets, longer delays before restoration of production conditions, and higher productivity losses. All this must be set against the low cost of the raw materials [13].

The success of the one-step technology, which replaces the use of the raw materials NaOH and HNO_3 , is founded on EDTA, which is able to pull metals out of the deposit and allow the caustic soda easier attack on the loosened soil. The EDTA technology requires a lower alkali concentration (0.5% instead of 3%) and no added acidic step. Besides cleaning and preventing scale, the additional benefit of the EDTA technology is that the extent of thoroughness of the cleaning procedure can be gauged without dismantling the plant (Figure 8.14). The equipment is thoroughly cleaned only when free EDTA is still detectable at the end of the wash, that is, cleaning is assessed from the residual EDTA.

The single-step technology usually uses a detergent concentration of 3%. This gives a solution with an initial EDTA concentration of $\geq 4 \text{ g L}^{-1}$ and an alkalinity of 0.5% (minimum alkalinity to solubilize proteins). The EDTA loosens the structure of the deposit by breaking the calcium bonds. The calcium-free deposit then readily undergoes cleaning at low alkalinity as shown schematically in Figure 8.15.

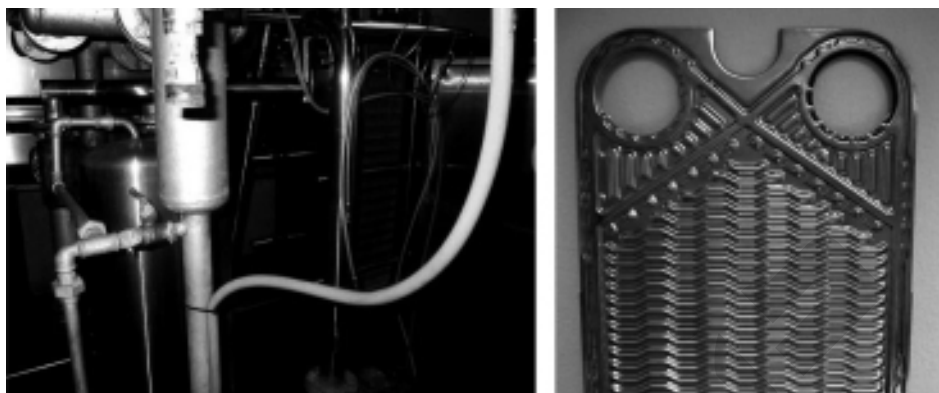


Figure 8.14 Milk pasteurizer and a clean pasteurizer plate.

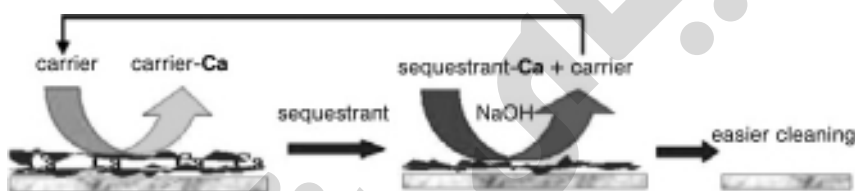


Figure 8.15 Carrier mechanism of sequestrants.

To assess the effectiveness of the cleaning, EDTA is detected according to the following procedure:

- **Reagents:** calcium acetate 4 g L^{-1} , ammoniacal buffer, ammonium chloride, Eriochrome Black T indicator (EBT).
- **Equipment:** 150 mL flask, burette.
- **Procedure:** Place 30 mL of the washing solution in the flask. Add 20 mL of buffer, and small amounts of ammonium chloride and EBT. The solution changes to blue. Titrate with calcium acetate up to violet.
- **Calculation:** $\text{EDTA (g L}^{-1}\text{)} = \text{mL of titrant} \times 0.3$.
- **Comment:** Solutions of high alkalinity must first be neutralized to the phenolphthalein end point with HCl.

EDTA and caustic soda are the basic constituents of the one-step detergent. NTA, MGDA, GLDA, HEDTA, and even IDS can be used as alternatives. However, detergents based on these sequestrants need a periodic but more frequent acidic step. Only the presence of EDTA defines a detergent as a true one-step cleaner.

EDTA is a pure stoichiometric sequestant without any dispersing or suspending ability. The risk of arriving at a sub-stoichiometric condition is always present.

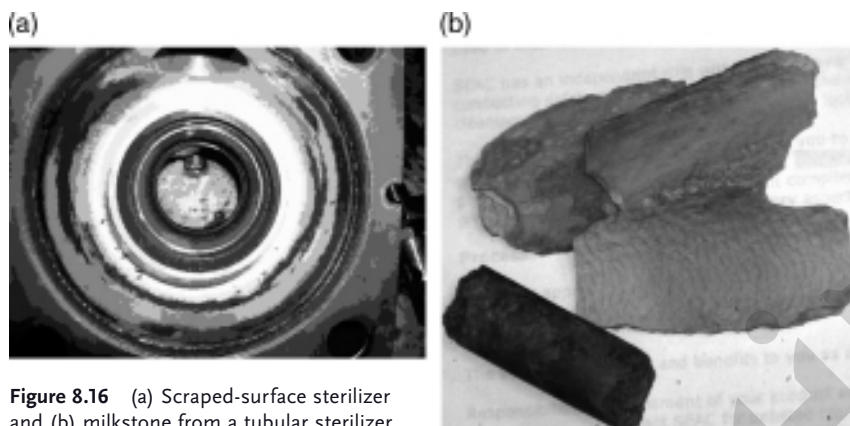


Figure 8.16 (a) Scraped-surface sterilizer and (b) milkstone from a tubular sterilizer.

Therefore, the sequestering system is boosted with threshold and dispersing sequestrants. Phosphonates (ATMP and PBTC) and polyacrylates (4500MW) complete the sequestering blend. Suitable defoamers suppress the foam arising from the accumulation of proteic and fatty contamination. Although the one-step detergent is more expensive than the raw materials caustic soda plus nitric acid, its comprehensive benefits are so considerable as to make the cost of chemicals insignificant in the whole economy of the process.

More tenacious contamination comes from sterilizers because of advanced carbonization and thicker contamination, as Figure 8.16 shows.

To clean sterilizers, the EDTA technology needs to be boosted by using higher alkalinity than that used in cleaning pasteurizers. However, a slight residual ash-like deposit remains on the inner surface, but a rapid treatment with nitric acid following the alkaline treatment gives thorough removal of soil. The use of EDTA to clean sterilizers gives the further benefits of less stressed conditions and saving of time.

Cleaning of equipment used in a heat exchange process is frequently assisted by adding an oxidant to the caustic solution. This facilitates the removal of starch, proteins, fibers, pectins, and fats. Chlorinated detergents are still used at low temperatures ($<50^{\circ}\text{C}$), but hydrogen peroxide is replacing the chlorine technology.

Peracetic acid and chlorine dioxide perform the task of disinfection. Chlorine brings the risk of pitting corrosion, although chlorine/chloride (≤ 1000 ppm) only starts to cause pitting corrosion after a delay of about 1.5 h, after which time the passivation barrier of the chromium oxide is crossed. Temperature influences the corrosion rate. Although peracids and hydrogen peroxide are corrosion safe, this is no longer true if the chloride concentration exceeds 25 ppm. The released oxygen accelerates the kinetics of pitting. This is extremely important in the soak process. No oxygen donors should be present in water containing chloride at a level exceeding 25 mg L^{-1} if this used to soak a plant. An example of corrosion on a sterilization plate is shown in Figure 8.17.

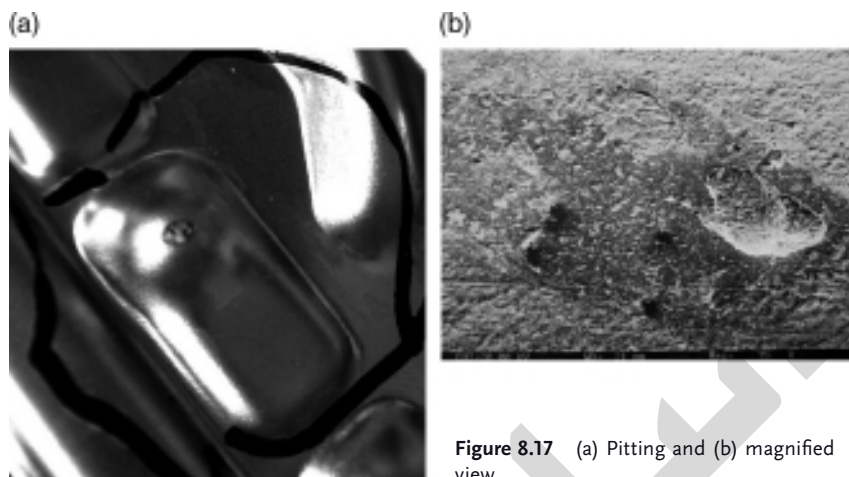


Figure 8.17 (a) Pitting and (b) magnified view.

This example of localized corrosion actually originates from plates touching each other. This contact between plates often occurs in a pasteurizer. Vibrations of the running plant induce loss of chromium oxide by abrasion at the point of contact causing de-passivation. Micro-anodic areas are set up at these depassivated points. Corrosion starts, forming a voltaic cell between the micro-anodic and the remaining cathodic area still passivated. Chlorides, stray currents, and conductive solutions in general accelerate corrosion.

8.3.1.1 Conversion of Stainless Steel Oxides

When alkaline solutions containing high levels of EDTA, HEDTA, MGDA, NTA, IDS, GLDA, and other stoichiometric sequestrants run at high temperatures, a darkening on stainless steel occasionally becomes evident with time. This phenomenon has been discussed in Section 3.4.5. The dark layer is attached to the steel surface and is only dissolved by strong chemicals such as hydrofluoric acid and permanganate technology. Figure 8.18 show an example of the gradual increase in the intensity of the darkening.

This effect has been found to be associated with poor quality of the stainless steel. The conversion to black oxides is safe and compatible with the processed foods. There is therefore no need to remove it except for aesthetic reasons.

8.3.2

Raw Milk Line

The constituents of nonthermally treated milk are in an aqueous dispersion, and the plant can even be cleaned with water. A good pre-rinse removes most of the residue. Only calcium phosphate precipitation and casein denaturation by heating are responsible for any tenacity of the soil. On the other hand, sugar, fat globules

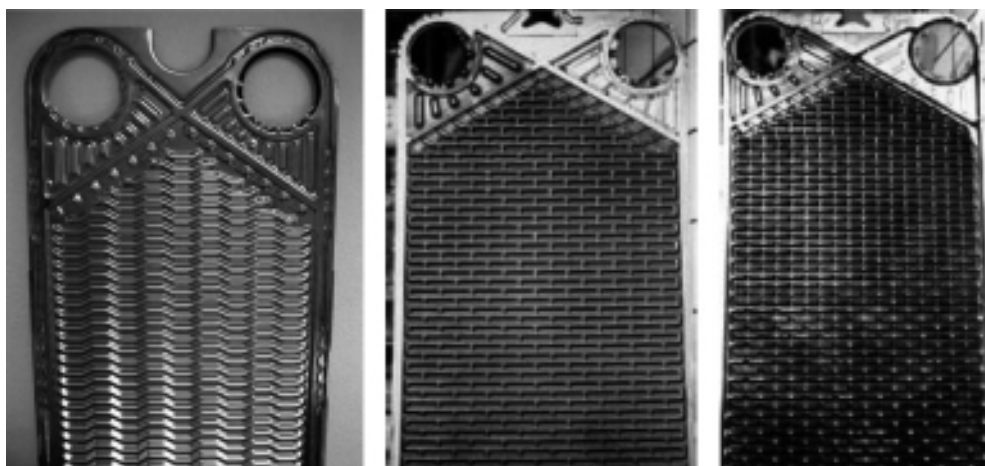


Figure 8.18 Gradual increase in intensity of darkening on pasteurizer plate.

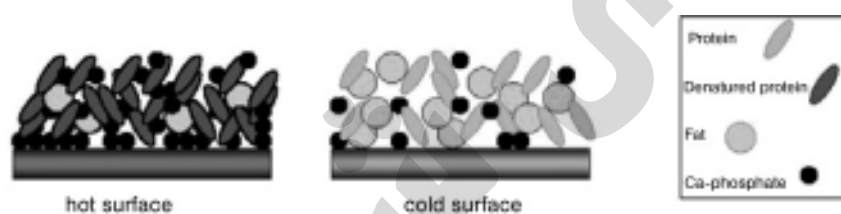


Figure 8.19 Models of milk soil (adapted from Refs [15] and [16]).

Table 8.4 Composition of cow's milk and milk soil.

Soils (%)	Whole milk	Cold milk soil	Hot milk soil	Milkstone Min Max	
Protein	3.6	26.6	30.3	4.1	43.8
Sugar	5.0	38.1	Trace	None	Trace
Fat	3.7	29.9	23.1	3.6	17.6
Minerals	0.7	5.3	46.6	42.3	67.3

(only traces in the heated soil [14]) and dispersed native proteins are readily cleaned off. Several researchers have proposed models for the composition of the milk soil. Burton 1968 [15] and Kane 1985 [16] suggested the widely accepted model illustrated in Figure 8.19 [14, 17].

It is obvious that soils in holding tanks for raw milk are quite different from those found on pasteurizer plates. Harper [18] and Belitz [19] quantify the average composition of cow's milk and milk soils in Table 8.4.

Although an alkaline solution is the ideal medium to clean in the food industry, the cleaning of raw milk residues is so easy as that an acidic detergent is also acceptable. Its peptizing ability makes phosphoric the most suitable acid. Phosphorus-free acids (citric, glycolic, tartaric, sulfamic) perform cleaning when formulated together with surfactants. Wetting and emulsifying surfactants lessen hydrophobic effects and allow the acid to clean.

Acidity is thermodynamically unfavorable to inorganic precipitation. Scale does not occur in such a system. However, the rinse moves the solution toward neutrality, where scaling cannot be prevented. As the acidic anion increasingly gets closer to the sub-stoichiometry with the hardness of the rinse water, it could precipitate depending on its solubility product. It is therefore useful to include a threshold sequestrant in acidic products just to prevent salt precipitation during the infinite dilution typical of the rinse. Without threshold agents, a white deposit appears no later than a few applications, as a function of the hardness (e.g., calcium phosphate from phosphoric acid and calcium oxalate from oxalic acid).

Threshold sequestrants often behave as corrosion inhibitors as well.

When alkaline detergents are applied, the presence of EDTA or any hydroxy-acid sequestrant (as a second choice) is recommended in addition to phosphonates. Hydroxy acids succeed in competing for calcium with phosphate and fatty acids (hydrolyzed from triglycerides). Adding a small amount of wetting agent (surfactant) completes the approach to soil removal.

8.3.3

Separator

Centrifugal force replaces gravity in centrifugal separators (Figure 8.20a) in order to succeed in removing particles that are almost as light as the liquid itself. The reverse-bowl separator exploits rotating conical discs to separate fat cream particles from the liquid part of milk. Dirt, sludge, udder cells, leukocytes, red blood corpuscles, and bacteria simultaneously move to the bowl surface while cream slides along the discs. The total amount of sediment normally is 1 kg/10000 liters [20], and this is removed at regular intervals.



Figure 8.20 Separator and example of incomplete cleaning.

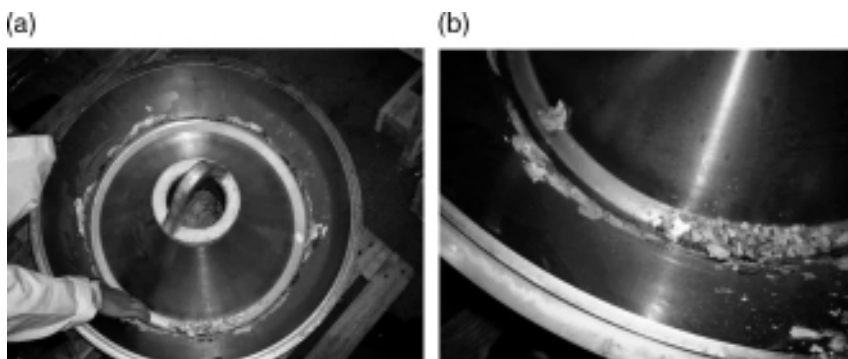


Figure 8.21 Residue after (a) 1% caustic soda and (b) 1% nitric acid cleaning.

Excessive build-up of sludge, fat and casein deposits seriously affect the skimming efficiency and give a base for the growth of bacteria. Deposits are difficult to remove as the centrifugal force stretches and presses them (Figure 8.20b). Self-cleaning separators, able to automatically discharge the sludge while the machine is running, are cleaned in place (CIP). The CIP technology avoids the need for daily dismantling for cleaning. Soil is so firmly attached as to require robust detergents (caustic with strong sequestering agents). Raw materials such as caustic soda and nitric acid are frequently used. This basic technology implies five steps and often fails to clean. One-step detergents specific for emulsifying fats and solubilizing and dispersing casein are more suitable. Removal, emulsification, and dispersion are made easier with sequestrants fast acting on calcium, phosphates, and fatty acids. Blends of tripolyphosphate and EDTA provide the most used system. EDTA competes with fatty acids and calcium, and tripolyphosphate provides the system with threshold and dispersing efficiency as well as peptizing ability on proteins.

Hydrophobicity demands suitable low-foaming surfactants with appropriate HLB (hydrophilic-lipophilic balance) in order to allow the cleaning solution to penetrate the contamination and work efficiently. Figure 8.21 shows what frequently happens with raw materials as cleaners.

Powder detergents are still widely used, as it is possible to produce caustic soda plus EDTA and tripolyphosphate plus surfactants in powder form. Liquid detergents frequently need to be fortified with hydrogen peroxide.

8.3.4

Churning

Butter making (churning) consists in modifying the suspension of fat globules so as to achieve phase inversion, changing from fat-in-water to water-in-fat [21] through the coagulation of the fat globules by agitation.

The churning environment is fatty and sticky. The detachment of from the churn walls represents the main problem and point of assessment of the cleaning quality. The chemical reasons for the butter coming off are not easy to understand. It is clear that four components of the detergent are involved: silicate, triphosphate, surfactants, and chlorine. Surfactants are not the primary agents and chlorine provides sanitation rather than cleaning. Consequently, silicate and triphosphate fulfil most of the washing demands. Silicate, in particular, is reputed to be the main agent responsible for detaching the butter. However, if one of the two components is absent or their ratio is not appropriate, butter removal suffers. For the reasons mentioned, detergents for washing churns derive their efficacy from the large amount of silicate and adequate quantity of triphosphate (approximately 2:1 ratio). Surfactants and chlorine are considered to be auxiliary components.

8.3.5

Curdmaking Process

The majority of curdmaking processes are carried out in mechanized tanks where the coagulum is induced (renneting), cut (knife blades or wires), and stirred (shovels). In addition to the traditional curdmaking (Figure 8.22), micro-curdmaking processes enhance productivity by a continuous moving-round process of cleaning, renneting, cutting, discharging, and cleaning again.

Stirring must be gentle but fast enough to keep the grains suspended. Any curd settling down to the bottom causes lumps to be formed, loss of casein, and insufficient drainage, which affects the texture of the cheese.

The coagulation process involves the hydrolysis of the casein complex and its rearrangement into a new structure that calcium helps to bind. The structure looks like casein-based glue and possesses its sticky behavior. Thus, preventing curd from sticking on the surface is the most important aim when operating the curdmaking tanks. Gentle movements leading to the desired drained agglomera-

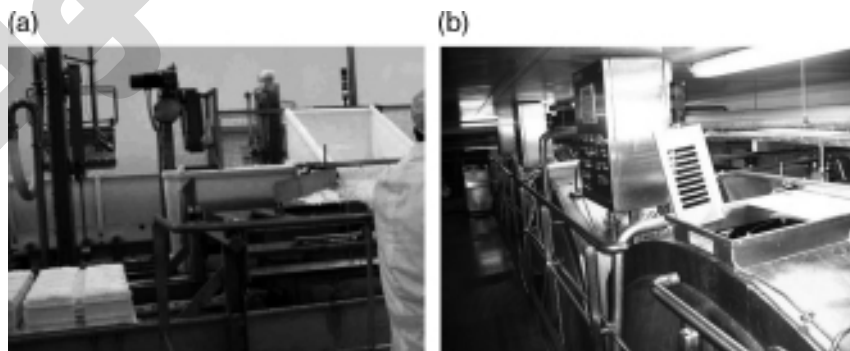


Figure 8.22 Micro-curdmaking sequential process (a) and traditional process (b).

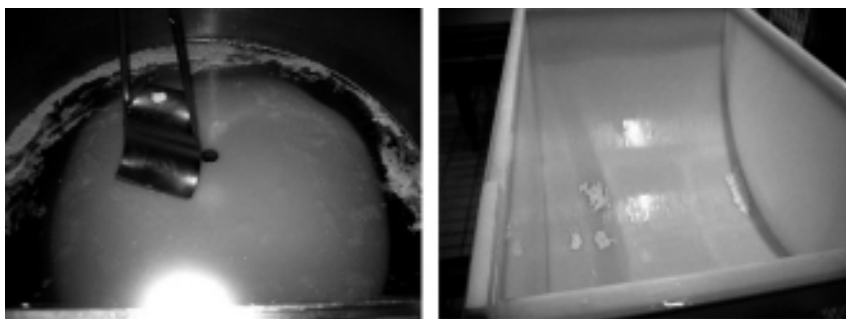


Figure 8.23 Lump formation because of sticky surfaces.

tion give a suitable texture to the curd. Lump formation on stainless steel and plastic show that the surface is sticky (Figure 8.23).

Since the process does not treat thermally stressed substances, the curdmaking plant should theoretically be easy to clean. Besides cleaning, however, it is mandatory to leave a nonsticky surface at the end of the sanitation. As in several other applications, the key to the problem depends either on the sequestration mechanism or on leaving an acidic surface. As surfactant-free detergents enhance anti-stickiness, the occurrence of stickiness has the same explanation as that for the plastic molds of soft cheese and, generally speaking, every surface in contact with soft cheese and curd. The cleaning of soft cheese molds is carried out either with acidic detergents or alkaline ones followed by an acidic step. The process ends with a disinfecting step, usually spraying peracetic or peracetic acid (hydrogen peroxide in citric acid). The acidic step does not give surface stickiness. The alkaline step does not give any problem on new molds, but only for a limited number of cleaning cycles. Anti-stickiness is therefore actually attained only after the acidic step.

Stickiness derives from physical and chemical mechanisms, which help us to understand why the acidic step solves the problem. The physical mechanism causes thermal stress. Repeated hot cleanings and cold rinses generate stress, which modifies the shape of the surface, as shown in Figure 8.24a–c, which shows the ageing path of a polyethylene mat of a mold.

Plastic passes from a linear structure (a) of the original extrusion to a wavy form (middle-aged mold, b) and then to a wavy-creviced surface typical of the aged mold (coarse surface, c). However, a rough surface is necessary but not sufficient to lead to stickiness. The infrared reflectance analysis of the polymeric surface reveals the presence of a peak of oxygen adsorbed as a consequence of the disinfection treatment with peracetic acid. Oxygen forms one of the strongest bridges with hydrogen and polarized molecular sites. Moreover, the more the valence of cations increases, the more the compression of the electrical double layer increases (described as the potential energy of the interface). The high concentration of calcium thus causes the attractive forces to become predominant over the repulsive ones, leading to a significant increase in attraction [22]. Thus,

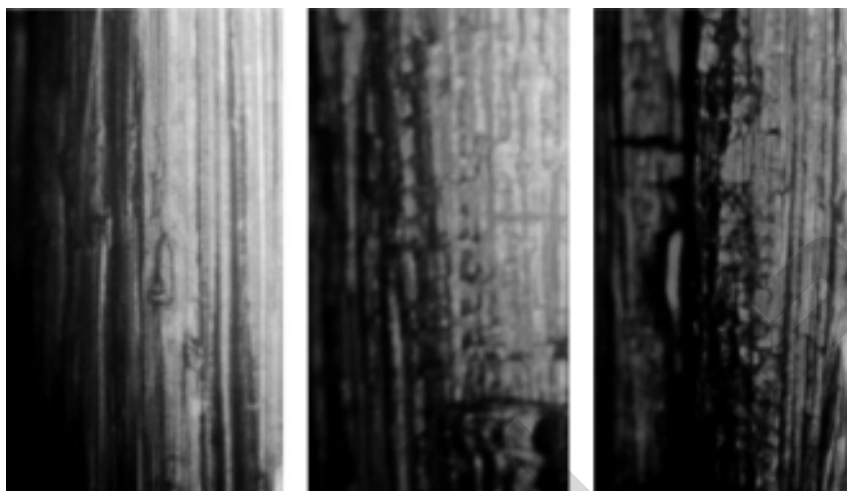


Figure 8.24 Surface modified by ageing (photomicrograph).

bridges due to the presence of oxygen, multivalent cations, Van der Waals forces, and physically modified surfaces contribute to stickiness. Even though these conditions occur, stickiness disappears when the surface tension rises above 55 mNm^{-1} . The rise in surface tension explains why the stickiness on molds vanishes after an acidic clean or an alkaline clean followed by the acidic one. As a matter of fact, acids are not the ideal means of achieving detergency in food processes, as they tend to keep or generate hydrophobicity. Thus, the application of an acidic cleaning raises the surface hydrophobicity. Hydrophobicity moves the surface tension above that critical limit where stickiness vanishes. For the same reason, a citric acid solution sprayed on the surface before the curdmaking process gives an anti-sticking effect.

The anti-sticking effect is also a property of alkaline detergents highly concentrated in acrylic homopolymers (4500 MW). Anti-stickiness takes place only when such sequestrants are still found in free form at the end of the cleaning. In particular, if the acrylic homopolymer is co-formulated with EDTA, anti-stickiness is accomplished when EDTA is still detectable in free form at the end of the process. As the EDTA stability constant is predominant on polyacrylate, most of the polymer occurs in free form when free EDTA is detected. Thus, the polymeric carboxylic group links the surface in a thin layer having the hydrocarbon chains turned outwards. The free charges on the surface are saturated, the free energy of surface lowered, and a higher surface tension established. All of this results in an anti-stickiness effect.

What happens in curdmaking is also confirmed when the curd-filtering sheets (Figure 8.25) are washed.

Alkaline detergents based on acrylic homopolymers make curd readily removable from sheets. In practice, there is no need to manually scrape curd off sheets before washing.



Figure 8.25 Curd-filtering sheets (picture on the right by courtesy of 'Il Latte' Tecnica Nuove Ed., Italy).

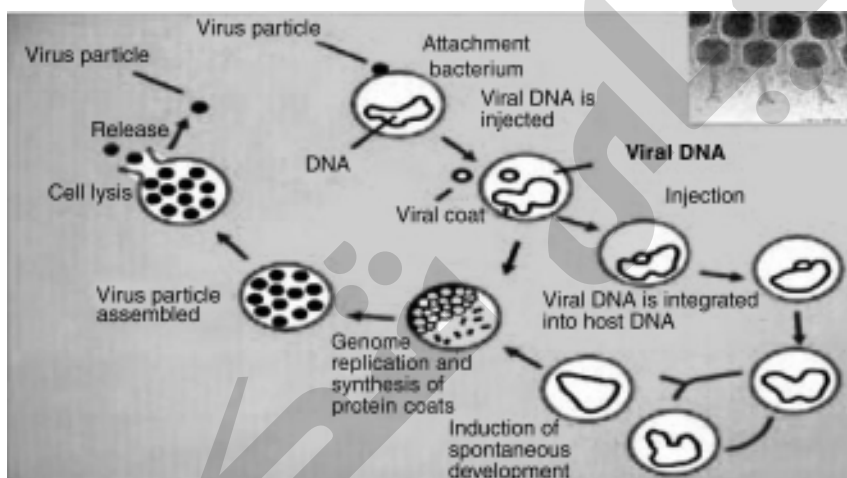


Figure 8.26 Bacteriophages and the rolling circle of the replication mechanism [courtesy of Marc Adrian (1985)].

A serious problem in cheese making arises from bacteriophages. Cheese-making industries use bacteria-containing starter cultures to acidify milk. Bacteriophages are parasitic viruses that attack and kill bacteria. Each virus is host-specific and will only attack one particular type of bacteria. If bacteriophages destroy bacteria, the cheese-making process will slow down or even stop.

Bacteriophages cause the bacterial cell to gradually break down (lysis) by penetrating the cell wall and injecting their own DNA into the cell. They then replicate before rupturing the bacteria cell walls, thereby being released into the environment to attack more bacteria (Figure 8.26). As more and more bacteria are infected and ruptured, fewer remain available for the cheese making. Thus, the process slows or stops. As bacteriophage is species specific, one way of reducing the likely damage is to use a multiple bacterial strain type. However, this does

not solve the problem. Ultimately, the only one way to ensure that the cheese making remains efficient is to make sure bacteriophage is destroyed. A thorough cleaning will remove any soils capable of hiding phage. Disinfectants must be used to eradicate the phage altogether. Three main groups of disinfectant are available:

- quaternary ammonium compounds (QACs) and amphoters
- peracetic acid and chlorine
- glutaraldehyde and glutaraldehyde added to QACs.

Combinations of these ensure bacterial, fungal, and viral disinfection. Advice on minimum exposure limits, controls, and concentrations are directly obtainable from the chemical manufacturer.

8.4

Processed Food

The idea that foods vary in terms of molecular structure was developed in 1834 when the universal nutrient for man known as food was found to contain three major molecular groupings or components: carbohydrates, proteins, and fats [23]. Generally, plants and animals are water systems made up of carbohydrates, proteins, fats, and mineral salts of calcium, potassium, iron, magnesium, sodium, chlorine, phosphorus, sulfur, and most of the chemical elements in traces.

The chemical composition of food and, consequently, its contamination (soil in plant after the process) are usually described in terms of percentages of carbohydrates, proteins, fats, ash (mineral salts), and water, there being an important difference between plant and animal tissues. Plant tissues are the main source of carbohydrates, whereas animal tissues are usually a source of fats and proteins.

There are various methods of grouping foods. According to the chemistry of detergency, foods can be codified into 6 groups:

- 1) **Meats, fish, and eggs:** This group is made up of every kind of raw meat (beef, veal, pork, lamb, horse, chicken, duck, turkey. ...) and processed meat (ham, sausages, canned meat. ...), every kind of fish, shellfish, and molluscs, raw eggs, and processed yolk and albumen. It represents a homogeneous group which is source of proteins (on average: 20% in meat, 16% in fish, and 13% in hen's eggs [8]) and fats. Their sensitivity to denaturing, gelatinization (collagen), polymerization, and drying makes proteins hard to clean. The hydrolysis of fats yields fatty acids, which precipitate on reacting with polyvalent metals and polymerize by oxidation and reaction with proteins. Iron and sulfide together with calcium (water hardness) exacerbate the difficulty in cleaning.
- 2) **Milk and its derivatives:** The milk group differs from the previous one by being the source of one predominant protein (casein), phosphate, and calcium. Casein, phosphate and calcium generate milkstone. Milkstone is one of the most resistant soils when it grows on heat exchanging surfaces.

Table 8.5 Composition of materials causing cleaning problems. Courtesy of Quaglia [8].

g/100g	Dry legume	Vegetable	Fruit
Protein (g/100g)	20–25	0.6–4.6	0.1–1.2
Lipid (g/100g)	2–6	0.1–1	0–1
Fiber (g/100g)	11–25	0.2–9.4	0.2–1.7
Calcium (mg/100g)	98–120	9–220	4–49
Iron (mg/100g)	4–6	0.2–8	0.1–1
Phosphorus (mg/100g)	300–480	11–90	2–52

- 3) **Cereals and tubers:** All kinds of flour and their derivatives (bread, pasta, bakery products, pizza, cereals, crisps, rice, potatoes. ...) are included in this group. Although cereals and tubers are essentially sources of starch (carbohydrates), they contribute to the availability of proteins (on average: wheat 12%, rice 7.5%, potato 2% [8]). In the presence of water, gliadin and glutenin (wheat proteins) form a structure known as gluten, which provides dough with elasticity. Besides complexing polyvalent cations, starch gel generates a sticky layer and slows the cleaning down.
- 4) **Vegetables, legumes and herbs:** Peeling, blanching, and cooking lead to the deposition of fibers, proteins (legumes), calcium, magnesium, iron, oxalate, phosphate, sulfate, and clay. These collectively cause the contamination known as vegetablestone. In terms of cleaning, vegetablestone represents the most resistant deposit found in food detergency. The deposit of contamination on a heat exchanger (blanching) becomes like marble, slowly re-hydratable, and barely attackable by chemicals. Average compositions of matter causing cleaning problems are given in Table 8.5 [8].
- 5) **Fruit:** This group includes all types of fruit and its derivatives such as juices, jams, fruit jellies, and preserves. From Table 8.5 it is evident that the concentration of critical substances is relatively low. Thus, detergency is relatively easy. However, fruit is source of pectin, fragrances (smell), and dyes. For this reason cleaning needs the addition of oxidizing agents (hydrogen peroxide or chlorine) in order to remove entirely, make inert, or deodorize the contamination. The manufacture of fruit and vegetable preserves involves complex processes, as listed in Table 8.6 [24]. Besides the risk of thermal damage, repeated heat exchange processes precipitate a contamination increasingly resistant to cleaning as its thickness and the heating time increases.
- 6) **Seasoning and cooking fats:** This group identifies applications processing or using fats (lard) and oil (olive, corn, sunflower, soybean, grape-stone). Fats are a source of fatty acids by hydrolysis. Their derivatives can polymerize with proteins at high temperature and turn into a contamination resembling resin.

Table 8.6 Manufacture of preserves. Courtesy of Pompei. [24]).

Receiving	Preparation	Pre-treatment	Packing ^{a)}	Thermal treatment	Stowage	Distribution
	Washing	Scalding ^{a)}		Pasteurization ^{a)}	Chilling	
	Sorting	Pre-cooking ^{a)}		Sterilization ^{a)}	Freezing	
	Cleansing	Sizing				
	De-stalking	Sieving				
	De-stoning	Evaporation ^{a)}				
	De-coring	Juice extraction				
	Peeling ^{a)}	Filtration				
	Trimming					

a) Heat exchange involvement.

Fatty acids react with calcium and form a whitish deposit. The absorption of fats into cooking residues increases their hydrophobicity. Polymerization, calcium soaps, carbonized contamination, and hydrophobicity lead to considerable difficulties in cleaning.

The aforementioned groupings have been deliberately simplified. Processed foods include a huge mix of those categories. New mixes are also the result of new ideas intended to enable increasingly tempting foods to be offered to consumers.

8.4.1

Evaporator

Evaporation is the process where a food increasingly loses its water content. Proteins, fats, carbohydrates, and salts are found in larger amounts per weight unit at the end of the concentration process. Even when the process is carried out at low pressure, heat is always used. The exposure to temperature makes proteins less soluble, fats hydrolyzed and oxidized, carbohydrates more subjected to chemical and enzymatic browning, fibers more compacted, and salts more insoluble. The damage to the food is directly proportional to the time of thermal exposure in the plant, and the damage rate increases by one factor for every 25 °C of rise in temperature [25]. In order to prevent thermal deterioration, the traditional evaporators can be replaced with tangential filtration technology (ultrafiltration (UF), NF, and, mainly, RO). Crossflow filtration operates at room temperature, does not cause damage, and enhances productivity (see Chapter 12).

The contamination in the evaporation process includes every physical state, from aqueous-like fresh food to dehydrated, compacted, and carbonized material. The presence of fibers and salts (oxalate and clay) reinforces the soil lattice and slows down its rehydration. Cleaning is often influenced by the rehydration time, meaning that in most cases soil removal is achievable only when the contamina-

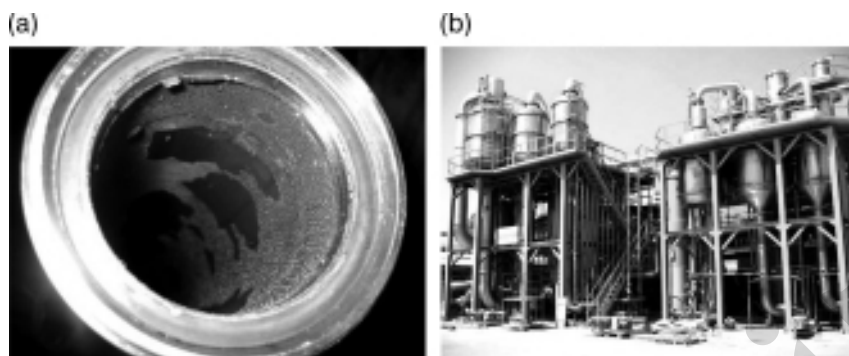


Figure 8.27 View of (a) deposition in a process pipeline and (b) plant for concentration of tomato juice.

tion is entirely rehydrated. Two different approaches to cleaning are recommended for productivity reasons:

- routine cleaning (daily) in order to remove most of the fresh deposits and permit a rapid resumption of work (rapid removal of loose deposits so as not to lose productivity)
- periodic cleaning (weekly or more) to achieve thorough removal of soil.

The different procedures result from the fact that no time is usually available for a daily thorough cleaning. Several hours devoted to cleaning in depth can only be at longer intervals. The deposit forms a typical self-protected contamination. Sequestrants play a great role in accelerating rehydration and dissolution. As mentioned, the sequestrants, mainly EDTA, NTA and MGDA, are able to weaken the lattice (desorption of polyvalent metals) and ensure more rapid cleaning of the soil, as shown in Figure 8.27.

Secondary and tertiary additives based on EDTA, blends of EDTA with phosphonates, and oxidizing agents (chlorine or hydrogen peroxide) are frequently added to reinforce the cleaning power of the primary detergent. Even with this support, the re-solubilization of soil needs time. Thus, a periodic procedure involving 3–4 hours of alkaline oxidizing and subsequently 1–2 hours of acidic treatment is customary to obtain a satisfactory result. The rapid procedure only aims to remove loose deposits in order to maintain productivity during the campaign.

The more the soil is carbonized, the more the alkalinity is necessary. Causticity, hydrogen peroxide, and time become the key factors in cleaning rather than sequestrants. Since the wet condition facilitates cleaning, it is mandatory to clean these plants before they dry, that is, immediately after the end of the campaign, at least. This kind of care is a general rule in detergency and becomes essential if fibers, salts, clay, and risk of polymerization are some of the features of the process.

8.4.2

Dough-Kneading Machine and Extruder

Cereals and legumes are transformed into numerous food products. The process usually starts from a dough-kneading machine and is followed by shaping by extruders in many cases. As well as the traditional process of extrusion such as pasta making (forming smooth, hollow tubes, corrugated pieces, flat ribbons, and fancy shapes ...), extrusion-cooking is the technology used to prepare a large number of foods based on cereals. Pre-cooked, ready-to-use, shaped foods are made available for human and animal consumption and as industrial raw materials (cornflakes, oatflakes, pre-cooked flour, crispbread, instantaneous purée, pellets to expand, mixed dry soups, pre-treated malt for breweries, textured vegetable proteins ...). The majority of the products are based on flour enriched with eggs, proteins, fibers, vitamins, and mineral salts in order to satisfy both normal and dietetic demands. This converts local food resources into complete nourishment systems [26, 27]. A summary of mixes is shown in the simplified flow chart Figure 8.28.

Although starches, proteins, salts, and vegetables leave residues [28], contamination is easy to clean off because dough comes off the surface when it is ready. Moreover, several extruders are self-cleaning and can be manually dismantled.

The dough-kneading and extrusion process is divided into wettable (closed zones) and dry sections (open surfaces), each of which requiring a different procedure. The closed part is suitable for CIP, and CIP detergents are usually applied. Sequestrants have no significant influence on the cleaning result, except for control of the water hardness. Basic sequestrants, such as tripolyphosphate, phosphonates, and gluconate, accompanied by good alkalinity together with wetting agents (surfactants) accomplish the sanitation in most of the applications. When necessary, hydrogen peroxide reinforces the primary detergent. An alkaline chlorinated detergent can perform rapid cleaning, taking away smells (e.g., egg, herbs, and fragrances) and giving disinfection if any traces of free chlorine are still detected at the end of the cleaning process. The presence of starch sometimes makes acidic cleaning necessary.

Dry zones cannot be wetted with aqueous solutions. As a consequence, soil has to be removed by brush, cloth, and paper sometimes steeped in mild detergents. Afterward, surfaces are wiped or sprayed with ready-to-use alcoholic detergents. If the alcoholic detergent includes traces of biocide (quaternary, amphoteric disinfectant), evaporation of the alcohol leaves the surface covered with a thin layer of disinfectant. Such a layer hygienizes and preserves the surface from airborne microbial re-contamination.

8.4.3

Pasteurizer and Sterilizer

The concepts of pasteurization and sterilization have a different meaning for each group, that is, milk, fruit, or vegetable preserves. Where milk is concerned,

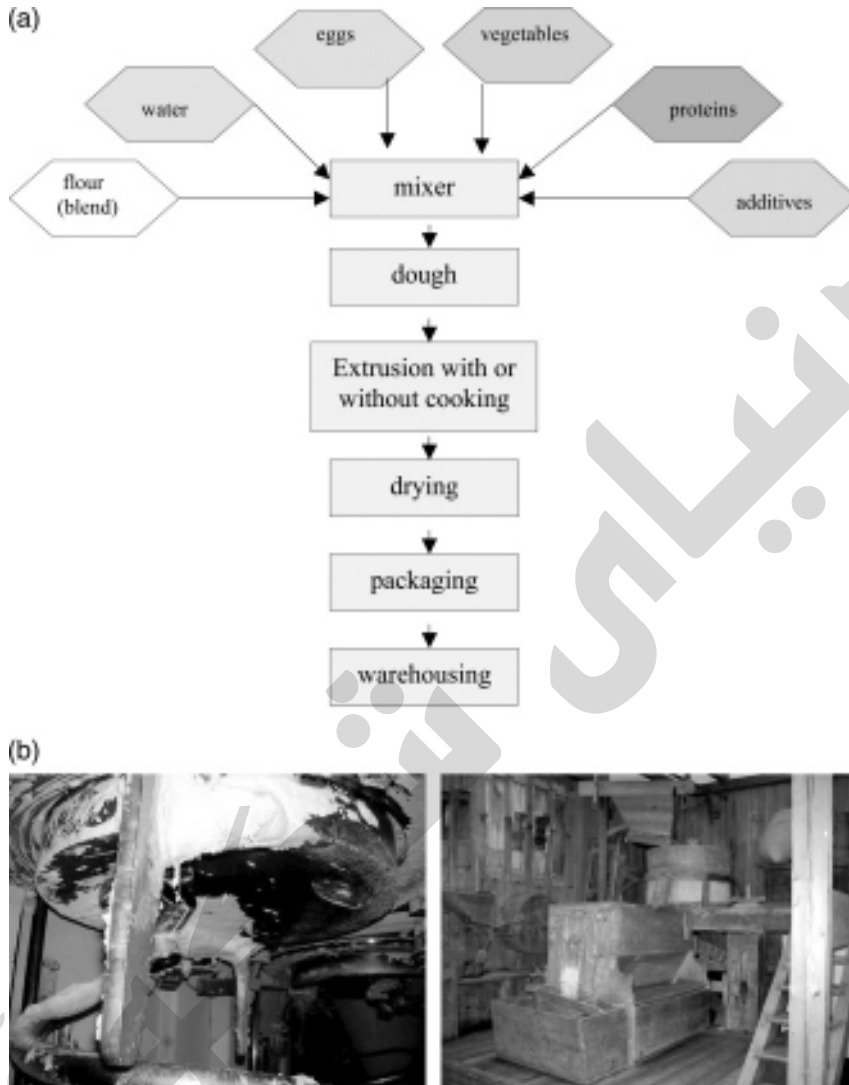


Figure 8.28 (a) Dough process and dough-kneading machine (courtesy of Grisenti-Barilla) and mill producing flour (b) (Deutsches Museum–Munich).

pasteurization gives a short life and sterilization a prolonged life. When referred to fruit and vegetable preserves, pasteurization and sterilization have the same meaning, producing long-life food, even if the pasteurization is performed below 100°C and sterilization above this temperature. This depends on the microbial population in preserves. The pH of preserves establishes well-defined limits of microbial growth (Table 8.7):

Table 8.7 Growth of microorganisms in preserves.

$a_w = 1$		
pH < 4.3	4.3 > pH < 4.6	pH > 4.6
Juices and pulps of citrus fruit, vinegar preserves of vegetables	Juices and pulps of fruit, juices and puréed tomatoes, water preserves of fruit, pickled preserves	Natural preserves of nonfermented vegetables and nonacidified oil preserves
4.3 is the ultimate pH of growth for sporigen microorganisms both pathogenic and nonpathogenic	Among sporigens, 4.6 is the ultimate pH of growth for pathogenic microorganisms. No growth of sporigen pathogens below 4.6	Above pH 4.6, pathogen microorganisms may freely grow in preserves

Treatment of preserves having a pH < 4.3 at temperature below 100°C is regarded as pasteurization, whereas treatment of preserves with a pH > 4.6 at temperatures exceeding 100°C produces a sterilizing effect. The latter is done to kill pathogen spores and prevent their growth. Theoretically speaking, pasteurization is the thermal treatment which destroys all the pathogens and most of the vegetative forms and inactivates enzymes. Sterilization adds the concept of spore killer. In treating preserves, temperature and pH act synergistically to give sterility, or better, no bacterial growth. Nevertheless, the final product cannot be defined as a sterile food but rather a food having commercial sterility. As *Clostridium botulinum* generates heat-resisting spores, a 12 log reduction of the population of its spores is conventionally designated as the reference standard of industrial sterilization [24]. Thus, the final step in preparing preserves involves a targeted thermal treatment to make longer-lasting food with a 'best before' date. Apart from cold aseptic filling and mass sterilization, the thermal treatment is applied directly to the containers just after filling (see Section 18.4.1).

The main cleaning aims at keeping containers looking shiny and preventing incrustations inside the treatment plant. In both cases, hardness needs to be controlled and spillage from damaged containers emulsified and dispersed. A correct balance of surfactants (HLB) is used, and sequestrants help containers to look shiny by

- complexation of metals causing hardness
- dispersion of the salinity of the system
- prevention of re-deposition of overall contamination (salts, organic matter, oil, dyes).

Sequestrants themselves must be as invisible as possible on the dried containers. The choice of sequestrants requires particular care. Sequestrants react with salinity and lead either to a shining surface or to more evident deposits. Wrong



Figure 8.29 27 dF hardness and 100ppm of sequestrants: comparison between citric-tartaric acid and hexametaphosphate-ATMP.

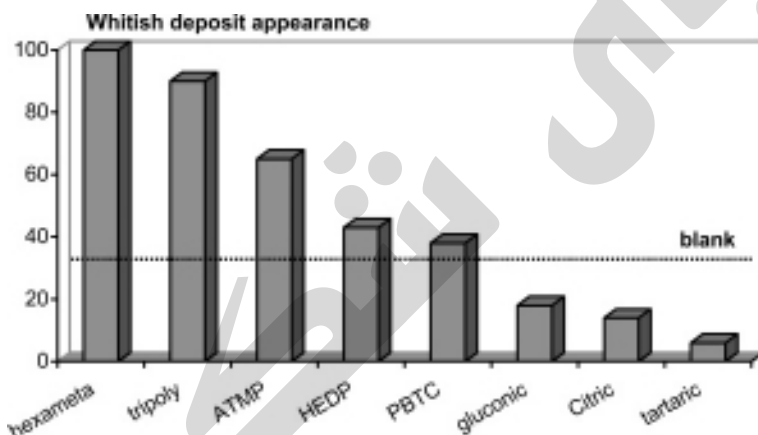


Figure 8.30 Prevention of whitish deposit. Water hardness 25 dF, sequestrant 200ppm, autoclave 120°C, sterilization time 15 min. Blank is sterilization free of sequestrants. The figure for the hexametaphosphate deposit is arbitrarily set at 100%

sequestrants can contribute to increased salinity. Pasteurization (tunnel soaking) and sterilization in an autoclave are processes sensitive to salinity. The investigation of salinity dispersion shows that some sequestrants increase the whitish deposits on tins and jars. A typical laboratory result is shown in Figure 8.29.

Generally speaking, all the compounds containing phosphorus (ATMP, HEDP, PBTC, EDTMP, and polyphosphates) tend to increase visible deposits although they are excellent threshold chemicals. On the other hand, blends of tartaric, citric and gluconic acids mask salinity. They prevent the formation of whitish spots, seeming to transform a potential bulky and porous incrustation into a shiny surface after draining (draining with dispersion). The Figure 8.30 compares tuna

(painted) and tomato (tinned band) containers sterilized in an autoclave at 25 dF hardness and using different sequestrants.

The ability to drain and give a shiny result typical of hydroxyacids (see Section 3.4.3) is confirmed not only in the sterilization of preserves but also in bottle-washer rinsing (Section 6.3.2).

Some applications, such as cleaning chocolate molds and the tunnel pasteurization of glass containers, require rinse-aid products based on surfactants (e.g., fatty alcohols EO-PO and EO-BO) both to disperse salinity (prevention of concentrations of salinity in the form of spots) and to maintain a thin film of water for rapid drainage. The risk of fading of the paint on caps, jars, and tins means that mild surfactants and alkaline products must be applied. For this reason, disinfectants are carefully chosen both to kill bacteria in cold areas and avoid fading. Halogens (chlorine, bromine) corrode, and QAC monomers cause fading of paint. On the other hand, polymeric QAC, isothiazolone, glutaraldehyde and bromonitrilopropionamide prove to be compounds suitable for the tunnel pasteurizer treatment.

8.4.4

Cooking, Baking, and Frying

Modifications of the original structure of foods by heating can be produced by water, steam, air, metals, and temperatures (from 60 to 230 °C). Positive and negative changes in protein-bound aminoacids, interaction of proteins with carbohydrates and carbonyl groups, peroxidation and polymerization of lipids and fatty acids, caramelization, carbonization, and precipitation of salts have already been discussed in detail.

Table 8.8, taken from Quaglia's paper, shows an example of the influence of temperature on a starch system (bread baking) [8].

Flour, proteins, fats, metal salts, flavorings, and aromatic materials can be found on all items of equipment (trays, baking tins, fryers, and grills) in every

Table 8.8 Events as a function of temperature in the bread baking process.

Temperature (°C)	Reactions
30	Gas expansion and enzymatic production of sugar
45–50	Death of <i>Saccharomyces</i>
50–60	Vigorous enzymatic activity, start up of the starch water
60–80	Starch water completion, reduction and ending of the enzymatic activity
100	Steam development
110–120	Starch conversion into dextrins in the crust
130–140	Formation of brown dextrins
140–150	Caramelization
150–200	Aromatic products, carbonization

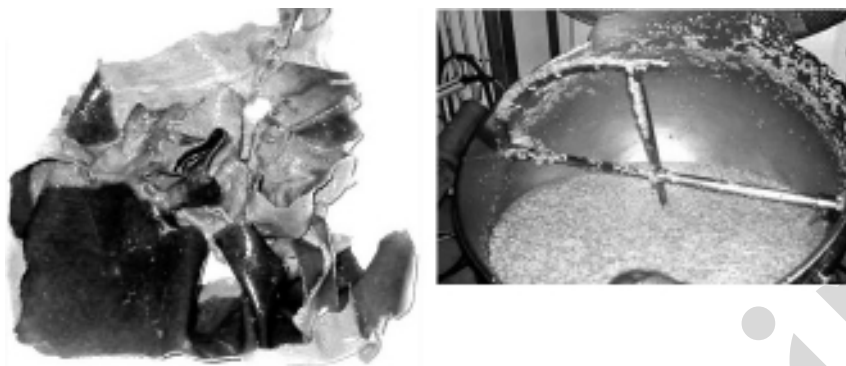


Figure 8.31 Soil from a cooked vegetable-cheese sauce and industrial pot (courtesy of Muschio–Antica Pasteria).

state of alteration. Supports and equipment are not usually cleaned after every cooking cycle, and consequently the process accumulates a residue having the worst hydrophobic and inert properties typical of carbonized soil.

From the point of view of the chemistry of detergency, three different cooking systems can be recognized:

- 1) **Wet cooking**, where temperatures do not exceed 100°C ($>100^{\circ}\text{C}$ in steam pressure cooking). Stewing, boiling, and pressure cooking tools are usually cleaned either manually, frequently after soaking, or by foam and gel technology. Sequestrants do not play a significant role, being simply employed for controlling the water hardness. Conversely, surfactants, secondary additives (e.g., hydrogen peroxide), manual energy, and high rinsing pressure are the key factors of cleaning. Strong caustic detergents (alkalinity in neat products $\geq 30\%$ for CIP and $>10\%$ for foam) boosted with hydrogen peroxide are able to accomplish cleaning in every condition and application (Figure 8.31).
- 2) **Dry cooking**, where temperatures reach values even above 200°C . Roasting, grilling, toasting and baking lead to extreme conditions wherein the external structure of food alters and loses part of its surface components. Quaglia [8] reports a loss of superficial substances for potatoes after 60 minutes in an oven at 200°C as follows:

4% of total nitrogen	15% of potassium
15% of total aminoacids	12% of iron

A sizeable proportion of the released substances precipitate and form typical soils. Trays and baking tins are usually exploited to excess, until particles of carbonized soil come away carried along by the food. The resulting soil is a mixture of carbonized and caramelized food hard to remove because of a hydrophobic inert carbon skeleton left behind by the over-cooked material. Instead of aqueous solutions, chlorinated solvents have been widely applied

on steel and aluminium molds to obtain rapid cleaning. Ecological restrictions, however, no longer permit their use. Strong caustic detergents have replaced them. Caustic detergents include silicates to protect aluminum (corrosion inhibitors). An acidic pickling frequently follows the alkaline step. Gluconate, EDTA, wetting agents (e.g., alkylpolyglucoside) and hydrogen peroxide decrease the time of cleaning.

Baking pans are often made of stainless steel and aluminum coated with teflon or silicone resins. Suitable detergents and temperatures have to be carefully selected in order to preserve the protective coating. Figure 8.32 shows a blistered surface caused by incorrect cleaning.

- 3) **Frying**, where food is immersed in oil (olive, seeds, lard) at high temperature (up to 200°C). Proteins, starch, and metals migrate from the food surface into the oil. Oil degradation generates dimers, trimers, epoxides, aldehydes, alcohols, and hydrocarbons. Barbanti [29] summarizes the agents responsible for degradation (Table 8.9).

Table 8.9 Degradation during frying. Courtesy of Barbanti [29].

Deterioration	Responsible agent	Products of reaction
Hydrolytic	Water	Fatty acids
Oxidant	Air (O ₂)	Monoglycerides
Thermal	Temperature	Diglycerides
		Glycerol
		Oxidized monomers
		Dimers and polymers
		Volatile compounds
		(hydrocarbons, aldehydes, ketones, alcohols, acids)
		Cyclic monomers
		Dimers and polymers

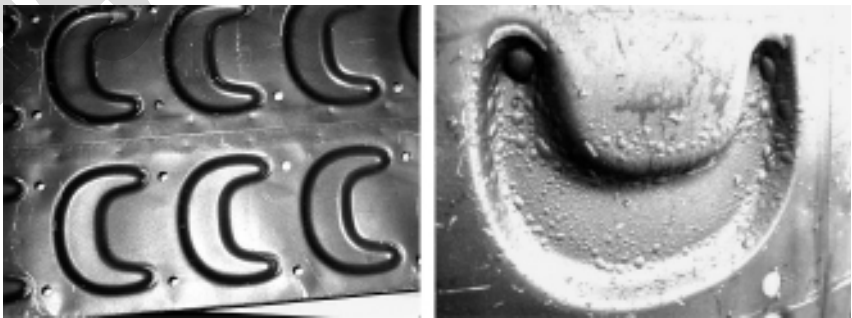


Figure 8.32 Temperature and wrong detergent cause blistering of the protective coat.

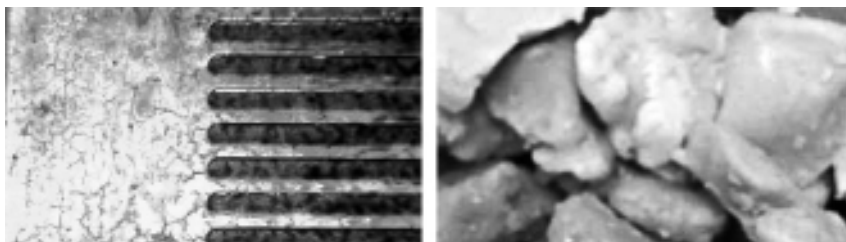


Figure 8.33 Wall of fryer and starch-oil-detergent lumps causing pollution of the process.

More than 400 compounds produced by the decomposition of oil have been identified [8]. Vigorous boiling distributes these substances to wherever the steam goes. The surface of a potato fryer reveals the oily, hydrophobic, caramelized, and sticky condition of the contamination (Figure 8.33). Hydrolyzed free fatty acids react with metals (calcium) in the course of the cleaning and, in the absence of suitable sequestrants, leave whitish surfaces. Thus, strong causticity associated with EDTA, tripolyphosphate, and phosphonates achieves the thorough removal of the fatty contamination. EDTA keeps the calcium in solution, fatty acids are neutralized with sodium, and the sodium soaps produced, being surfactants, take an active part in cleaning.

The temperature must be carefully adapted to the different steps of cleaning. The released carbohydrates absorb oil, forming lumps at cold temperatures. The rinse after cleaning is the critical step. The cold temperature of the rinse can also form lumps like those visible in Figure 8.33. Starch-oil lumps absorb some of the detergent. Lumps trapped on filters remain in the fryer and generate foam when a new frying process starts. Foam means pollution and leads to rejection of the potatoes produced.

8.4.5

Smoke Chambers

Smoked meat, fish, and cheese are produced by exposure to the smoke produced from smouldering sawdust and blown into a chamber where the food is placed. This operation impregnates food and chamber with the smoke constituents and fats extracted from food. More than 200 chemical compounds have been identified in wood smoke, mainly organic acids and bases, phenols, alcohols, aromatic polycyclic hydrocarbons, carbon monoxide and dioxide, and aldehydes [8]. Among these, aldehydes, phenols, and aliphatic acids absorbed into the food act as preservatives [30].

Besides the preservative action, smoke and its derivatives (extracts and smoke moisture) provide food with fragrance and color. The smoke chambers are periodically cleaned with detergents in which generic sequestrants do not play any significant role. The key factor in cleaning is the surfactant alkylpolyglucoside in the caustic medium, which specifically operates on the oily smoked soil. The

same surfactant performs as a sequestrant like gluconate. Threshold sequestrants help to prevent scale in rinsing. Smoke chambers are small open plants whose cleaning is usually based on foam and gel detergents. CIP technology is available in those chambers having an automatic cleaning plant (spray cleaning).

8.4.6

Blanching

Many vegetables and fruit are blanched in hot water or steam at temperatures in the range 70–100°C with the purpose of

- **Enzymes inactivation:** Enzymatic activity causes severe damage to the packaged vegetables. Peroxidase is one of the most resistant enzymes and is the reference standard used to assess the efficacy of the treatment [8].
- **Superficial microbial charge reduction:** The vegetable surface is hydrophobic, so part of the microbial charge (e.g., coliforms) remain on the surface even after a good cleaning. Blanching becomes a kind of pasteurization, extending the duration of preservation.
- **Degassing:** Temperature and shrinkage promote the removal of gas dissolved in the cellular tissue, which affects the vacuum if it evolves after the packaging process. Peas, beans, and carrots, for instance, contain from 18 to 38 mL of gas per 100 g, and is potentially able to disturb the vacuum [31].
- **Color stabilization:** Packaging protects foods from oxygen and light, and blanching prevents variations of color after packing. The blanching of tubers and leaves can be seen in Figure 8.34.

The blanching process extracts many components from the outside and inside of the tissue by mechanical energy (fibers and pieces of vegetable) and aqueous extraction (soluble organic substances, salts such as oxalate, phosphate, and clay, together with calcium, magnesium, and iron). High temperatures and hard water cause oxalate to precipitate. Deposits of silicate (clay), oxalate and organic fibers



Figure 8.34 Blanching of carrots and spinach.

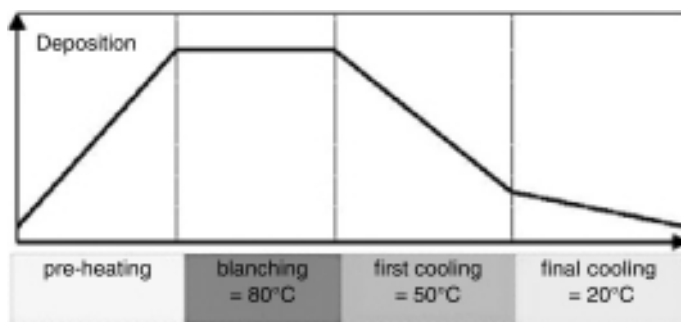


Figure 8.35 Tendency toward soil precipitation in blanching equipment.

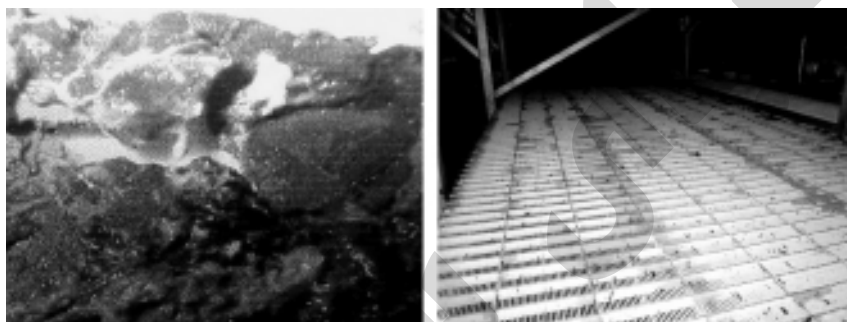


Figure 8.36 Vegetable-stone and soiled chain of spinach blanching equipment.

are as resistant as rock. Figure 8.35 schematically represents soil precipitation in blanching equipment.

The hard vegetable stone only occurs in the blanching area. The preheating and cooling zones are not particularly difficult to clean. The hot zone extracts material and cements the deposit to form a rock-like soil as shown in Figure 8.36.

Vegetable stone is a typical self-protected contamination, practically inert to caustic and acid detergents. Its dissolution by acceptable chemicals (nontoxic and nondisruptive, such as hydrofluoric acid) is only possible by applying the competitive action of the strongest stoichiometric sequestrant (EDTA) combined with a powerful oxidant (hydrogen peroxide). As soil increases daily and rapidly reaches a rocky condition, cleaning needs several hours of contact with the most active chemicals (caustic soda, EDTA, wetting surfactants, hydrogen peroxide, and nitric acid). There is usually not enough time to clean the blanching equipment daily during the harvest-time campaign. Then, different procedures are put in place. A short cleaning is given daily, just enough to roughly remove the loose deposit. This procedure rapidly restores productivity. The periodic cleaning (weekly or more) aims at cleaning thoroughly and allowing the equipment to finish the harvest campaign. Effective and adapted procedures are described below.

Daily:

- 5–10% solution of nitric or nitric-phosphoric acid.
- Recycle 1 h at 60 °C.
- Solution recovered and re-used after restoring acidity.

Periodic (weekly or more):

- 10% EDTA and 2% hydrogen peroxide in 1% alkalinity
- Recycle 4–6 h at 60 °C. Maintain the hydrogen peroxide concentration during running.
- Rinse.
- Recycle for 1 h, 5–10% nitric or nitric-phosphoric acid solution.
- Final rinse.

Conveyor belts are even more difficult to clean. They are sometimes wetted with neat nitric acid for 10–15 min and rinsed with high-pressure water. It is evident that a deep clean in a blanching process needs time and energy.

8.4.7

High-Temperature Scraped Sterilizer

Sterilization is the result of a combination of temperature and time according to the mortality graph shown in Figure 8.37 [8].

The overall thermal treatment is equal to the sterilizing power which derives from the sum of each theoretical instantaneous heating and cooling. The thermal industrial process in which the temperature gradually increases can be considered as a succession of single contiguous theoretical treatments [8]. Since natural convection is too slow for viscous foods, heat transfer mainly occurs by conduction. Temperature takes long time to reach the cold point in the middle of the viscous mass. Thus, damage to the food in contact with the heated wall become

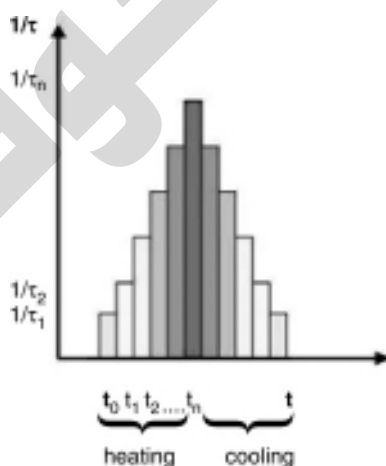


Figure 8.37 Steps of the sterilization process.

severe before the whole food mass is sterilized [24]. In order to obtain sterilization without harming the food, the sterilizer is provided with an axial motion suitable to mix the doughy food and scrape the heat exchanging surfaces.

Scraping-plate sterilizers reach temperatures above 100 °C. The same temperature can be applied to the cleaning step. At these temperatures some components of the detergent could undergo chemical and physical alterations, giving an adverse effect on the cleaning. Antifoam surfactants are an example of this negative behavior. They move from solubility to dispersed micelles and final to a hydrophobic oil, which converts a surfactant into a barrier to the cleaning. Moreover, some sequestrants can rapidly hydrolyze and lose their sequestering capacity. Thus, it is crucial to select a caustic detergent ($\geq 30\%$ alkalinity) devoid of surfactants and heatproof sequestrants such as phosphonates (ATMP, PBTC) and acrylic homopolymers.

When milk, cheese, and egg derivatives are incorporated into viscous foods, even good detergents could be inadequate for cleaning. Then, hydrogen peroxide successfully assists the cleaning even better than chlorine.

8.4.8

Fresh Cut Produce (4th Gamme)

Fresh cut foods, minimally processed refrigerated fruit and vegetable (MPR), also known as '4th gamme', are ready-to-eat freshly packed vegetables with a relative short life. The industrial harvesting (sorting, cleaning, cutting, mixing, and packaging) moves the fresh vegetables and fruit from the field to fresh-cut food on the table.

The term 4th gamme is taken from the list of food categories:

- **1st gamme:** natural fresh vegetables and fruit
- **2nd gamme:** preserved vegetables and fruit (e.g., tinned, pickled, dehydrated, and in oil)
- **3rd gamme:** deep-frozen vegetables and fruit
- **4th gamme:** fresh cut vegetables and ready-to-eat fruit.

This last group includes leaf vegetables, root crops and tubers, sprouts, and any fresh fruit and vegetables that have been physically altered from their original form but are still in a fresh state (*International Fresh-Cut Produce Association-IFPA*). Preservation in an edible state lasts for ca. 10 days after packaging. Shelf life depends on physical effects of preparation, as reported in Table 8.10 [32], but mainly on the temperature of preservation.

High quality raw material, low mechanical damage, good rinsing and drying, strict sanitation, appropriate packaging and atmosphere, control of enzymatic oxidative browning, and temperature maintained within 2–5 °C are absolutely necessary for high quality fresh-cut products. The enzymatic oxidative browning originates from the polyphenoloxidase (PPO)/O₂ activity on diphenol groups, formation of quinines, and subsequent reaction with aminoacids and proteins to give brown complex polymers. However, a modified atmosphere, edible coatings,

Table 8.10 From Brecht et al, Hort Rev. 30: 185 (2006) in [32]. Effect of cutting in preparation.

Immediate effects	Subsequent effects
Wound signal propagation	Elevated ethylene production
Membrane depolarization	Elevated respiration
Membrane disorganization	Oxidative reactions
Loss protoplasmic streaming	Altered phenolic metabolism
	Altered protein synthesis
	Compositional changes

Table 8.11 Examples of microorganisms in received raw material.

Microorganisms	Number	Comment
Pseudomonadaceae	10^5 – 10^8	Depending on temperature
Enterobacteriaceae	10^4 – 10^6	Depending on temperature
Faecal coliforms	10^3	Decreasing in preservation
Yeasts	10^3 – 10^4	Root crops and tubers
Molds (spores)	10^4	Depending on climatic condition
Lactic bacteria	10^4 – 10^5	Carrots. Gasogen bacteria
Corynebacteriaceae		Gasogen bacteria
Pathogens	Unusual	L. monocytogenes, E. coli, Y. enterocolitica, S. aureus, Salmonella

antioxidants (ascorbic acid), sequestrants (EDTA, cyclodextrins), and acidulants (citric acid) can reduce the oxygen access to tissues. Yellowing is decreased by inhibiting the ethylene effect (by means of inhibitors and a modified atmosphere).

The flow chart includes the following steps for fresh-cut manufacturing:

- pre-cooling
- sorting, cleansing, and temporarily preservation
- washing, brushing, and drying
- cutting
- washing (rinsing) with disinfectant
- drying and sorting
- blending, weighing, and packaging
- cool warehousing
- cool delivering.

Contamination and deposits are derived from ground soil, clay, dyestuffs, organic fibers, oxalate, and rotten parts together with microorganisms such as coliforms, fungi, and pseudomonas (biofilm). Table 8.11 shows average numbers of various microorganisms in the received raw material [33].

Biofilm and reactions leading to decline in quality are exponentially affected by temperature according to Arrhenius's law [$K = K_0 \exp(-E_a/RT)$]. Thus, short

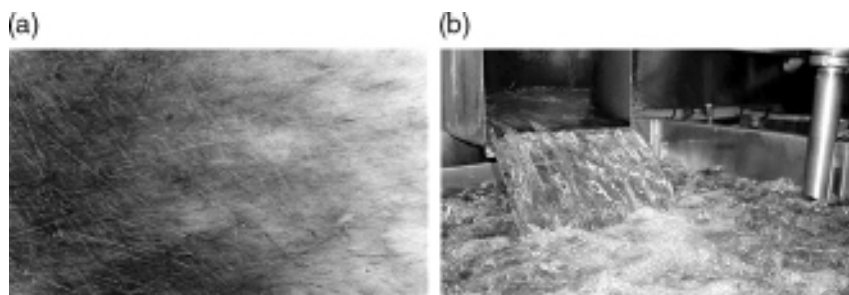


Figure 8.38 (a) Soiled PTFE surface with crevices. (b) Cascade washer (courtesy of Gurnari–Il Melograno).

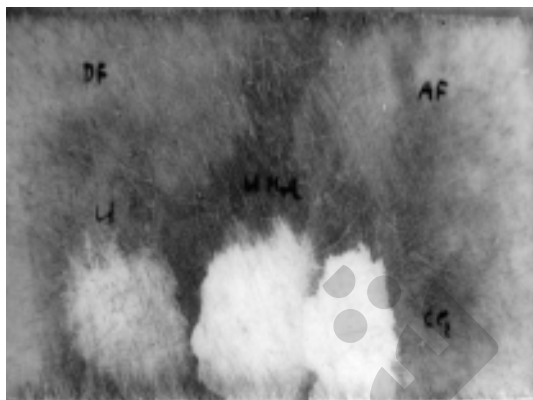


Figure 8.39 Cleaning test on PTFE work table.

storage of the raw material, good cleaning, and a refrigerated process ($<5^{\circ}\text{C}$ from harvest to haulage and sale) are the key factors in obtaining the desired shelf life.

Being protected by ground soil, clay, porosity, and crevices, the microbial contamination is fairly inert to chemicals. Mechanical removal rather than chemical attack is desirable. Thus, cleaning by agitation (e.g., cascade and ultrasounds washers, air bubbling) helps to remove chemical soil and macro-organisms (e.g., insects and nematodes). A PTFE worktop badly damaged by cutting is one of the obstacles to cleaning (Figure 8.38).

Although this type of contamination would seem to require acidic cleaning, alkaline detergents boosted with an oxidant give the best result. Hypochlorite and hydrogen peroxide in an alkaline medium produce gases (chlorine and oxygen). This oxidizing gas mixture penetrates inside the contamination and cleans wrinkles and crevices in depth. Sequestrants (EDTA, NTA, MGDA, IDS, GLDA ...) assist in the soil removal in the presence of hydrogen peroxide. STP and PBTC complete the action of chlorinated detergents. Acrylic polymers can be added to prevent redeposition. The PTFE worktop in Figure 8.39 shows the efficacy of different detergents in cleaning off the contamination.

Table 8.12 Low activity of disinfectants on 4th gamme.

Log reduction of microorganisms in lettuce washing ^{a)}				
10 g/L Na-bicarbonate	6 mg/L Chlorine	70 mg/L Chlorine	40 mg/L Peracetic acid	80 mg/L Percitric acid
0.32	1.15	1.61	1.34	1.86

a) Stomacher procedure.

Fresh-cut foods need gentle cleaning to preserve their original freshness and careful disinfection to be safe to eat. Sanitation benefits from chlorine, bicarbonate, peracids (peracetic and percitric acid), hydrogen peroxide, chlorine dioxide, and ozone.

Sodium bicarbonate has a negligible effect, so should not be considered.

Hypochlorite and peroxides have strong bactericidal action but also remarkable aggressiveness on the vegetable tissue if the concentration exceeds a well-defined limit. Vegetables have a hydrophobic cuticle like a waxy coat generating an intrinsic contact angle above $\pi/2$. Complex morphology of surfaces and abrasions on the epidermal tissue constitute obstacles to reaching the sites where microorganisms are lodged. Cleaning with bicarbonate, chlorine, and peroxides (chemicals with poor wetting power) does not give a significant reduction in the number of microorganisms [34]. No improvement is obtained if chlorine dioxide and ozone replace chlorine. Examples of this difficulty in reducing bacteria are shown in Table 8.12.

As the vegetable surface is hydrophobic and behaves as a barrier which resists wetting, aqueous solutions contact the surface as a function of their capacity to wet. The hygienic result depends on the wetting power of the chemicals (Figure 8.40). Thus, the reduction of microorganisms is achieved by a cleaning process rather than a direct disinfection. Disinfectants only help in keeping the process water in a bacteriostatic (hopefully potable) condition.

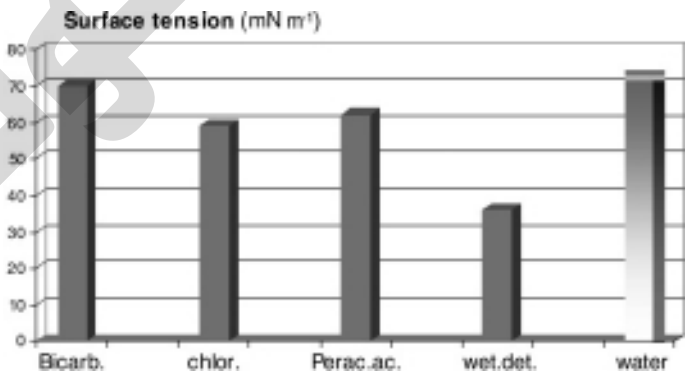


Figure 8.40 Sodium bicarbonate: 10 g L⁻¹; peracetic acid: 50 mg L⁻¹; chlorine: 75 mg L⁻¹; wetting detergent: 5 g L⁻¹.

The statistical results of microbiological analysis repeated on 15 samples of lettuce are plotted in Figure 8.41; the microbial pollution is persistent.

Thus, it is worth concentrating the effort toward reducing hydrophobicity rather than increasing the concentration of disinfectant. Gentle detergents formulated with food-compatible ingredients (e.g., lactic and phosphoric acid, sodium chloride, alcohols) and wetting surfactants (e.g., C_{12} -sulfate) are more effective in decreasing microorganisms than disinfectants. If the test of Figure 8.41 is repeated with a wetting detergent made up of lactic acid and C_{12} -sulfate (Figure 8.42), the reduction of the microbial charge improves.

Disinfectants should be added to the system in the final steps before packaging to keep water in a bacteriostatic condition.

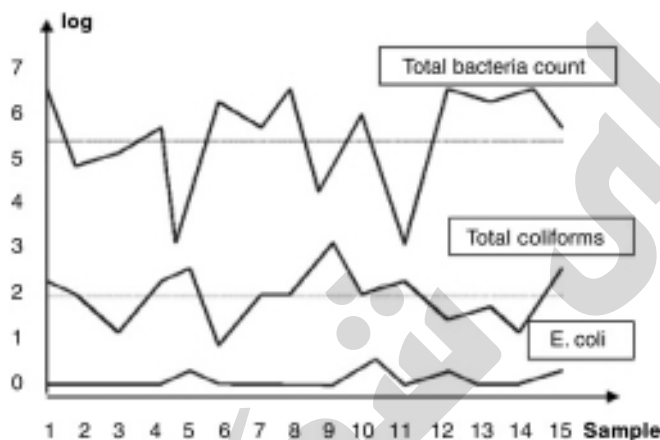


Figure 8.41 Persistence of microbial pollution (15 ppm of chlorine in wash water).

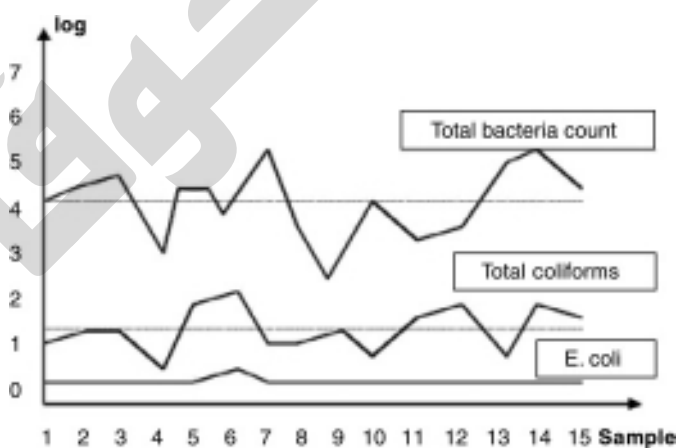


Figure 8.42 Persistence of microbial pollution (5 g L^{-1} of a wetting detergent in wash water).

Besides the cleaning activity, the pH of the solution is fundamental to reduce the microbial charge. A pH value of 3 is considered an upper limit. The microbial charge decreases more rapidly below pH 3. For this reason, phosphoric acid can be added to lactic acid to reach such a pH (lower concentration of lactic acid needed).

Lactic acid ($\text{CH}_3\text{--CHOH--COOH}$) is known for its nonirritant, bactericidal, and bacteriostatic properties and food compatibility. It is also used in cosmetics and gentle detergents directly in contact with skin. The carboxylic and hydroxyl groups provide lactic acid with sequestering behavior also. Therefore, lactic acid associated with dodecylsulfate is widely used in the fresh-cut detergency. The anionic surfactant wets and the lactic and phosphoric acids decrease the microbial charge and also prevent microbial spreading and recontamination on uncontaminated parts of the vegetable.

The replacement of the traditional technology of disinfection (chlorine) with a gentler one complies with the general requirement to reduce the use of chlorine in contact with foods. It follows that cleaning with mild wetting detergents (e.g., citric/lactic/phosphoric acid and surfactant) and disinfection with peroxide (e.g., peracetic acid, percitric acid, chlorine dioxide, hydrogen peroxide, and ozone) effectively combine sanitation with safety. Air bubbling and ultrasonic devices can complete the treatment. Such an approach is more expensive, but quality and safety of prepared fresh cut vegetables should be the priority.

The sanitation of the water in contact with food is carried out by means of physical systems also. Crossflow microfiltration is a procedure that enables clean and sterile water to be re-used. It also allows either chemical-free treatments or a lower concentration of disinfectant. Moreover, microfiltration also fulfils the fundamental objective of saving water, which is not only environmentally friendly but also saves money.

8.4.8.1 Cleaning and Disinfection Procedures

Cleaning and disinfection are performed on different areas of the process:

- fresh cut food
- equipment and tools in contact with food
- surfaces not in contact with food
- premises.

It is useful to recollect that

- Fibers and gels are easy to remove only when hydrated (before drying)
- Pectins and gums are easy to clean off before polymerization and oxidation
- Microorganisms are more easily killed before the biofilm develops, that is, before they are protected in their organic metabolites.

The first rule of a good result in sanitation states that dirt should be prevented from growing, drying, and polymerizing. Thus, it is mandatory to clean immediately after producing. Good cleaning is crucial because it removes up to 97% of microorganisms and allows for easier subsequent disinfection. Tables 8.13 and 8.14 summarize the sanitation processes.

Table 8.13 Traditional technology.

Foam/gel cleaning of open surface, traditional technology			
Alkaline	4%	Room temperature	Alkaline cleaning
Basic chlorinated alkaline	4%	Room temperature	Alkaline oxidizing cleaning
High chlorinated alkaline	4%	Room temperature	Alkaline oxidizing cleaning and disinfection
Acid	4%	Room temperature	Descaling detergent for periodic maintenance

Table 8.14 Advanced technology.

Foam/gel cleaning of open surface, chlorine-free advanced technology			
Alkaline	4%	Room temperature	Alkaline cleaning
Alkaline + H ₂ O ₂ additive	4% >0.5%	Room temperature	Alkaline oxidizing cleaning (disinfection depending on the % of hydrogen peroxide)
Alkaline + QAC amphoterics	4%	Room temperature	Chlorine-free alkaline cleaning and disinfection
Acid	4%	Room temperature	Descaling detergent for periodic maintenance

Hydrogen peroxide replaces the traditional technology based on chlorine. Chlorine adds organoleptic, environmental, and health risks due to by-products chlorotannins (medicine taste), chloramines (persistent off-taste and harmful compounds) and chlorocarbons (AOX, NPOX and THM, compounds also responsible for the hole in the ozone layer). No food alteration and no negative environmental impact are to be expected from hydrogen peroxide. For this reason, peroxides replace chlorine even in contact with fresh cut foods, according to Table 8.15.

Peracetic acid replaces chlorine, but its limit of application is below 50 mg L⁻¹ in order to prevent vegetable tissue damages (loss of crispness). On the other hand, the concentration of peracetic acid can increase up to 100 ppm without negative effects on tissues. Therefore, peracetic acid is considered to be a further advance in sanitation of fresh cut food.

Organic acids (e.g., lactic acid), blended with surfactants (e.g., C₁₂-sulfate) and reinforced in acidity (phosphoric acid) are suitable for the primary cleaning of dirty vegetable and tubers. The first cleaning aims at removing soil and biofilm. This stage removes dirt and macro-organisms (e.g., nematodes) and prevents bacteria from spreading. Chloride forces the detachment of nematodes,

Table 8.15 Different methods of cleaning and disinfection.

Fresh-cut food cleaning and disinfection			
Chlorine	70–90 ppm	Room temperature	Cleaning and disinfection
Peracetic acid	20–40 ppm	Room temperature	Disinfection
Percitric acid (H ₂ O ₂ in citric acid)	40–80 ppm	Room temperature	Disinfection
Hydrogen peroxide	100 ppm	Room temperature	Bacteriostaticity
Chlorine dioxide	1–3 ppm	Room temperature	Disinfection
Organic acids (lactic) and food-compatible surfactants	1–5 g/L	Room temperature	Cleaning under bacteriostatic activity.

Table 8.16 CIP advanced technology.

CIP cleaning, chlorine-free advanced technology			
Alkaline (30% NaOH)	2%	Hot and cold	Surfactant-free alkaline cleaning
Alkaline (30% NaOH)	2%	≥60 °C	Defoamed alkaline cleaning. Solution recovered and suitable to be re-used.
Alkaline + H ₂ O ₂ additive	1% > 0.5%	Room temperature	Alkaline oxidizing cleaning. Disinfection according to the hydrogen peroxide percentage
Alkaline + QAC or amphoterics	2%	≥60 °C	Chlorine-free alkaline cleaning and disinfection
Acid	2%	Room temperature	Descaling detergent for periodic maintenance

surfactants help soil removal, organic acids maintain bacteriostaticity, and the whole detergent prevents soil redeposition.

Details of the advanced technologies of sanitation that include a CIP system are given in Table 8.16.

Parts of equipments are sanitized after dismantling, often keeping them soaked until the subsequent production. The dismantled parts are treated as shown in Table 8.17.

Table 8.17 Soak cleaning and disinfection technology.

Soak cleaning and disinfection of dismantled parts			
Neutral/buffered detergent disinfectant	0.5–2%	Room temperature	Manual and soak cleaning and disinfection
Neutral disinfectants (amphoteric/QAC)	0.5–1%	Room temperature	Disinfectant for soak preservation of dismantled part and tools
Neutral eudermic detergent	0.5–2%	Room temperature	Universal manual skin compatible detergent

8.4.9

Mechanical Cleaning of Equipment

Changing from manual to mechanical cleaning of equipment in a CIP process not only improves the sanitation result and productivity but also adds savings in water and energy. OEMs (equipment manufacturers) copied the concept of the dishwashing machine and tunnel pasteurizer to develop one-step cleaning (cleaning in a box) and uninterrupted loading and downloading (cleaning in a tunnel).

The procedure, which utilizes compact spray machines, is as follows:

- pre-wash re-using water of the final rinse
- hot cleaning, recycling the solution of a CIP detergent
- hot final rinse
- disinfection, if needed.

Pressurized water (10–20 bars) and detergent solution are piped to the spray nozzles, which project them at all the sides of the piece in order to remove the contamination by a combination of chemical and mechanical energy. Tunnel machines are preferred when there are large numbers of tools, each tool being cleaned for a few seconds (e.g., cleaning of molds). Discontinuous systems are used if pieces of equipment are bulky and there are fewer (e.g., trolleys). There are innumerable types of equipment and dismantled parts found in food preparation. Some of them are mentioned in Table 8.18.

Products and procedures are decided as a function of the type of contamination. Fats, proteins, and starches blended with inorganic materials precipitate together in denatured, dehydrated, caramelized, and carbonized structures. They need careful selection of detergents and procedures to achieve the best result of cleaning and sanitation (alkaline, acid, and oxidant, often in sequence).

The addition of hydrogen peroxide to the alkaline step facilitates the removal of highly adhesive contaminations. At the same time, adding hydrogen peroxide to the final hot rinse performs disinfection. Table 8.19 shows various detergent systems and the corresponding types of contamination for which they are used.

Table 8.18 Example of tools and dismantled parts.

Industry	Equipment
Meat and fish manufacturing cycle	Trolleys, wagons, box containers, cages, trays,
Processed vegetables	bowls, aluminium and stainless steel molds,
Milk and cheese process	block molds, scales, knives, hooks, bins,
Baking foods and delicatessen	dismantled parts of equipment, crates, cases,
Ready-to-use foods	hooks, plastic molds, PTFE worktables,
Pharmaceutical and sanitary facilities	shelves, pots and pans, baking tins, scale
Large-scale retail trade, organized services	pans ...

Table 8.19 Targeted detergents for equipment cleaning.

Detergent	Contamination
Strong caustic detergents (free NaOH and/or KOH)	Fats, proteins, blood and starch removal from compatible surfaces (stainless steel and plastic)
SMS alkaline detergents (inhibited alkalinity)	Removal of organic contamination from soft metals (aluminium, galvanized and painted surfaces, polycarbonate)
Strong acidic detergents (phosphoric and phosphonitric cleaning)	Removal of mixed organic and inorganic contamination from compatible surfaces (stainless steel and plastic)
SMS and eco-compatible acidic detergents (organic acids)	Removal of mixed organic and inorganic contamination from soft metals. Phosphorus and nitrogen decreasing in sewage
Alkaline detergent disinfectant (amphoteric/QAC)	Soil removal and sanitation with nitrogen derivatives (chlorine-free procedure)
Acidic detergent disinfectant (short-chain fatty acids)	Soil removal and sanitation with organic acids (chlorine-free procedure)
Alkaline chlorinated detergents	Removal of tenacious soil and sanitation by chlorine
Alkaline detergents and hydrogen peroxide	Removal of tenacious soil and sanitation by peroxide

The washing machine needs periodic maintenance in order to remove internal deposits not removed during the cleaning step. This self-cleaning of the empty machine is carried out either by increasing concentration or changing the detergent in favor of stronger one.

The process validation involves a number of basic parameters:

- choice of detergent
- optimization of its concentration
- defining the wash and rinse temperatures
- specifying times spent in the different sections of machine
- setting the automatic control of concentration
- checking carryover, efficiency of the rinse, and water cycle
- checking sprays for homogeneous covering of equipment
- defining products and procedures for periodic maintenance
- checking results of cleaning and sanitation
- personnel training.

Experience confirms that the washing machine frequently does not receive enough attention. It is often covered with scale even when too much detergent is used; spray nozzles are clogged, do not cover tools, or are wrongly located; temperature is different from that displayed. Training enhances awareness, and auditing of control procedures can prevent inaccuracy.

8.5

Winery

Galileo Galilei said: 'Wine is a blend of humor and light' [35]. Good soil well exposed to sun swells the grapes into bunches of humor, catches the rays of light, and transfers fragrance and body to the wine. Later, the complexity of the micro-life (yeasts and bacteria) on the skin of the grapes induces the extraordinary metamorphosis from a fruit to one of the most enjoyable drinks. In terms of detergency requirements, two types of deposits, arising from two different phases of wine production, need to be dealt with:

- Wine making (pressing, fermenting, decanting, storing)
- wine clarification and stabilization (filtration).

8.5.1

Cleaning in the Cellar

Tartrate and dye are the residues of the wine-making phases. The complex group of polyphenols (flavonoids) covers surfaces with violet or yellow colors, while potassium and calcium tartrate crystals grow on surfaces in contact with wine. Examples of deposits from red and white wine are shown in Figure 8.43.

Oxidizing agents rapidly decolorize (destroy) polyphenols [anthocyanins (red color) and flavones (yellow color)]. Hydrogen peroxide in alkaline solutions successfully replaces chlorine, the traditional cheap decolorizing agent. Hydrogen peroxide avoids the undesirable secondary reactions of chlorine such as the formation of halo-derivatives and their off-odor ('medicinal') and cork taste.

Caustic soda solution dissolves potassium tartrate and bi-tartrate, which are the main components of the deposit on the walls of the tank.



Figure 8.43 Deposits from red and white wine.

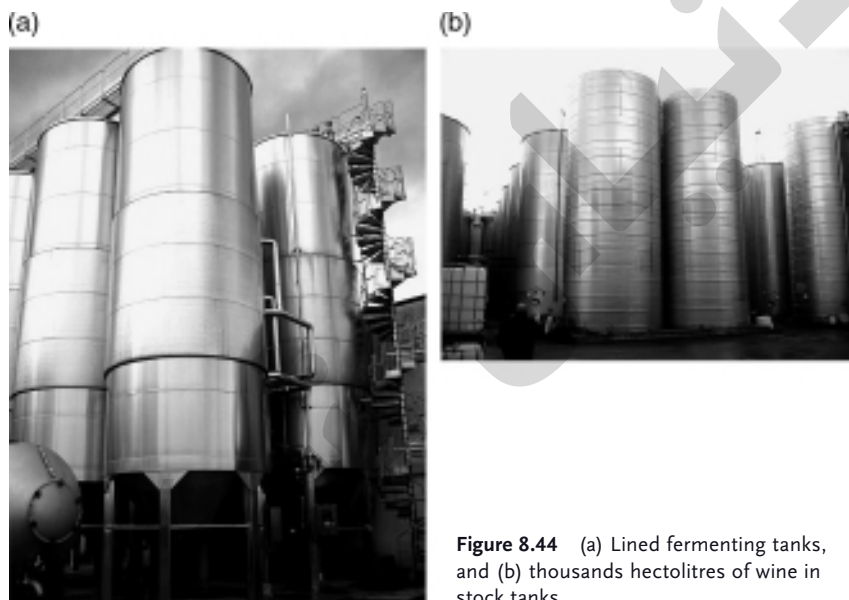


Figure 8.44 (a) Lined fermenting tanks, and (b) thousands hectolitres of wine in stock tanks.

An estimation of the quantity of tartrate in the tank enables the correct amount of caustic soda to be dissolved in water in order to clean the tanks rapidly. The weight of deposit in a given tank can be estimated accurately enough by first estimating its volume by multiplying its area by its thickness, and as its density is approximately 2, its weight is found by doubling this volume. A kilogram of caustic soda will dissolve 4 kg of deposit, so the weight of caustic soda required is a quarter of the weight of deposit.

The caustic soda is rapidly consumed, and the neutral solution is no longer able to dissolve tartrate. A poor result in removing tartrate often indicates an incorrect calculation of the quantity of tartrate actually present on the walls of the tank. Some typical tanks are shown in Figure 8.44.

Even though their surface area is considerable, cleaning tanks does not usually present problems. Alkalinity and oxidizing agents readily accomplish the task, while sequestrants play a subordinate role.

Although potassium tartrate is not a problem in wine processing, calcium tartrate can become a serious problem in bottles. Unlike potassium tartrate, predominant in the cellar and soluble in caustic soda, calcium tartrate (predominant in bottles) is insoluble in alkaline media and soluble in strong acids. Bottle-washers perform alkaline cleaning. Thus, it is crucial to ensure that the wine is stable before filling in order to prevent precipitation of calcium tartrate in the bottles (see Section 1.3.4).

8.5.2

Stabilization of Wine

Stabilization must be achieved during the final stages of the wine-making process before bottling. Wine is a living and unstable system. The final physical form must be such as to maintain the characteristics of the wine for a long time and prevent any modifications with time. Clarity and a clear color free of crystals or any violet coating on the glass should be the first agreeable impressions of a bottle of wine. Removal of the excess of tartrate by cooling, and reducing levels of proteins, colloids, and metals by judicious adsorption on bentonite, casein, gelatin, albumin, and activated carbon are typical procedures adopted to produce a stable wine. The traditional alluvial filter and centrifuge are coupled with dead-end filtration or replaced by electrodialysis and crossflow microfiltration.

The presence of filtering membranes, in particular crossflow filtration, introduces a different concept of cleaning. Dealing with a membrane is rather complex both in terms of cleaning and membrane preservation (see Chapter 12). Detergents should be efficient and keep the claimed shelf life of membrane. For this reason the membrane manufacturers previously approve products and procedures and authorize their application.

Crossflow microfiltration membranes, used to stabilize and preserve wine (bulk sterilization), are usually made up of hollow fibers. Adsorbed carbohydrates (pectin, gums, carrageenans ...), bentonite and colloids need alkaline treatments strengthened with chlorine or hydrogen peroxide (Figure 8.45). While enzymes break down the polymeric structure of the deposit, oxidation comes with micro-



Figure 8.45 Hollow-fiber membrane fouled by an excess of bentonite.

The *Brettanomyces* species produce β -glucosidase enzyme, which cleaves the disaccharide cellobiose to produce glucose molecules. Glucose is used by *Brettanomyces* to grow [36, 40]. Hence, as well as feeding on the sugars of wine, *Brettanomyces* can survive inside wood using cellobiose. Wood protects *Brettanomyces* inside it in spite of cleaning and disinfection. Wine makers are concerned about pollution by *Brettanomyces*. The risk of losing years of work and a reputation is well known, but it is difficult to succeed in disinfecting wood thoroughly and without damage. Several disinfectants seem effective when wine is artificially polluted in the laboratory (hot water, peracetic acid, ozone, dimethyl/diethyl dicarbonate, pimaricine, UV rays, pasteurization, filtration ...) but few of them succeed in sterilizing the spongy structure of wood. Aside from high concentrations of sulfur dioxide gas [>7 g/barrel [40]], potassium permanganate is one of the best chemicals able to provide sterilization in depth without damaging wood. The routine cleaning and disinfection are carried out using a CIP-like process lasting from 3 minutes (high pressure >50 bar) to 10 minutes (low pressure <10 bar) per barrique. Nevertheless, seriously polluted containers need two days of soak to be regenerated. The majority of disinfectants are unacceptable if they are in contact with wood for a long time (Section 8.5.3.1). Soaking in permanganate solution for 48 h is an effective and safe procedure to restore a seriously infected barrique to its clean state. The alternative is to dispose of it and spend the money on a new one.

8.5.3.1 Disinfection of Wood

Wood is a living material. It increases and decreases in volume, exchanges gases with the environment (oxygen), releases components (tannins and resins), has a surface shaped like a sponge, reduces heat transfer, prevents UV penetration, absorbs chemicals, and protects microbes. Disinfectants can modify its ability to age and refine wine and, mainly, have difficulty in performing in depth (beneath surface). From all of this, disinfectants cannot be freely used on wood. They can give rise to wood damage, wine organoleptic modification and microbial persistence.

Typical organoleptic hazards include

- **Cork off-taste:** (chloroanisole formation)
- **Medicine off-taste:** (chlorophenols formation)
- **Fading and brilliance loss:** (chloro-compounds inclusive of chloramines)
- **Oxygenation prevention:** (sulfide residue)
- **Oxidative shock:** (peroxide residue from cellulose peroxidation).

Typical microbial hazards include

- **Acetobacters:** (sour taste)
- ***Brettanomyces* yeast:** (excess of phenolic character, dung and leather off-taste).

In order to understand the principles of disinfection, the wooden vessels are divided into vessels only superficially contaminated and those seriously polluted

(sick in depth). A microbiological analysis and, more frequently, the oenologist's nose decide on the intensity of the microbial contamination. This evaluation is not a mere exercise. It directs the disinfection procedure toward either rapid treatment or a long soak. Rapid treatments can be carried out even with disinfectants not strictly safe on wood. A long soak must be performed with disinfectants that do not affect the integrity of the wood and preserve its effectiveness in maturing wine for a long time. In addition to sulfur dioxide, the proposed disinfectants are summarized in the following list:

- hot water and steam
- hydrogen peroxide and persalts added to caustics
- peracetic and peracetic acids and ozone
- organic acids (sorbic, benzoic, salicylic) and pimaric
- dimethyl and diethyl carbonate
- UV lamp
- potassium permanganate.

Hot Water and Steam Wood is a bad conductor. Heat penetrates in depth with difficulty. Thus, either microbes are not killed in depth or too long a time of contact is required. Cellulose is hydrolyzed, and tannin and resins are extracted under humid heat. Thus, hot water and steam should be used for a short time only. They can be applied on wooden vessels which are not sick in depth.

Hydrogen Peroxide and Persalts Activated by Caustics Wood is sensitive to caustics and oxygen. Caustics (sodium and potassium hydroxides) hydrolyze cellulose, generating caustic gel (chemical rottenness), and this gel remains caustic when it dries, so pH modification is to be expected at the point of contact of wine with wood. Hydrogen peroxide and persalts have to be activated with caustics or temperature to release oxygen, and the active oxygen peroxidizes cellulose (O, OH and COO groups). An oxidative shock may occur at the point of contact of wine with wood. Chemical rottenness and oxidative shock are good enough reasons to reject this treatment.

Peracetic and Percitric Acids and Ozone The released oxygen is extremely reactive as both a disinfectant and an oxidant. Thus, these chemicals are very effective on the wood surface, as both killers of microorganisms and cellulose oxidants. Owing to its rapid action, oxygen does not penetrate wood. Thus, peracetic acid and ozone are excellent surface disinfectants and also effective peroxidants of cellulose. Oxidative shock may occur at the point of contact of wine with wood. Hence, these chemicals can be applied as a brief treatment only.

Organic Acids (Sorbic, Benzoic, Salicylic) and Pimaric The disinfecting activity is affected by the components of the wine (pH and polarized organic soil). Sanitation is not reproducible. Therefore, these chemicals should be rejected on account of their lack of reliability.

Dimethyl and Diethyl Carbonate The biocidal and wood-preserving effect of these compounds are good. However, they hydrolyze to very hazardous by-products such as methanol (a toxic alcohol) and carbamates (suspected carcinogens). Because of these harmful by-products, this treatment should not be used.

UV Lamp UV lamps of wavelength 254 nm, inserted into the vessel for 1.5–3 min, are effective against microorganisms. However, penetration in depth of the UV-rays is negligible. Thus, a UV lamp is good for superficial sanitation and is applicable to wooden vessels that are not sick in. The eyes should be protected and the limited life of the lamp should be borne in mind.

Potassium Permanganate Effective as a biocide, permanganate does not affect wood. It can be kept in contact for a long time so as to have time to penetrate and disinfect in depth. Permanganate does not produce peroxide and does not extract fragrances from wood. Thus, it is the best disinfectant to sanitize sick-in-depth vessels. This is achieved by soaking vessels for 48 h in 0.5–1.0% solution.

Instead of disposing of vessels, they can be restored by the following procedure:

- rinse with water
- clean with a suitable noncaustic detergent (0.5%, usually with a pressurized solution)
- rinse
- soak for 48 hours in 0.5% permanganate (slightly alkaline solution)
- rinse
- fill with wine or preserve the vessel (closed) with sulfur dioxide.

Examples of unchanged parameters of wine matured in wood vessel sanitized with permanganate are listed in Table 8.20.

8.6

Enzymatic Cleaning in Food Detergency

Enzymes typically end in the *ase* suffix, for example, *protease*, *lipase* and *amylase*. They are substrate specific. An enzyme acting on one substrate will not work on another so that, for instance, *protease* or *peptidase* breaks the peptide bonds in proteins and does not work on starch. *Amylase* will break starch down, and *lipase* hydrolyzes fats. There are thousands of known enzymes, each of which performs one specific chemical reaction. They function as organic catalysts and are chemically involved but not chemically changed. Many enzymes function by lowering the activation energy of a reaction. The activation energy is the minimum energy required for a given reaction to occur and varies from one reaction to another. Cofactors are nonprotein substances essential to the enzyme's stability and activity. Ions such as potassium (K^+), calcium (Ca^{2+}), selenium (Se^{2+}), copper (Cu^{2+}), zinc (Zn^{2+}) and iron (Fe^{3+}) are examples of cofactors activating the enzymatic process.

Table 8.20 Test on red wine aged in wooded vessel.**Wine sanitation****Sample: Cabernet Sauvignon Protocol n°1 (reported procedure)**

Test	Unit of measurement	Wine before maturing in vessel	Wine after maturing in vessel (40 days)	Analytical procedure
Sodium	mg/L	8	11	Reg. CEE 2676/90 All. 26 p. 2
Manganese	mg/L	1.12	1.29	POP_107 rev 1 2002
Potassium	mg/L	1297	1188	Reg. CEE 2676/90 All. 27 p. 2
Sulfate (K_2SO_4)	mg/L	400	421	POP_003 rev 3 2003
Phosphate(PO_4) ³⁻	mg/L	451	427	POP_103 rev 3 2003

The nature of an enzyme is proteic, and, even if it is modified, it follows the chemistry of proteins. The enzyme activity is also determined by the shape of its protein. Modification of the shape denatures the enzyme. Therefore:

- **Enzymes are unstable in an aqueous medium.** Storage stability (enzymatic activity) is still a problem though less so than in the past. Nonionic ethoxylated surfactants, calcium salts, and glycols (propylene) enhance stability and contribute to the enzyme's shelf life in liquid detergents. Encapsulation is a further advanced approach pursued by producers. The encapsulated enzymes remain intact when blended into the detergent base and are only released upon dilution in the cleaning application.
- **Enzymes are unstable away from their designated pH, being adapted to operate at this specific pH.** Strong caustics and acids suppress their activity. The pH range 5–10 is ideal to maintain an activity sufficiently long to promote cleaning. Therefore, enzymes are used either in mild detergents or together with a buffer suitable to establish and maintain the correct pH.
- **Enzymes are unstable at high temperatures.** Rise in temperature will speed up the rate of enzyme-mediated reactions, but only to a limited extent. Heating denatures their structure too much and has a harmful effect on their activity. A temperature within the range 30–50°C is ideally suited to promoting rapid cleaning.

Also known as biocatalysts, enzymes perform applications as diverse as detergents, converting starch to sweeteners, producing fuel ethanol, stonewashing

blue jeans, enhancing the nutritional value of animal feeds, removing trans fats from food [41]. The investigation of enzymes as cleaning agents dates from the early 1960s, when enzymes from bacteria became available. Enzymes are now well accepted as ingredients of powdered and liquid detergents for laundry applications and for specific applications in the food industry, such as membrane cleaners in crossflow filtration (e.g., dairy). The desire to reduce environmental impact and the development of eco-compatible methods of detergency led the way to broadening the scope of enzymatic application, even toward the replacement of harsh conventional procedures (e.g., the use of caustic and corrosive solutions) with milder ones in CIP. However, time and cost-in-use constraints reduce their attractiveness in comparison with the traditional strong detergents.

Safety is one of the requisites in handling enzymes, as they are hazardous by inhalation and contact. They can cause

- **Allergy** Like many other proteins, enzymes can act as allergens. The formation of specific antibodies is known as sensitization. Thus, exposure to enzymes leads to respiratory symptoms like asthma and sinus congestion.
- **Irritation** Proteolytic enzymes are capable of causing irritation of eyes, mucous membranes, and skin.

Detergency in the food industry makes use of three groups of enzymes:

8.6.1

Protease

A protease performs proteolysis by breaking the peptide bonds that link the amino acids together in the polypeptide chain. Proteases occur naturally in all organisms and are involved in innumerable physiological reactions. In terms of detergency, splitting up big molecules into small pieces makes cleaning easier. Big molecules located inside small pores of sensitive surfaces (e.g., filtering systems) are difficult to remove. For this reason, cleaning of the membrane used in crossflow filtration of milk and its fractionated components is the main user of proteases. The concentration of proteins and fats from milk by ultrafiltration (UF) and reverse osmosis (RO) and also the separation and concentration of whey (by NF and RO respectively) all cause fouling of membranes with a proteic deposit, the removal of which by heavy detergents is not possible because polyamide membranes have pH limitations and do not tolerate oxidizing agents. However, enzymatic treatment (recycling or soaking process) recovers functionality (ratio of permeate to retentate) without damaging the filtering polymeric layer (see Chapter 12).

Protease is included in formulations of liquid products where water is partially replaced with glycols and surfactants. The enzyme performs cleaning with the help of an ancillary additive (buffer) which maintains the pH at the optimum value for achieving sequestration, solubilization, and antiredeposition.

8.6.2

Lipase

Lipase is a water-soluble enzyme which catalyzes the hydrolysis of ester bonds of lipidic substrates. Acting on the ester group, lipases are a subclass of esterases. Most lipases act specifically at the 1,2,3 glycerol positions, degrading lipids by converting the triglyceride substrate from fats and oils to simpler glycerides, glycerol, and free fatty acids. A multitude of glycerides (triglycerides, phosphoglycerides ...) and several different lipases exist in nature.

Lipases from fungi and bacteria find a role in food preparation (yogurt, cheese fermentation ...), in converting vegetable oil into fuel, and in freeing surfaces from fats and oils in a laundry. The same concept of the use of protease in detergency is applicable to lipase when fats and vegetable oils are to be removed.

8.6.3

Amylase

Amylases break down starch into shorter chains, ultimately yielding glucose molecules. They act on glycosidic bonds, in particular, α -1,4-glycosidic bonds. The group comprises α -, β -, and γ -amylases, each of which breaks down long chains of carbohydrates to form dextrin, maltose, glucose, and other simple sugars. It has a role in bread making, since the addition of amylase enzyme to dough makes the process faster. Detergency exploits amylase to dissolve starches from fabrics and to help in the removal of pectin, gums, carrageenan, and other polysaccharides from membrane filtration in vegetable and fruit processes. Cellulase performs on cellulosic deposits (fibers) in an acidic medium (pH 4–5).

8.7

Chemicals for Cleaning Tenacious Contamination

This section focuses attention on chemicals that provide the best in CIP result in the presence of tenacious contamination. Processed foods leave various residues that differ according to the origin of the food. Some components are modified by precipitation, denaturing, polymerization, coagulation, and caramelization. They are sometimes found combined together, sometimes blended with insoluble clay and trapped inside pectins and gums, but usually compacted and dehydrated by heat. The cleaning of such contamination would require a long time of contact with caustic detergents followed by acidic ones, high concentrations, and high temperatures. There is often a need for repeating cleaning steps. However, the removal of such contamination is simplified when the correct chemicals are used for each type of contamination. Tenacious types of contamination include

- **Calcium phosphate**

Precipitation occurs every time milk or milk derivatives are included in the processed food and undergo heat exchange. EDTA and nitric acid solubilize calcium phosphate. The presence of calcium phosphate requires either strong chemicals (caustic soda and nitric acid) or caustic soda with strong sequestration chiefly based on EDTA (one-step cleaners). The latter do not require the acidic step (nitric acid), which is only used in periodic maintenance. If EDTA is not permitted, other stoichiometric sequestrants can be used if they are assisted by an additive based on hydrogen peroxide.

- **Calcium soap**

Precipitation occurs every time meat and milk are processed or included in the processed food.. The presence of calcium soaps (≥ 12 carbons) means that strong sequestration, mainly based on EDTA, will be necessary. Acids are less effective because of generation of a hydrophobic system. Soap-based lubricants give the same problem when diluted in hard water. If EDTA is not permitted, other stoichiometric sequestrants can be used if they are assisted by additive based on hydrogen peroxide.

- **Calcium oxalate**

Precipitation occurs every time trees (tannin extraction), vegetables, seeds and fruit are processed or included in the processed food and beverage. Beer, tea, tomato processing, and vegetable blanching lead to oxalate precipitation. High alkalinity, hydrogen peroxide, EDTA, and nitric acid succeed in re-dissolving it.

- **Eggs pasteurization**

Heat coagulates egg contamination and causes it to adhere. Thermally treated egg requires treatment with alkalinity and hydrogen peroxide.

- **Gums, pectins, carrageenans, and xanthans**

Fruit processing (e.g., fruit juices and wine) leads to contamination rich in polysaccharides. Crossflow filtration also suffers from this deposit. Cleaning requires alkalinity and hydrogen peroxide or chlorinated detergents.

- **Potassium tartrate**

This is the typical residue from wine and is deposited on tank walls during the manufacture and stabilization of the wine. Potassium (bi)tartrate is soluble in caustic soda in the correct ratio (4 of tartrate to 1 of caustic), so the quantity of tartrate in the vessels must be correctly calculated to establish the correct concentration of the alkaline detergent.

- **Calcium tartrate**

This is the typical deposit found in bottled wine. Precipitation occurs if the wine is unstable. As calcium tartrate is insoluble in caustic detergent, an alkaline bottlewasher will not succeed in cleaning the recovered bottle.

Therefore, careful stabilization in cellar is mandatory to prevent precipitation in the bottles from occurring.

- **Preparation of sauces**

The cooking of sauces leaves a contamination whose cleanability depends on the type of ingredients. Cheese, egg, and starch generate a deposit which becomes stressed and adherent on heating. High alkalinity accompanied by hydrogen peroxide usually accomplishes cleaning.

- **Pasteurization of cream**

The addition of hydrogen peroxide to highly sequestered caustic solution facilitates the removal of the deposits formed.

- **Pasteurization of caramel**

The key to success in the cleaning of any deposits formed in this process is the addition of hydrogen peroxide to the caustic solution used.

As will be apparent from the above discussion, the key to a rapid and thorough cleaning operation is often the use of an effective oxidant. Chlorine itself is a good oxidant for cleaning, but hydrogen peroxide has to be preferred because of its efficacy and absence of negative effects on food (off-taste), plant (corrosion) and environment (formation of chlorinated derivatives).

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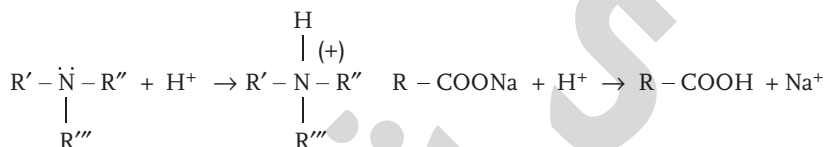
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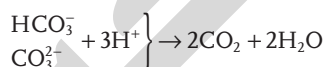
9

Acidic Cleaning

An acidic medium transforms organic soil into a hydrophobic system. Soluble soaps, for instance, are converted into insoluble fatty acids, and the protonation of organic nitrogen strengthens the cationic charge. According to the zeta potential, as the hydrophobicity and cationic charge increase, more matter is adsorbed onto the surface and its desorption becomes more difficult.



Generally speaking, cationic charge and hydrophobicity increase the attractive force. This conflicts with detergency. Thus, the acidic medium is not an ideal system for cleaning. However, acids have useful properties. First of all, the acidic pH makes carbonate and bicarbonate thermodynamically unstable by moving the equilibrium to carbon dioxide, a gas. When this leaves the system, these troublesome anions are removed for good.



Its acidity and oxidizing properties make nitric acid able to re-solubilize calcium phosphate. The peptizing ability of phosphoric acid makes it very effective in removing proteins. And although an acidic medium transforms the organic soil into a hydrophobic system, a shrewd choice of wetting agents (surfactants) to use in conjunction with the acids counteracts the hydrophobicity. Surfactants possess an HLB (hydrophilic-lipophilic balance, see Chapter 5), which allows them to be adsorbed on both hydrophilic and hydrophobic materials. They 'wrap up' the attractive force of the contamination, and the hydrophobic soil becomes more hydrophilic and therefore more susceptible to being rapidly removed.

According to the 'roll-up' mechanism [1], wettability, and contact angle [2], the cleaning of oily contamination is accomplished through surface-active molecules being adsorbed and displacing oil in micro-spherical form, which is the state of minimum energy (Figure 9.1). The modified soil does not redeposit even if it



Figure 9.1 Roll-up theory for treatment of oily contamination.

comes into contact with the surface again. Surfactants modify this same surface, forming a barrier which prevents soil redeposition [3]. Thus, surfactants play a fundamental role in allowing acids to perform as cleaners.

9.1

Infinite Dilution

When cleaning is complete, rinsing concludes operations. Rinsing means diluting the cleaning solution to infinity so as to have water at the end. The acid ions move toward neutrality, increasingly neutralized by the metals of the hardness until substoichiometry is reached. Depending on their solubility product, the formed salts could precipitate and form scale on the surface. This phenomenon is a result of rinsing with hard water. At infinite dilution, the threshold ability of sequestrants is at its maximum, so that the presence of threshold agents in acidic detergents prevents possible negative effects arising at the rinse stage. However, nitric and hydrochloric acids form soluble salts and do not need sequestrants. Carbonate and bicarbonate are thermodynamically unstable and do not precipitate in acidic medium. Conversely, oxalic and phosphoric anions ($\text{C}_2\text{O}_4^{2-}$ and PO_4^{3-}) behave as precipitants because of their negligible solubility when neutralized by polyvalent cations (see Section 1.1.4.2). Thus, when an acidic detergent-descaler is based on phosphoric acid or includes oxalic acid, it is recommended that the formulation should also include a threshold sequestrant. Phosphonates are customarily selected because of their effectiveness in preventing the precipitation of calcium phosphate, their stability in an acidic medium, and their being corrosion inhibitors.

9.2

Sequestrants

HEDP and PBTC are typical examples of threshold sequestrants suitable for preventing deposits at neutrality. Stoichiometric sequestrants are useless as they soon arrive at substoichiometry because of the water hardness and precipitate as scale. EDTA is furthermore unstable at acidic pH and crystallizes even in neat detergent.

Sequestrants perform various roles in acidic cleaning. Besides controlling hardness, they are useful as corrosion inhibitors. Several of them (phosphonates and

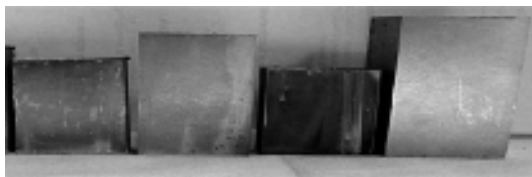


Figure 9.2 Inhibiting activity on aluminum in phosphoric acid solutions. Conditions: 50°C and 72 h soak. Phosphoric acid 2%, +(20h), +2 g L⁻¹ HEMP (72h), +2 g L⁻¹ ATMP.

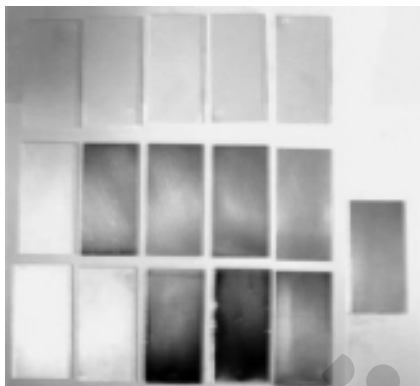


Figure 9.3 Coupons clearer than the blank means an attack on Al and complexation. Coupons darker than the blank means an attack on Al with Fe-Mn oxides deposition.

polyphosphates) are claimed to behave as cathodic inhibitors. However, nitric acid does not always need inhibitors because it passivates and protects stainless steel. On the other hand, phosphoric acid corrodes aluminium, forming a dark deposit (iron and manganese oxides impurity) which covers the aluminium surface. The deposit is unstable and can be transferred to the processed food. Hexametaphosphate (HEMP) and ATMP show specific inhibiting activity on aluminium in phosphoric acid solutions, as shown in Figure 9.2.

When aluminium is soaked in phosphoric acid, the corrosion reaction starts immediately. The hydrogen release slows down within a few minutes in those solutions containing hexametaphosphate or ATMP and the aluminium darkening increases with time except in the sequestered solutions. However, while ATMP keeps aluminium permanently protected, 2 g L⁻¹ of hexametaphosphate ceases to be an inhibitor after roughly 40h of soaking. This is explained by hydrolysis of the polyphosphate [4]. Hexametaphosphate proves to be an effective inhibitor only in its polymeric form (when it performs as a sequestrant). When it is hydrolyzed to monomeric orthophosphate, it does not protect the aluminium any longer. ATMP is stable and behaves as a weak corrosion inhibitor. HEMP performs better than ATMP, but only for a relatively short period of time. Hence, the choice must be carefully assessed as a function of the application, as shown in the Figure 9.3.

9.3

Cleaning of Molds

Acidic cleaners are regularly used to wash molds for cheese and cooked ham, some of which are shown in Figure 9.4.

They are cleaned either in a tunnel machine or by soaking in an air bubbling tank. A significant percentage of molds are made of aluminium, and silicate can be used to inhibit corrosion by alkaline detergents. An acidic pickling sometimes follows a long cleaning operation in alkaline soak in order to remove agglomerates of aluminium hydroxide formed, even in the presence of silicate. This is typical of aluminium molds for cooked ham after repeated cooking cycles. EDTA and tripolyphosphate in alkaline detergents synergize the buffered alkalinity in loosening and removing the baked-on contamination (Figure 9.5).

Phosphoric acid-based detergents are mainly applied in soak tanks where the mechanical force to detach the contamination is supplied by bubbling air. The contamination is sometimes so resistant as to need several hours to soften it and clean it off. Rather than sequestrants, wetting surfactants can help in achieving a successful clean.

Plastic and stainless steel molds can be washed with blends of phosphoric and nitric acids. There is a lower limit for phosphoric acid (roughly 10%) below which cleaning is unlikely to be achieved. The cleaning of cheese molds with these acids



Figure 9.4 Cheese and ham molds.

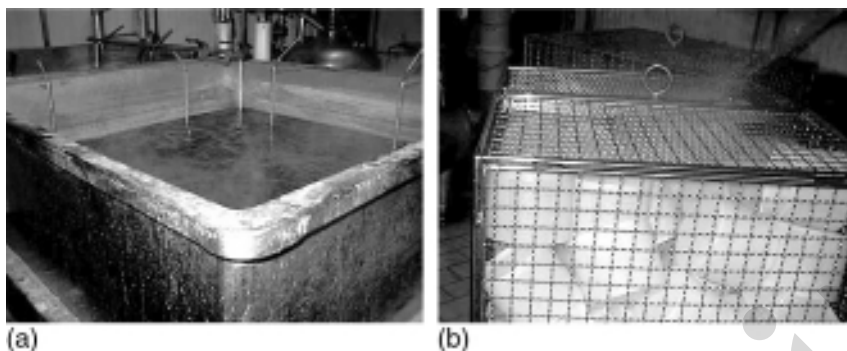


Figure 9.5 (a) Soak tank and (b) cheese molds cage.

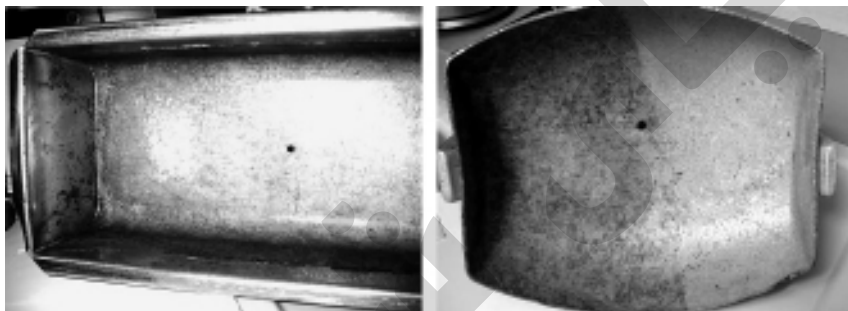


Figure 9.6 Aluminium and stainless steel molds.

strictly depends on the ability of phosphoric acid to peptize and detach caseinic deposits from the surface. In tunnel cleaning, surfactants and soft contamination enable phosphoric acid-free detergents to perform.

The type of metal is of great importance in achieving a satisfactory cleaning. Evolution of gas from the aluminium surface facilitates the soil removal. Solutions of phosphoric acid slightly attack aluminium, and hydrogen gas is released. Unlike aluminium, stainless steel molds remain dirty when phosphoric acid is applied (no attack and gas release). The Figure 9.6 prove the different result after 2 h of soaking at 50°C in 10% solution of a phosphoric based detergent.

The influence of the metal is confirmed when alkaline detergents inhibited with silicate are used for cleaning (no gas release). However, if hydrogen peroxide is added to the alkaline solution, the cleaning is rapidly accomplished even on a stainless steel mold (oxygen gas release) as Figure 9.7 shows.

Thus, the mechanical force of gas release is a basic requirement for achieving a thorough cleaning by the soaking procedure.

Dry contamination needs a long soak to achieve rehydration to enable chemicals to clean. In this way, cleaning in a tunnel machine, in which only a few

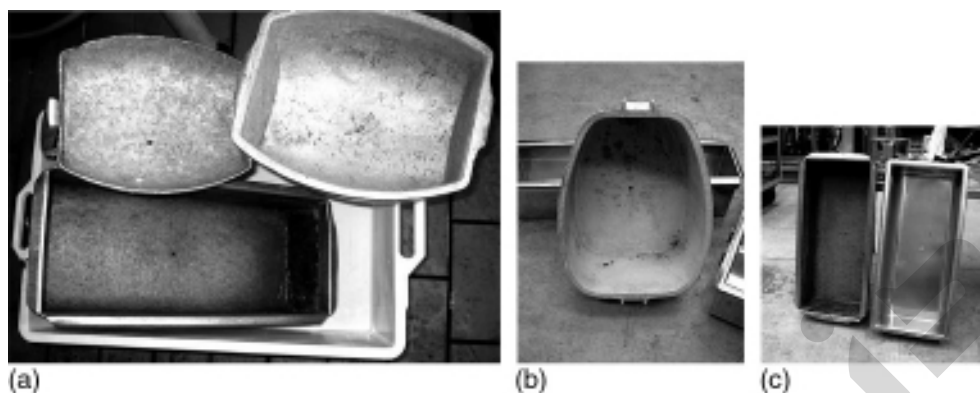


Figure 9.7 (a) Soiled molds and molds treated with alkaline cleaning solution without (b) and with (c) 0.3% hydrogen peroxide added to the solution.

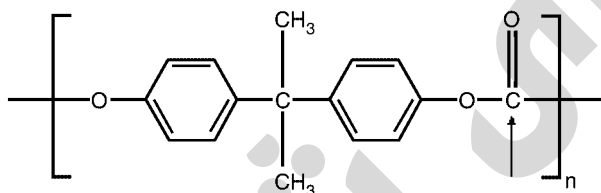


Figure 9.8 The polycarbonate structure is the polymerized ester of 2,2-bis-(4-hydroxyphenyl)-propane (Bisphenol A) with carbonic acid.

minutes of contact are available, is possible when fresh or re-hydrated contaminations are washed.

Soil condition (fresh or dry) and type of molds (aluminium, stainless steel and plastic) are parameters of reference for the selection of suitable detergents and procedures for cleaning.

9.4

Cleaning of Chocolate Molds

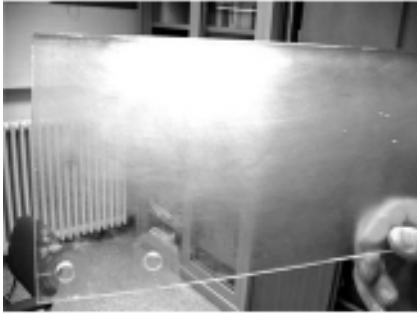
Molds for shaping chocolate are usually manufactured of polycarbonate material, the chemical structure of which is shown in Figure 9.8.

Polycarbonate (PC) is a plastic sensitive to chemicals and temperature. Contact with unsuitable chemicals causes two types of severe damage to polycarbonate, namely hazing and stress cracking. This can be seen in Figure 9.9.

Stress cracking is produced by two concurrent events:

- contact with detergents able to de-structure the polymer (chemical attack)
- mechanical force (pressure or tension) acting on the plastic (physical attack).

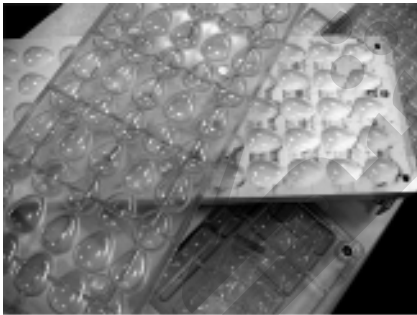
Figure 9.9 (a) Hazing and (b) stress cracking.



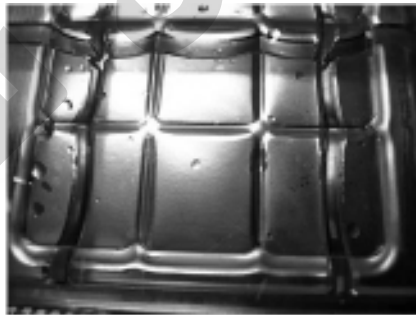
(a)



(b)



(a)



(b)

Figure 9.10 Chocolate molds (a) before and (b) after cleaning. Drops of water are visible after the rinse.

In the absence of mechanical force, unsuitable detergents and temperature generate haze. Nonionic surfactants, caustics, and chlorine are the main agents responsible for damage. They attack the ester groups, break down the polymeric structure, and shorten the polymer shelf life.

PC molds suffer damage after rinsing as well as by direct contact with cleaning chemicals. The hydrophobic surface tends to form drops inside which traces of impurities concentrate, including detergent traces, and these locally damage the polycarbonate when they dry. The damaged area leaves a white stain on the molded chocolate, leading to rejection of the chocolate. Figure 9.10 shows what happens.

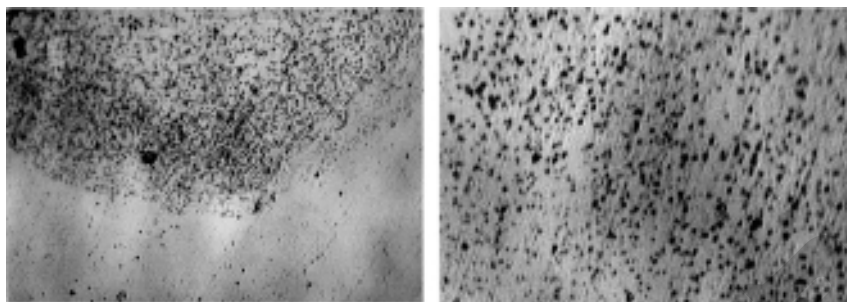


Figure 9.11 Spot with corrosion holes on polycarbonate surface (photomicrograph).

A photomicrograph of the dried drops reveals many holes due to corrosion (haze) (Figure 9.11). This localized haze is responsible for the white stains.

The application of mild detergents, suitable surfactants during rinsing, and gentle procedures (short time of contact at temperatures below 65°C) ensure molds with a shiny appearance and long life.

9.5

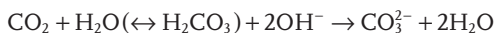
Acidic Cleaning in a Brewery

A total or partial carbon dioxide atmosphere (fermentation and bright beer tanks) means that breweries are obliged to make intensive use of acidic detergency.

When dissolved in water, carbon dioxide is in equilibrium with the corresponding acid:



In water, a ternary equilibrium between environmental carbon dioxide (gas) and carbon dioxide/carbonic acid (solution in the liquid) is established as a function of temperature and pressure. As tanks contain a carbon dioxide atmosphere even during cleaning, the use of alkaline detergents would make tanks implode because of the change state of the CO_2 gas to sodium carbonate solution:



On the other hand, displacement of the CO_2 with air would make the process more expensive, and the beer would undergo oxidative shock. Thus, the policy of maintaining the CO_2 environment during cleaning is driven by economic considerations (cost of raw material and time saving) as well as better quality of beer. Acidic cleaning satisfies these requirements.

In practice, while the cleaning of the beer residue is easy in bright beer tanks (BBT), the cleaning of the fermenting beer ring is extremely difficult because of proteins, hop resins, polyphenols, calcium, oxalate, and polysaccharide

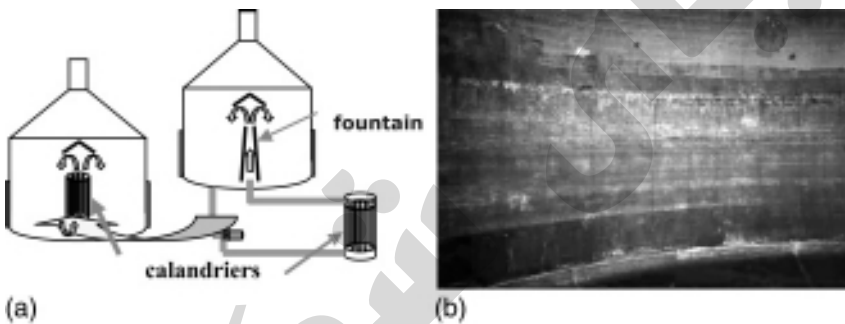
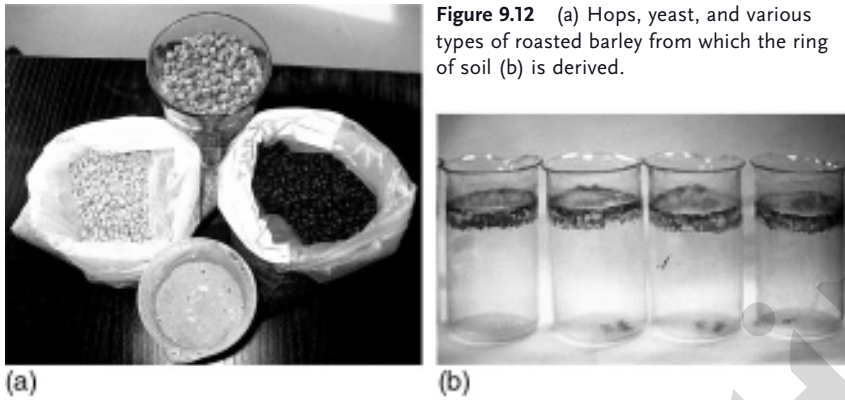


Figure 9.13 (a) Schematic diagram of kettles and (b) their soil [Courtesy of JohnsonDiversey from 'Brewing: foundation and advanced course' Brew Training, JohnsonDiversey Training Department, Italy (Jan. 2003)].

linked and polymerized in the course of the wort fermentation [5]. The Figure 9.12 shows dirt rings from wort fermentation in the laboratory.

In terms of detergency, brewing is divided into three zones according to how difficult they are to clean: kettle, fermenting, and BBTs. Kettle and fermenting tanks need caustic cleaning reinforced with hydrogen peroxide because of highly resistant contamination (Figure 9.13). The acidic step alone does not give a thorough cleaning.

Conversely, soil in BBTs is sufficiently light to be removed with an acidic detergent. The type of acid (e.g., phospho-nitric), sequestrants behaving also as corrosion inhibitors (e.g., ATMP and PBTC), a mixture of surfactants to improve cleaning (e.g., fatty alcohol 6EO), and defoamers effective at low temperatures (e.g., condensed PO) are carefully selected in order to enhance the poor effectiveness of acids on the organic contamination.

9.5.1

Acids

Phosphoric acid gives the best detergency. Glycolic, citric, and formic acids complete its activity. Organic acids also constitute the basis for ecological detergents (N and P free). Since organic acids do not give sufficient conductivity, sulfuric/sulfamic acid can be added to make up for this. Sulfuric acid shows slight detergency and, furthermore, exhibits aggressiveness toward metals and coated surfaces as shown in Figure 9.14.

Sulfuric acid has no cleaning activity. However, it is used as a cheap carrier for bromoacetic acid, a disinfectant still in use in spite of being harmful to health and the environment.

Acidic detergents with disinfecting properties can be used for primary cleaning or can follow alkaline cleaning to complete the process. Short C_7 – C_{10} fatty acids, octenylsuccinic, salicylic, and peracetic acids, and polybiguanide in phosphoric and nitric acids combine detergency and disinfection in one step.

9.5.2

Sequestrants

Sequestrants prevent scale precipitation from water hardness and beer, promote re-solubilization of salts (calcium oxalate), and add corrosion inhibition on aluminium surfaces. In particular, the ATMP and PBTC anticorrosion property has been described in Section 3.4.2.3.

Acidic detergents benefit from threshold sequestrants. Thresholds are reinforced with EDTA, NTA, IDS, MGDA and GLDA in alkaline cleaning. EDTA proves to be the best sequesterant for the resolubilization of calcium oxalate in alkaline detergents.

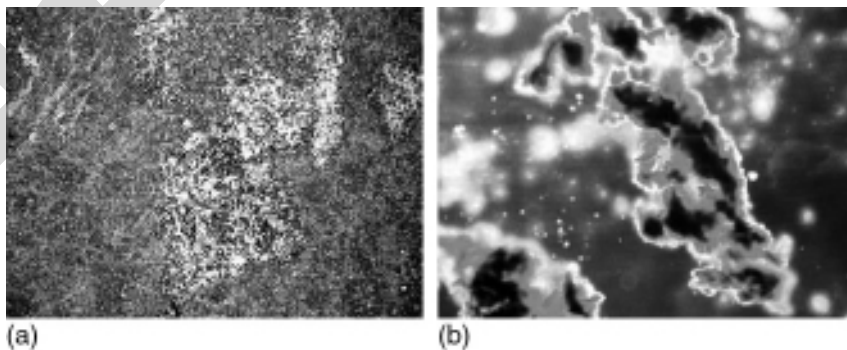


Figure 9.14 (a) Munkadur coating damaged by intensive use of sulfuric acid and (b) photomicrograph of the damaged coating.

9.5.3

Surfactants

Surfactants play an important role both as detergents and defoamers. As acids have difficulty in cleaning organic contamination, wetting and cleaning surfactants assist them (e.g., linear fatty alcohols with low ethoxylation ~6EO).

Highly foaming proteins and resins at low temperatures (<10 °C) require defoamers effective in depressing foam in a very cold environment (e.g., linear fatty alcohols ~3EO, EO-PO, and condensed PO).

Particular care is given to the choice of thoroughly rinsable surfactants. The final quality of a beer also depends on the retention of its foam. Foam is very sensitive to even traces of surfactant, which can quickly depress it.

Sanitizing agents added to the acid (e.g., short-chain fatty acids, octenylsuccinic acid, fatty alcohol monoethoxycarboxylate, bromoacetic, glycolic and salicylic acids, peracetic acid, and polybiguanide) perform cleaning with disinfection in a carbon dioxide atmosphere [6] using the following procedure:

- one single step on non-stressed contamination (e.g., BBT)
- a terminal step to provide the whole process of cleaning with disinfection.

Summing up:

- The key to success in one-step acidic cleaning is the use of blends of surfactants in phosphoric and nitric acid.
- Disinfection carried out in one-step acidic detergents is a further benefit (saving time and improving productivity).
- Resistant contamination, such as deposits in kettles and fermenting tanks, cannot be washed off with an acidic cleaning. They need concentrated caustic cleaners boosted with hydrogen peroxide and strong sequestrants, but removal of CO₂ is necessary.
- One-step descaling and disinfecting can follow alkaline cleaning

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10

Open Aqueous Systems Exchanging Heat

Tunnel pasteurizers for bottled and canned beverages and also cooling towers are items of equipment in which detergency and microbiology problems arise because heat is exchanged in open aqueous systems. Recycled warm and hot water, evaporation, and rather open plants make the process vulnerable in terms of both limestone precipitation and microbial growth. They are neutral systems where the increase in salinity places demands on the dispersing and suspending properties of the threshold sequestration, while the microbial growth demands a careful use of biocides. Corrosion, *Pseudomonas*, and algal growth involve both the plant and the containers passing through it. Aggressive chemicals cause paint on unprotected cans and caps to fade. Cans are involved in flash rusting (mild steel) and dome staining (aluminium). Sequestration, corrosion inhibition, pH, and microbial control constitute the main means of treating the running plants.

10.1

Tunnel Pasteurizers

The pasteurization of beverages in bottle and cans (beer, wine, ciders, fruit juices, soft drinks ...) is a relatively mild heat treatment carried out to extend shelf life by means of gradual heatings and coolings. Heating and cooling are performed by spraying water as the containers pass through the pasteurizer (Figure 10.1).

The goals of pasteurization are the inactivation of enzymes such as pectinesterase and polygalacturonase (fruit juices and vegetables) and the destruction of microorganisms such as fungi, *Lactobacillus* species, wild yeasts, and residual *Saccharomyces* species, nonsporigen bacteria, and molds (beer, wine, soft drinks). The inactivation is achieved by heating the beverage in its package at roughly 60°C for a predetermined time. Temperature modifies the equilibrium of the water salinity. Deposition and scale, biofouling, corrosion, and damage to containers require sequestration and sanitation treatments. Containers pass through sections where water at different temperatures causes heating and cooling to maintain a gradient moving from one section to its equivalent in temperature, as schematically shown in Figure 10.2.

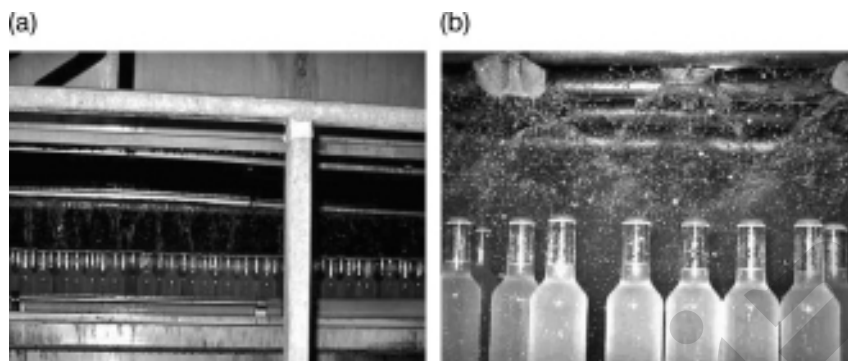


Figure 10.1 (a) Tunnel pasteurizer for soft drinks and (b) inner water spray.

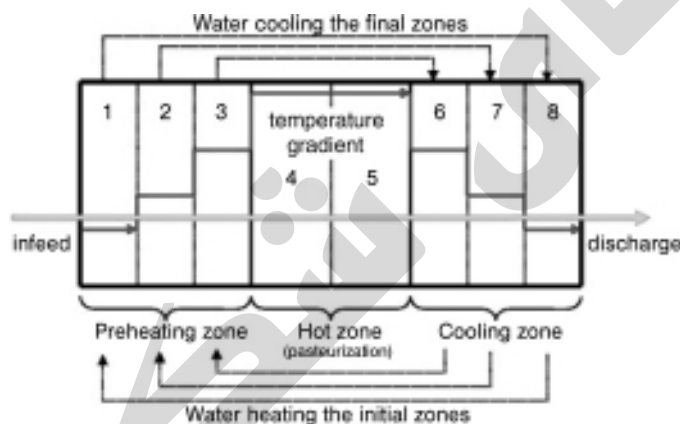


Figure 10.2 Sectors and temperature gradient in tunnel pasteurizers.

Pasteurizers fall into three main categories depending on their water consumption:

- **nonregenerative:** Each zone provides heating and cooling. Wastage of water and heating energy are considerable.
- **regenerative:** Hot and cold water are recycled to heat and cool equivalent zones of the pasteurizer. The water of the initial cold zones cools the hot ones after the pasteurization section. The hot water after the pasteurization is recycled into the initial cold sections to transfer heat ($1 \leftrightarrow 8$, $2 \leftrightarrow 7$, $3 \leftrightarrow 6$). This pasteurization cycle saves water and heating energy. Heat and water are lost only by maintaining a constant gradient in each section during the course of accidental long stoppages.

- **total regenerative:** The regenerative pasteurizer coupled to a cooling tower forms the total regenerative system. Water from the pasteurizer is cooled as it passes through the tower and is re-used. A small loss of water still occurs by evaporation.

10.1.1

Deposition and Scale

Water hardness, high temperature, and breakage of bottles and cans give rise to deposition and scale. Scale will be generally significant in hot zones, and deposition (biofilm) in pre-heating and cooling zones. Both have a number of effects on the pasteurizer:

- loss of indirect heat transfer
- increase in energy cost (friction, heat transfer)
- blockage of nozzles, screens, and valves
- poor container appearance (blooming and spotting on packaging)
- under-deposit corrosion
- high bottle breakage.

An excessive amount of scale in a tunnel pasteurizer is shown in Figure 10.3.

Table 10.1 compares the energy cost as a function of the scale thickness.

The main causes of deposition and scale are summarized below:

- hardness salts (calcium and magnesium salts)
- corrosion by-products (iron and aluminum oxides)
- temperature and pH
- biofouling (microorganisms and organic materials).

Langelier and Riznar indexes help to forecast the tendency of the water to generate scale or corrosion, as described in Section 1.1.1.6. As inorganic material forms scale and organic material causes fouling, different treatments are required to prevent trouble.



Figure 10.3 Scale in a tunnel pasteurizer.

Table 10.1 Energy increases as a function of the scale thickness.

Scale (mm)	Heat transfer depletion (%)	Increase in energy cost (%)
1	7	2
2	13	4
3	19	6
4	23	8

10.1.2

Microbiology

The ideal environment for growth of bacteria and biofouling is at temperatures within the range 10–45 °C (roughly mesophiles). The rate of growth is significantly reduced from 45 to 55 °C and does not usually occur above 55 °C. Microorganisms enter the pasteurizer from make-up, air, the conveyor feeding the pasteurizer, and the product being pasteurized (if the packaging breaks). The aerobic capsulated bacteria such as *Aerobacter*, *Flavobacterium*, and *Pseudomonas* are generally associated with slime problems (polysaccharides and polypeptides). Anaerobic sulfate-reducing bacteria, such as *Desulfovibrio desulfuricans*, are capable of reducing sulfates to hydrogen sulfide. Deposition of black iron sulfide and the offensive odor of hydrogen sulfide (H₂S) indicate the presence of these species. Filamentous molds (e.g., *Mucor* and *Fusarium*) and yeasts (e.g., *Torula* and *Saccharomyces*) are the organisms producing filaments that bind the slime formed by bacteria, resulting in a more bulky slime mass.

The growth of microorganisms has several effects on the pasteurizer:

- blockage of nozzles and flooding of the screen box
- accelerated corrosion
- offensive odors
- poor container appearance
- frequent maintenance.

Large numbers of bottle breakages either on the conveyor or in the pasteurizer significantly contribute to the formation of biofilm as the nutrient levels increase and high levels of other microorganisms enter the system. An example of biofilm growth can be seen in Figure 10.4.

10.1.3

Corrosion

Corrosion is an electrochemical process arising from a difference in electrical potential between two metals or different parts of a single metal, or direct attack on the metal by chemicals. Typical reactions of bivalent metals are given in Figure 10.5 [1].

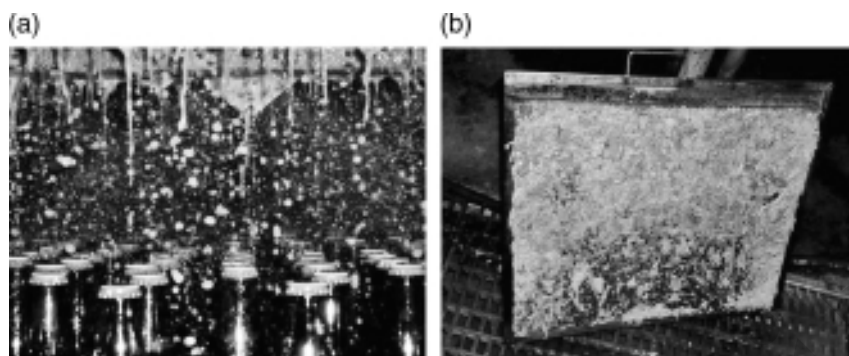


Figure 10.4 (a) Highly polluted water and (b) biofilm growth on the pasteurizer filter.

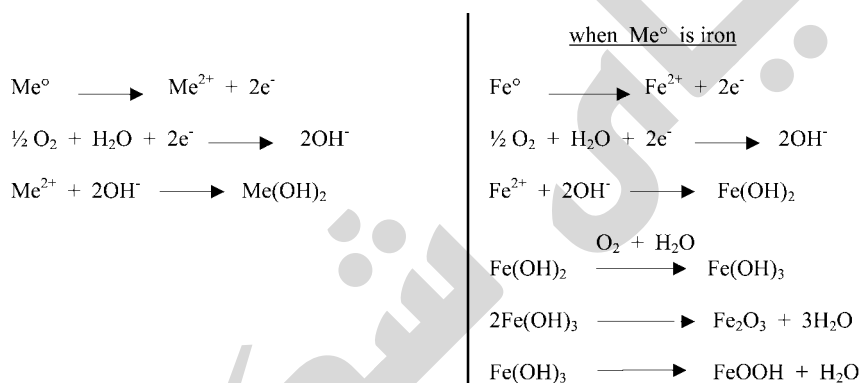


Figure 10.5 Reactions involved in the corrosion process.

Different types of corrosion produce iron oxides at the end of the process:

- uniform attack (general corrosion)
- pitting corrosion (presence of halogens)
- under-deposit corrosion (scale and biomass can lead to craters and pitting)
- galvanic corrosion (different metals in contact).

Galvanic corrosion is easily prevented by using the correct procedures when joining metals. Uniform corrosion is less dangerous. Under-deposit corrosion is the most dangerous as it can affect the integrity of the plant.

Treatment of the pasteurizer and cooling tower with corrosion inhibitors solves the immediate problem but does not attack its root cause. Since legal restrictions apply to most of the inhibitors (e.g., nitrates, chromium, zinc, phosphates ...) it is crucial to prevent corrosion by avoiding, for instance, halogen biocides (chlorine, iodine, bromine, halonitripropionamide). Surfaces must be kept clean with suitable sequestrants and environmentally friendly biocides [2].

As well as pasteurizers, steel on crowns caps and cans may undergo flash rusting when parts of them crimped by friction, are exposed to hot temperature, as shown in Figure 10.6.

Several factors influence corrosion:

- **dissolved gas:** Oxygen sustains and accelerates the corrosion reaction. Carbon dioxide attacks the metal surface as acid.
- **temperature:** The reaction rate speeds up with rise in temperature. For this reason, the hot zones are the most corrosive areas of the pasteurizer.
- **pH:** Iron and stainless steel benefit from alkaline conditions. As the pH increases, corrosion decreases. Unfortunately, aluminium cans cannot be exposed to a pH above 7.8. In order to prevent staining of the pull-tab and dome, it is mandatory to run below pH 7.5.
- **dissolved solids:** Chloride and sulfate speed up corrosion. Chloride causes pitting, and bacteria metabolize sulfate and give corrosive hydrogen sulfide.
- **microbial growth:** Reducing bacteria lead to hydrogen sulfide which causes pitting when it is evolved under biomass and limestone. Offensive odors are produced by microbes.
- **application of wrong chemicals:** Noninhibited hydrochloric, sulfuric, and sulfamic acids should be avoided as they reduce the passivated chromium oxide layer. Although the duration of the application is insufficient to trigger pitting, wrong application of acids causes the ferritic structure to corrode. When corrosion occurs, iron oxide increases the surface asperity. Asperities damage the paint on the cans (labels and color) when they move along the wall of the pasteurizer. Figure 10.7 shows intergranular corrosion on the stainless steel of a pasteurizer (AISI 304) 10 days after descaling with noninhibited hydrochloric acid.

If it is not prevented, corrosion leads to fouling, increase in the operational costs, and damage to containers and machines.

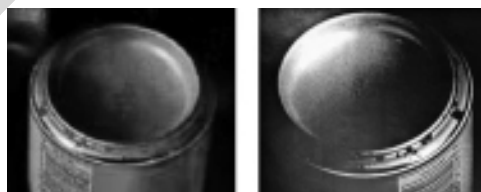


Figure 10.6 Flash rusted cans (courtesy of Diversey Food Group WHO).

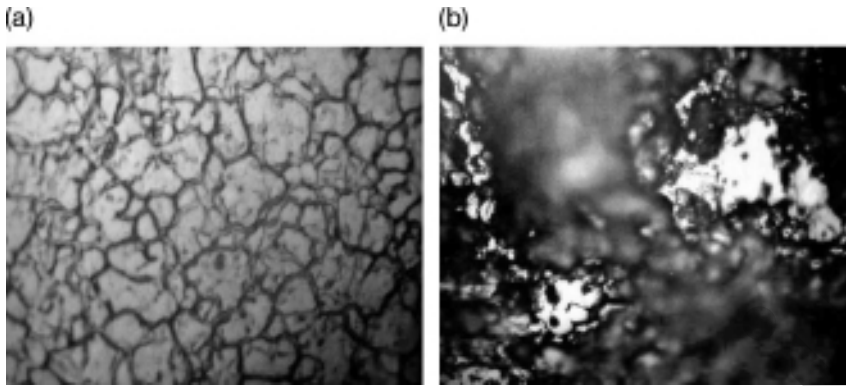


Figure 10.7 (a) Microstructure of a virgin AISI 304 stainless steel and (b) the same surface one week after descaling with HCl. The iron oxide is only visible under a microscope.

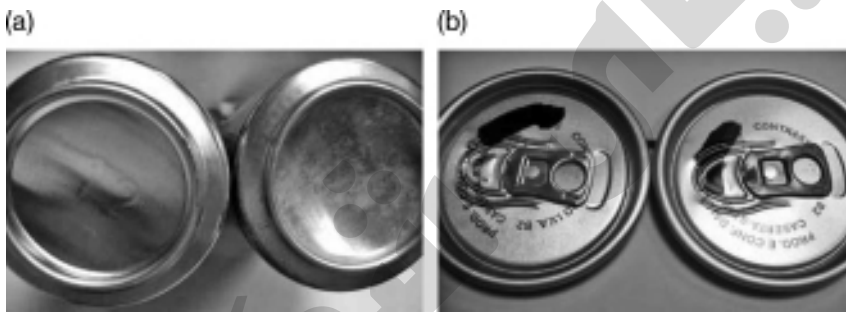


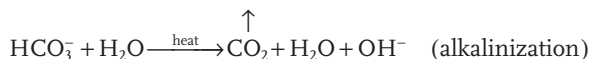
Figure 10.8 Staining on (a) dome and (b) pull-tab at pH 8.2.

10.1.4

Dome Staining

Iron and manganese oxides impurity in aluminium alloys can generate dome staining on pasteurized aluminium cans (Figure 10.8). Staining becomes evident as a dark brown layer when uncoated or unlacquered pull-tabs and domes are exposed to a pH above 7.8.

Aluminium is an amphoteric element. Its stability zone falls within pH 6.5 and 7.0 where it shows the highest resistance to corrosion [3]. Aluminium and aluminium oxide rapidly dissolve in alkaline media. Iron and manganese impurities come out, oxidize, and accumulate on the surface. Increase in alkalinity is produced by change in the water salinity promoted by temperature. The high temperature of pasteurization causes decomposition of bicarbonates and yields free hydroxyl ions and a higher pH:





The more the bicarbonate hardness increases, the more the high temperature causes the pH and deposit to increase. Hardness, pH, time of exposure, and purity of the aluminium alloy establish the degree of staining.

10.1.5

Chemical Treatments

The problems connected to a tunnel pasteurizer (scale, biofouling, corrosion, and packaging damage) originate from the process water. Therefore, the water is treated in order to avoid problems.

10.1.5.1 Scale and Biofouling

Tunnel pasteurizers are constructed to recycle raw water. Water is of neutral pH. Therefore, threshold sequestrants performing in neutral conditions are selected. A few ppm of HEDP or PBTC are enough to prevent scale in the hot sections and blooming on cans and bottles. Biocides prevent biofouling in cold-warm sections.

Sequestrants and biocides come into contact by carryover. They must be selected with care. Sequestrants could be incompatible with halogens (chemical destruction) and quaternary ammonium compounds (salt precipitation). Therefore, sequestrants and sanitizers must be selected having regard to the overall system, in particular:

- **as a function of the type of pasteurizer:** Each type of biocide needs a particular contact time to kill bacteria reliably. Therefore, each type of pasteurizer needs a biocide able to kill microorganisms at a rate matching the rate at which the water is changed. Nonregenerative (and even regenerative) pasteurizers renew their water rapidly. Hence, they require biocides acting faster than those used in pasteurizers which lose water slowly. Halogens, aldehydes (glutaraldehyde), and DBNPA (2,3-dibromo-3-nitrilopropionamide) act quickly, whereas isothiazolone is slow-acting. Quaternary Ammonium Compounds (QACs) can be applied in both systems, remembering that monomers cause the paint to fade on cans and caps. Conversely, polymeric QACs do not cause corrosion and can be used in place of monomers. Polymeric QACs, however, require higher concentrations in use (lower biocidal activity).
- **as a function of their chemical structure:** Sequestrants are anionic compounds whereas QACs are cationic. Even though they are, theoretically, chemically incompatible, their stability and efficacy in solution depend on their chemical structure. Polymeric structures react and yield insolubilization and precipitation. Thus, polymeric sequestrants (e.g., acrylic polymers) and polymeric biocides (e.g., polybiguanide and polyQAC) are mutually incompatible. On the other hand, combination of the monomers is possible even though a slight loss in activity is to be expected (e.g., PBTC and HEDP with monomeric QAC).

Chlorine and HEDP being incompatible, PBTC can successfully replace HEDP if chlorine is added or carried along with the process water.

10.1.5.2 Corrosion

The corrosion of tunnel pasteurizers is in practice controlled by biocide treatment, type of descaler, and concentration of chloride and bromide in the system. The presence of chloride ions above 25 ppm and biofilm inevitably give rise to corrosion, so that corrosion inhibitors must also be added. This anti-corrosion treatment does not stop corrosion but reduces its kinetics (cathodic inhibition). Polyphosphates (hexametaphosphate), zinc phosphate and phosphonate, molybdate, and nitrate are involved. As a result of adding corrosion inhibitors, blooming and spotting increase, as does the level of pollutants. Therefore the waste water treatment also becomes more expensive.

Halogen-based biocides should be avoided because of the impossibility of effectively controlling their corrosive effects. Corrosion would be one of the less important issues in the absence of halogens and biofilm. It follows that it is always recommended to prevent the cause of corrosion instead of looking for corrosion inhibitors to counteract corrosive treatment processes.

Descaling makes use of acids. Hydrochloric acid must be inhibited with the appropriate chemicals (e.g., alkylaryl nitrogen compounds) or replaced with phosphoric acid.

10.1.5.3 Packaging Damage

Heating causes dome and pull-tab staining on aluminium cans. Since staining occurs at pH values above 7.8, the recycled hard water needs an acidic treatment to keep the pH below that value. In practice, 7.5 is considered to be the upper pH limit for preventing black staining. Damage to aluminium occurs in the hot zones where limestone also precipitates. Thus, the simultaneous addition of acid and sequestrant (same formula or two additives) achieves both pH stabilization and scale control. Phosphoric acid precipitates calcium phosphate. Sulfuric acid is a cheap but highly corrosive chemical and takes part in the metabolism of sulfate-reducing bacteria. Thus, phosphoric and sulfuric acids are not recommended. Organic acids, such as citric acid, prove to be the most suitable chemicals. Citric acid together with HEDP or PBTC performs the single-step treatment.

10.2

Cooling Tower

Adding and removing heat are carefully governed in order to have water with an optimal capacity of exchange. When water is recycled to cause cooling, its temperature increases, and, to maintain the heat exchange efficiency, the accumulated heat must be removed. Total regenerative pasteurizers in meat and poultry chilling, refrigeration chains in domestic markets, wine cooling tanks, ice cream

factories, metal production, and metal working are examples where a cooling tower is usually installed.

The cooling tower provides the most efficient means of heat removal from open recirculation systems. Water is sprayed over packing, which forms a large surface where water and air move in opposite directions. Air-water contact evaporates part of water, which generates cooling. A simplified representation of the process is shown in Figure 10.9:

The evaporation mechanism concentrates salinity in the cooled water. The ratio between salts dissolved in circulating water and salts in the make-up water defines the cycles of concentration. As even the best suspending and dispersing sequestrants fail after a certain number of cycles (usually no more than 3 are acceptable), a partial renewal of water through an automatic blowdown [4] prevents scale precipitation on the gratings (see Figure 10.10).

A conductimeter automatically governs the blowdown. A pre-established conductivity signals the release of water with a high concentration of salinity while the level sensor makes up the loss.

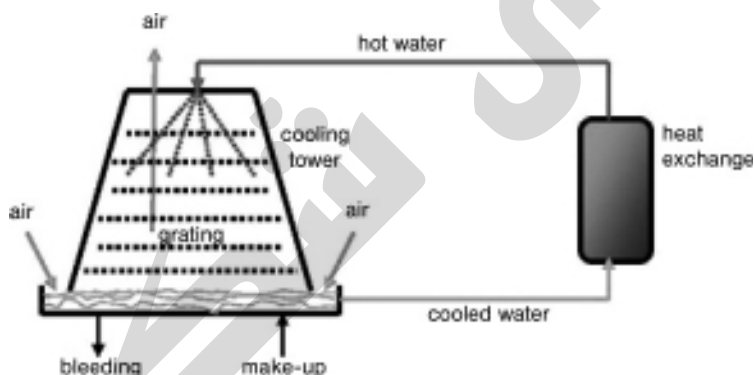


Figure 10.9 Schematic diagram of a cooling tower.

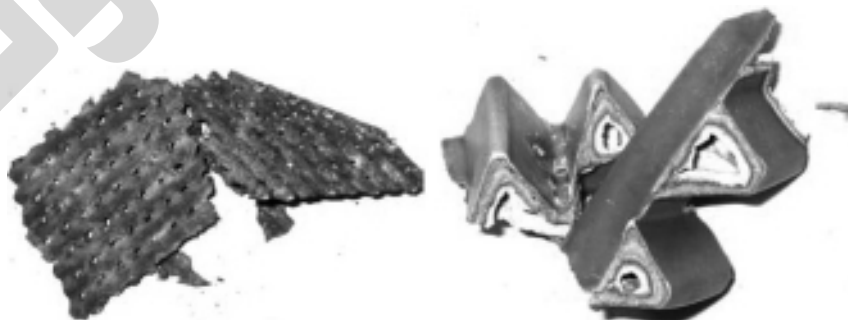


Figure 10.10 Scale precipitation on gratings.

Owing to the concentration of salinity, threshold and dispersing sequestrants are required. The suspending property of acrylic polymers (e.g., 4000–5000 MW) often synergizes the dispersing capacity of phosphonates (e.g., HEDP, PBTC and EDTMP) in keeping salts soluble and preventing deposition of the insoluble ones. Neutrality allows a very low concentration of sequestant. One of the practical rules recommends adding 10 ppm of sequestant boosted with a further 1 ppm for every 5 dF of hardness. If, for instance, the hardness is 20 dF, the concentration will be at least 14 ppm of sequestant as active matter.

As cooling towers are open plants exposed to sunlight, the microbial growth is considerable. Both pseudomonadaceae and algae are responsible for copious slime, which can even clog the strainer lattice. The common types of algae in a cooling tower are described as

- green chlorophyceae and cyanophyceae forming green/green-blue slime (multicellular algae producing gelatinous and stringy growth)
- diatomaceae, fouling with silica deposits.

Biocide added to the make-up water prevents biofouling. Cationic agents prove to be suitable in the absence of polymeric sequestrants (see Section 10.1.5). Isothiazolone and glutaraldehyde are suitable for every occurrence. Halogens and halogen-releasing chemicals (e.g., DBNPA) are not recommended because of corrosion problems.

If the cooling tower is coupled to a tunnel pasteurizer, its chemical treatment cannot be thought as a separate process. Sequestrants and disinfectants must be consistent with both plants and also with the containers to be pasteurized. There should be no mutual interference among chemicals; paint fading prevention and pH control should be managed as described in Section 10.1.5.

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دینی جای
مستطوف

11

Foam and Gel Cleaning

Open plants can be so complex that it would require too much time and manpower to accomplish satisfactory sanitation everywhere. Therefore, a modified type of cleaning has been developed in which structured detergents are spread so as to be retained on the surface for a long enough time to react with the contamination and afterwards to be thoroughly removed by a high-pressure rinse. Foam and gel detergents behave as described. Before the development of dedicated detergents, neutral foaming products were mixed in the workplace with existing caustic, acidic, and chlorinated detergents to provide them with foaming properties. The empirical handmade blends were sprayed in those parts which were morphologically complex, manually arduous, or impossible to reach. Examples are shown in Figure 11.1.

Sectors such as poultry and meat handling and sausage manufacturing, where cleaning is demanding, were the first to try foam technology. Soon after this, its use spread to the majority of food and beverage plants. Ease of operation, speed, effectiveness, and low involvement of personnel are the reasons for its success.

Gel cleaning evolved from the foam process. This technique prolongs the retention time, enhances the cleaning efficiency, and improves rinsability and waste processing.

In terms of detergency theory, foam and gel cannot be considered to be ideal physical systems to achieve cleaning. Cleaning is easily and rapidly achieved when the detergent solution moves. Such movement continuously replenishes the solution in contact with the contamination, facilitating its removal from the surface (e.g., CIP, spray, and air bubbling systems). On the other hand, in order to remain in contact with vertical surfaces, foam and gel form static structures sustained by air bubbles (foam) or a chemical lattice (gel). This condition reduces the volume of detergent at the soil-chemicals interface and, even worse, the soil is not progressively dissolved and carried into the solution. Chemicals in foam-gel treatments only act as soil conditioners rather than soil removers. The real agent of cleaning (soil removal) proves to be the mechanical force of the pressurized final rinse. Only the rinsing water transfers pressure (mechanical energy) and temperature (thermal energy) and promotes exchange of detergency agents (chemical energy) on the surface [1]. In contrast to manual application of cleaning agents, high retention detergents effectively reach every part of the equipment

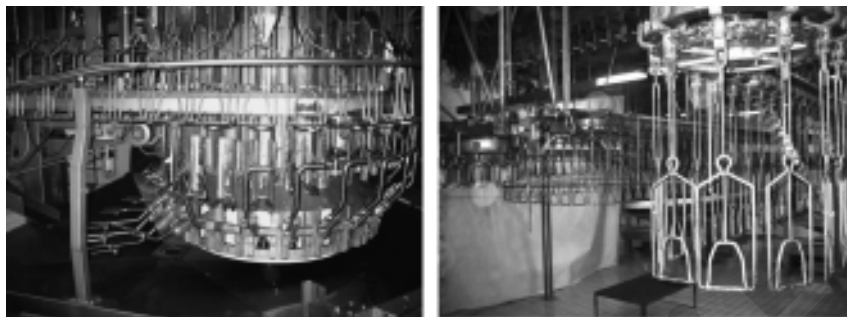


Figure 11.1 Complexity in the poultry process.

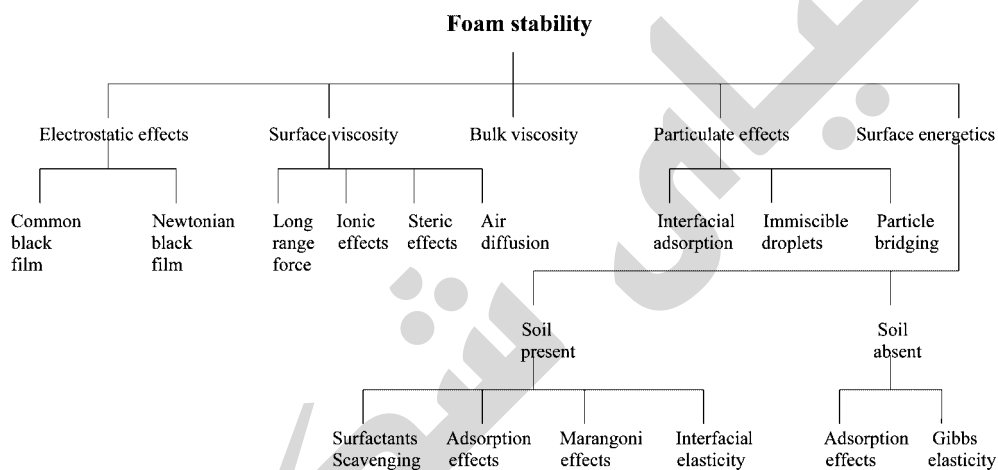


Figure 11.2 Production and stabilization of foam (courtesy of Wingrave [2]).

and, in conjunction with the water pressure, give a balance between efficiency in cleaning, saving of time, and low cost in use.

11.1 Foam

Since many surfactants can sustain foam, it would seem to be easy to produce effective foam detergents. However, the foam quality is determined by the type of detergent (e.g., acidic, alkaline), salts concentration (e.g., caustic soda, chlorine, sequestrants) and specific boosters able to keep the foam stable with time (e.g., short chain fatty acids). The mechanism through which foam is produced and stabilized is rather complex. Wingrave [2] sets out the contributing factors in Figure 11.2.

It is possible to obtain excellent bulky foam without cleaning efficacy and, conversely, excellent cleaning foam without a sufficient retention time. In neither

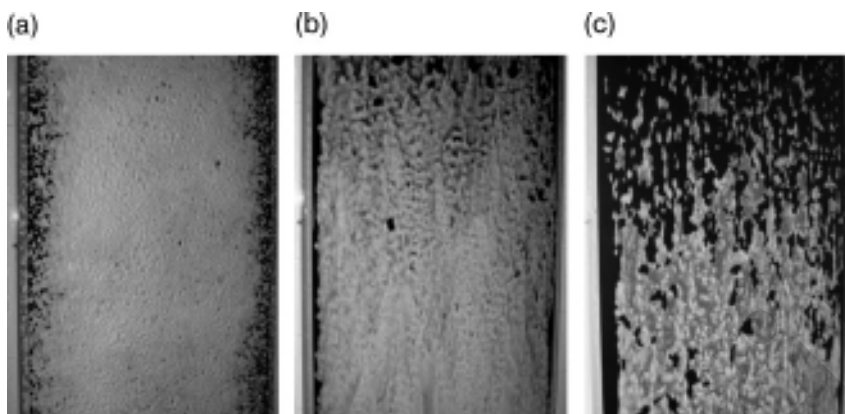


Figure 11.3 Retention time of a foam detergent: (a) just sprayed, (b) 2 min later, and (c) 4 min later.

case is detergency achieved. Foam cleans if it wets. However, there is a conflict between wetting property and retention time. The wetter the foam, the less is the retention on vertical surfaces. The more water left behind by the foam on the surfaces, the more cleaning is accomplished. The conflict is resolved with the aid of a group of chemicals (e.g., C_8 – C_{10} fatty acids, 2-ethylexanoic acid and gluconate) able to behave as foam and wettability regulators. They boost the retention time (bulky foam) without reducing the wetting power. The addition of short-chain fatty acids to foam formulations makes the foam change in viscosity according to the concentration of these compounds.

Short-chain fatty acids govern the qualitative appearance of the foam, but foam morphology is insufficient to provide cleaning. For instance, nonionic surfactants promote excellent detergency in CIP, manual, and soak systems and might be expected to give good cleaning properties in foam and gel products also. This is not the case. Even the best nonionic surfactants do not give the desired quality of foam. They lead to foam that flows away like an aqueous solution (no retention time). Therefore, foam cleaners make use of anionic surfactants as the primary foaming agents. Dodecylbenzenesulfonate, lauryl ether-sulfate, laurylsulfate, alkanesulfonates and α -olefinsulfonates are the most preferred surfactants to give foam with excellent cleaning properties. Laurylamine oxide is the only nonionic surfactant commonly included in the formulation. Laurylamine oxide does not have any cleaning properties but generates excellent foam at low cost and is compatible with any formulation, inclusive of chlorine. Blends of anionics and laurylamine oxide are regularly preferred as the best compromise in cleaning detergents (Figure 11.3). Blends of laurylamine oxide with QAC, fatty triamine, or chlorine form the basis of cleaning and disinfecting formulations.

Concentrations of salts (mainly caustics), EDTA, and chlorine make the foam heavier. The air bubbles have difficulty in expanding and cause the appearance and retention time of the foam to deteriorate considerably.

11.2

Gel

Gel detergents are considered to have evolved out of foam detergents in the course of technical development. Gels reproduce the same categories of products: heavy duty, soft-metal-safe and chlorinated alkaline detergents, acidic descalers, and nonchlorinated sanitizing detergents. Unlike foam detergents, where the addition of air physically generates the foam, gel formation depends on internal reactions occurring in contact with water. Gel forms when polymeric structures link together long chains of molecules in a liquid medium by branched bonds. The liquid prevents the polymeric lattice from collapsing into a compact mass, while the lattice prevents the liquid from sliding out. Opposite charges, such as partially cationic fatty amine oxide and anionic surfactants or soaps, produce a product which is nonviscous when undiluted but which changes into a gel when diluted in water [3]. The gel formed is partially stable and relaxes with time. However, it maintains its viscosity for some hours, time enough to clean successfully.

A gel is by itself almost invisible on an open surface. It is difficult to determine where and how the surface is actually covered. For this reason, a small quantity of air is added in order to produce a white gel. The white appearance, due to the formation of a micro-foam, renders the gel visible. Figure 11.4 shows how the gel changes in appearance with air injection.

When foam and gel are compared, the enhanced retention of the gel immediately stands out. Besides depressing the zeta potential and improving adsorption (cationic components), the thin volume on the surface curbs the effect of gravity as can be seen in Figure 11.5.

Gels carry a higher mass of chemicals per area of soil, which enhances detergency. This is illustrated by comparative laboratory tests measuring percentages of contamination removed by foam detergents and the corresponding percentages for equivalent gels. The results are shown graphically in Figure 11.6.

When it is rinsed off, gel generates less foam, which allows an easier drain. In spite of being richer in surfactants, the exhausted solutions of the gel are easier to deal with in waste processing. Suitable steps of chemical clarification remove the cationic components made inert and precipitated as sludge by reaction with anionic and polar compounds. This also facilitates the removal of anionics. On the other hand, the nitrogen group reacts with chlorine to give chloramines. Chloramines remain active longer and can disturb the biological step. Thus, nonchlorinated disinfectants should be preferred.

11.3

Foam-Gel Synergism

The technologies of pure foam and pure gel can be combined in order to reach an interesting compromise providing foam with the cleaning properties of gels in a formulation cheaper than gel. This means improving the retention time and

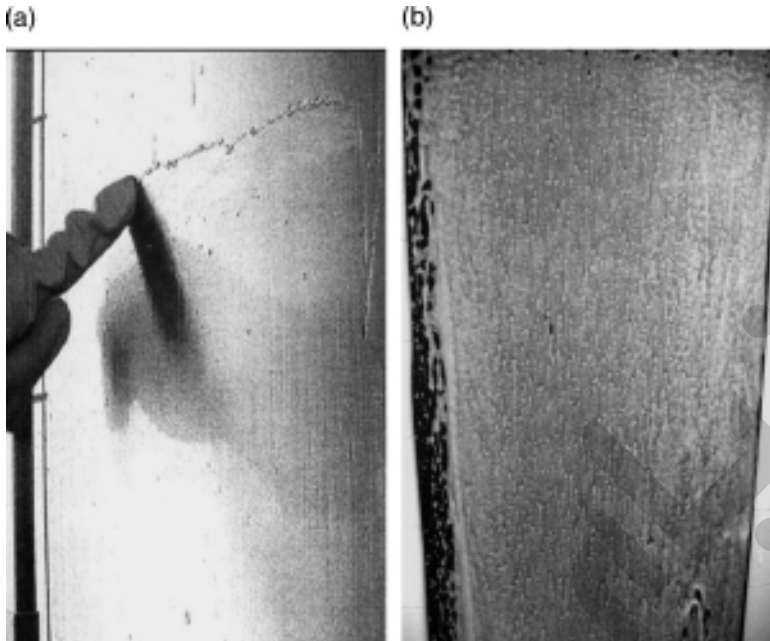


Figure 11.4 Appearance of foam (a) without and (b) with air injection (courtesy of JohnsonDiversey).

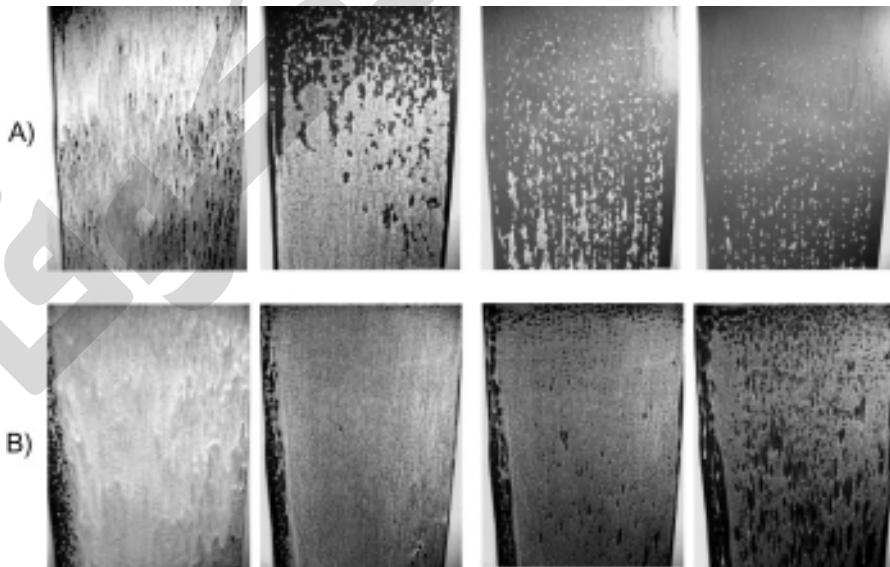


Figure 11.5 Difference in foam A) and gel retention B).

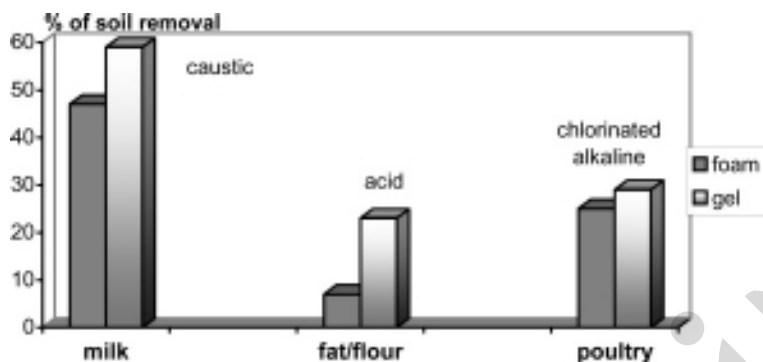


Figure 11.6 Contamination removal with three classes of detergents.

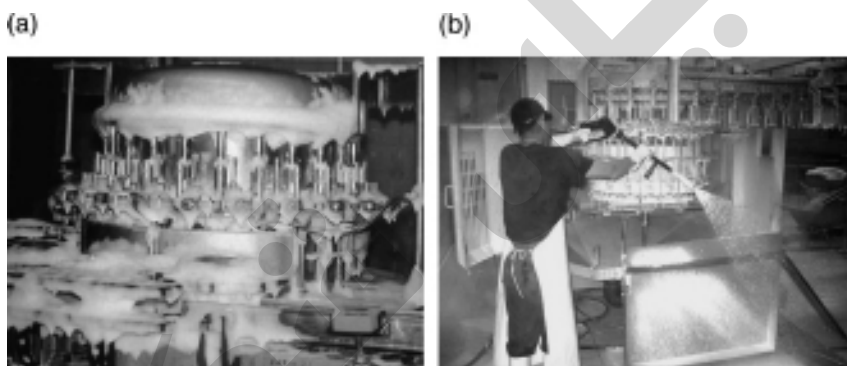


Figure 11.7 Cleaning of filler and poultry plant with (a) foam and (b) gel.

quality of the standard foam technology. Figure 11.7 shows the clear difference between the appearance of a bulky foam and that of a thin gel.

Gels involve cationic compounds reacting with anionic surfactants to give rod micelles as their basic structure. If we consider that

- cationic molecules lower the interaction energy (zeta potential) and increase the surface adsorption and retention time
- condensed nonionic surfactants in gel systems prevent the rod micelles from forming and make the system perform like foam products
- addition of short-chain fatty acids adjusts the foam quality and its wetting properties,

cationic chemicals (fatty amine oxides) and short-chain fatty acids can be added to foam systems in a small controlled quantity in order to reinforce the foam technology and obtain a product which has the benefits of a gel and the cost of a foam.

11.4

Body Structure

The complex structure of the plant in slaughterhouses for white and red meats benefits considerably from foam and gel cleaning. The dairy industry is the second large user, followed by bottling. The chemistry of the fats, which feature strongly in these industries, in particular the hydrolyzed fatty acids, assumes primary importance in deciding the type of product (body structure) which leads to the best cleaning result. Deposition starts to be apparent in the form of a hydrophobic surface and goes on growing as a whitish residue. Fatty acids, produced by the hydrolysis of fats, behave differently as a function of

- **Type of hydrocarbon chain.** Saturated lauric (C_{12}) and stearic (C_{18}) acids, for instance, are solid at room temperature, pasty above 35°C and liquid above 45°C .
- **Type of cations reacting and forming soaps.** Potassium and alkanolamines give soaps that are liquid at lower temperature than those formed with sodium. Calcium soaps have considerably higher melting temperatures, even up to 70°C (e.g., saturated C_{12} calcium soaps). Summing up their physical status at room temperature:

– R–K and alkanolamines	generally liquid and soluble
– R–Na	usually solid but soluble
– R_1 –Ca– R_2	certainly solid and insoluble.

The rate of cleaning of a solid contamination is less than that of liquid one. Detergents remove the solid contamination layer by layer (peeling) instead of rolling up liquid droplets. Prevention of the formation of a solid deposit is one of the basic rules in detergency. The popular saying that some detergents cook and fix fats on the surface is really a reference to the chemical precipitation of solid sodium and calcium soaps. Then, an alkaline soap based on caustic potash would be preferable to one based on caustic soda. The cold season may give rise to problems of the stability of products. Caustic potash enhances stability. Alone or blended with caustic soda, potash decreases the freezing point. For instance, the freezing point of a 45% sodium hydroxide solution is close to $+4^{\circ}\text{C}$, while 45% of alkalinity consisting of 30% sodium hydroxide and 15% potassium hydroxide freezes at -3°C . Furthermore, it is easier to stabilize chlorine in caustic potash than in caustic soda, and caustic potash is less aggressive toward aluminium than caustic soda (slower kinetics of corrosion).

Potassium hydroxide is more effective on fats while sodium hydroxide performs better on proteins. Thus, products based on potassium hydroxide should be preferred in the meat industry and those based on sodium hydroxide in the dairy industry. Unfortunately, potassium hydroxide is more expensive, so that judicious blends give a satisfactory balance between cleaning and cost in use.

Blends of stoichiometric and threshold sequestrants prevent calcium from precipitating. The stoichiometric sequestrants compete with fatty acids for

Table 11.1 Example of spread of microorganisms.

Point of sampling	Total bacterial count (ufc/cm)	Enterobacteriaceae (ufc/cm)	Escherichia coli (ufc/cm)
Before the final plucking with wax	Uncountable	7	3
After plucking	Uncountable	>100	44
After removing entrails	Uncountable	>100	57
After cleaning (water spray)	Uncountable	36	28
After chilling	43	1	0

calcium and the threshold ones (phosphonates) allow the stoichiometrics to perform even in sub-stoichiometry.

An alkaline detergent is usually formulated with silicate so as to be safe on aluminium (e.g., alkaline and chlorinated alkaline detergents, alkaline sanitizers based on quaternary ammonium compounds, fatty polyamines or fatty amphoteric polyamines). Some detergents exhibit soft-metal-safe (SMS) behavior though free of silicate. They exploit the mild technology based on calcium tartrate (citrate, acetate)–alkanolamine, which is effective enough in protecting aluminium from caustic attack. However, from the point of view of the overall economy of the treatment, the latter is so expensive that its use is reserved for specific needs (e.g., difficult rinse, ease of handling). Besides being components of SMS products, alkanolamines act as co-emulsifiers and help surfactants to prevent dirt from redepositing.

The meat processing industry usually adopts chlorinated foaming detergents since chlorine cleans and adds hygienic benefit. Table 11.1 shows an example of the spread of microorganisms from plucking to chilling.

Equipment remains severely contaminated. The presence or absence of *Salmonella*, *Escherichia coli*, and *Staphylococcus* is taken as the parameter to assess the hygiene of equipment and tools. The use of chlorinated products and a final disinfection with cationics after cleaning perform and maintain long-term sanitation.

11.5 Sequestrants

Competition for calcium takes place between water hardness and organic hydroxyacids in bottling, proteins and soaps in dairy and meat processes, and oxalate and silicate in vegetable processing. Although these competitors originate from fresh

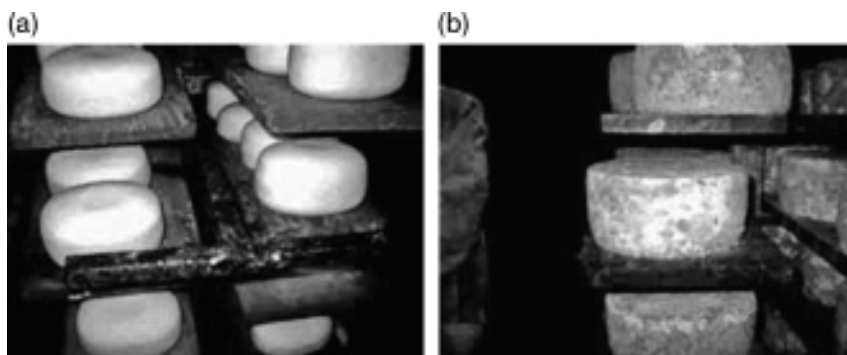


Figure 11.8 (a) Cheese free of unwanted mold. (b) Uncontrolled molds causes damage to seasoned cheese.

materials, they show remarkable stability constants and hydrophobic barriers. Thus, foams and gels include a sequestration system showing

- an affinity with metals stronger than that of competitors
- a carrier effect
- a cleaning property
- threshold ability.

No single sequestrant exists that is able to keep calcium salts soluble during the infinite dilution of rinse, to compete effectively with strong precipitants, and to remain active even in sub-stoichiometric conditions. Thus, foam and gel detergents have to be formulated with blends of sequestrants calculated to solve cleaning demands originating from diverse food industries.

EDTA is the best competitor for metals and the best carrier sequestrant. NTA, HEDTA, MGDA, GLDA, IDS can be used as alternatives if EDTA is not permitted. Tripolyphosphate provides the best balance between sequestration, antiredeposition and detergency because of its peptizing effect on proteins. In spite of restrictions on the use of phosphorus, it is still included in detergents. ATMP is the most common phosphonate blended with EDTA in the absence of chlorine. PBTC, sometimes together with homopolyacrylate (MW 4500) and STP, satisfies all the requirements inclusive of chlorine stability. The ratio between stoichiometric and threshold sequestrants is one of the key factors in cleaning success. An increase in EDTA concentration without adjusting types and concentration of threshold sequestrants could lead to worse cleaning in spite of the postulated rise in sequestering strength.

An example of what could happen without wise foam-gel sanitation in the cheese seasoning room is shown in Figure 11.8, where an abnormal growth of molds and bacteria is evident. Although molds take part in providing the complex body of cheese flavours, an excess of growth could spoil the final result.

11.6

Foam/Gel Free OPC

Open plant cleaning (OPC) is currently the domain of foam and gel technology. As already mentioned, in terms of the theory of detergency, foam and gel cannot be considered the best technology to accomplish cleaning, as in order to last longer on vertical surfaces, foam and gel form static structures including air bubbles (foam) and chemical lattice (gel) that do not permit the constant renewal of chemicals in contact with soil. Thus, immobility diminishes the chemical energy of the system. The real agent of cleaning (soil removal) is the mechanical force of the high-pressure rinse [1]. However, it is observed that good cleaning depends on the ability of the detergent to keep the surface wet. Foam and gel require complex formulations and specific equipment for delivering them. Therefore, one may innocently ask: 'Is it possible to apply conventional nonfoaming/nongelling detergents on open plants by prolonging the wetting time until it equals that associated with foam and gel?' The answer is positive only if the conventional detergents are formulated with chemicals able to delay drying. High-molecular weight carboxylic homo- and copolymers, polymaleic anhydride, carboxyalkylcellulose, polysaccharides, and heteropolysaccharides (e.g., xanthans, galactomannans, carrageenans, and alginates) behave like a sponge and absorb water as they swell up. The drying time of solutions containing such substances is delayed because the water release is slowed down. The detergent thus has more time to act as it does in foam and gel. The advantage follows from the ease of operation and flexibility of the delivery plants. Such detergents do not need specific equipment and pressurized pipelines. Thus, although the cleaning of open plants continues to be based on the use of foam and gel detergents, simpler applications sometimes seem attractive to reduce the complexity and costs of application.

11.7

Practical Problem Solving in OPC

The most frequent problems of cleaning in open plants concern different types of stains remaining on the surface after rinsing. Looking at the type of stain it is possible to infer the origin of the problem and how to solve it. In practice, three different categories of stains can occur.

11.7.1

Bluish Stains

The problem is connected to a protein-fat soil (mainly fat) incompletely removed by cleaning. The chemical reaction of fats (fatty acids) with stainless steel followed by oxidation yields a bluish stain (Figure 11.9). The adsorption of fats (triglycerides) converts the stain into a greasy deposit. The occurrence is ascribed to a wrong concentration of the detergent. Therefore, it is necessary either to check



Figure 11.9 Cleaning problem from unsuitable concentration of detergent.

the efficiency of the equipment in delivering the required concentration or to increase the detergent concentration to achieve complete cleaning.

11.7.2

Yellowish-White Stain

The problem is connected to uncontrolled hardness and detergent with a wrong balance between sequestration and caustic soda (sodium). High alkalinity from caustic soda must be balanced with an effective blend of sequestrant. Otherwise, sodium reacts with fats to give so-called cooked contamination. This rough definition indicates precipitation of a sodium-calcium-fat-protein mixture on the surface (Figure 11.10). The stain increases with time and has the appearance of wax easy to scratch with the fingernail.

The occurrence is ascribed to a wrong (unsuitable) formulation. The problem cannot be solved by modifying the concentration in use but rather by changing the detergent.

11.7.3

Fat Removal in Patches

The problem is caused by the inability of the final rinse to remove the layer of fat from the surface. This event is typical of the poultry industry. Figure 11.11

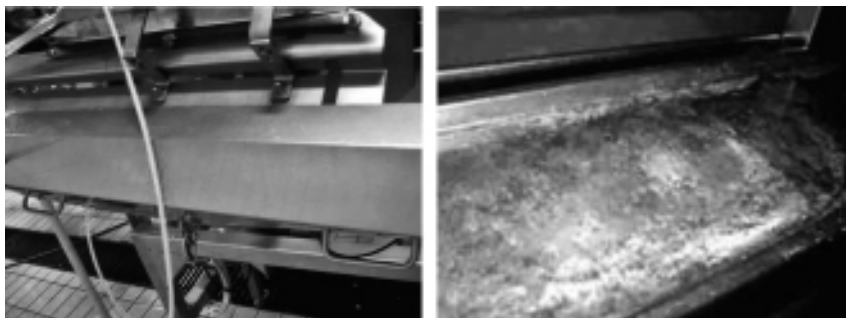


Figure 11.10 Cleaning problem from unsuitable formulation of detergent.



Figure 11.11 Cleaning problem from unsuitable temperature or worker negligence.

shows the cloacae-opening equipment where the difficulty of fat removal is evident.

There are various causes:

- 1) low temperature in pre-rinse and final rinse
- 2) low pressure of the rinse water
- 3) negligence of the worker.

Temperature and pressure play a considerable part in removing fats. A regular check on the efficiency of the delivery equipment is usually the key factor in obtaining a good cleaning result. The training of personnel is equally crucial.

11.8

Equipment for Pressure Washing

Equipment for generating pressurized liquids falls into two categories:

- **Pressure washer:** mobile (portable) equipment, usually providing one pressure only, specifically for a small plant or for hobby applications

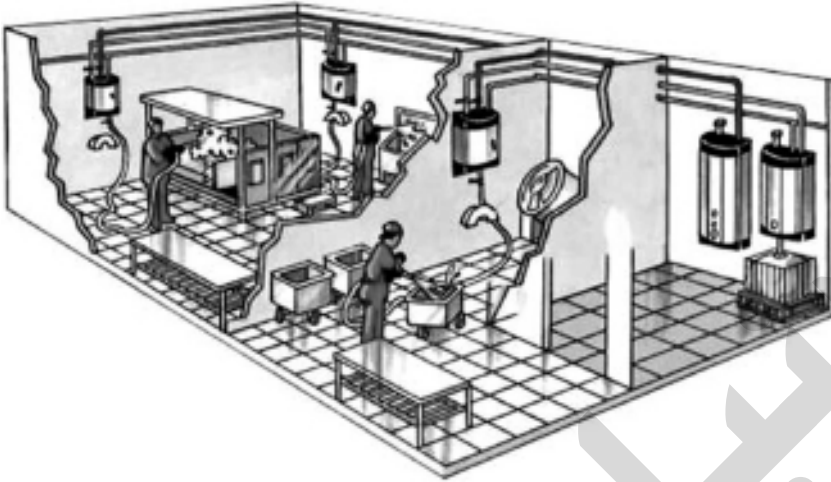


Figure 11.12 Centralized equipment (courtesy of JohnsonDiversey).

- **Modular equipment:** centralized or decentralized equipment for a large plant with a number of workers carrying out cleaning simultaneously.

11.8.1

Centralized Equipment

The system is said to be centralized when the equipment for preparing and pressurizing the cleaning solution is located in a separate room. Centralized systems as schematized in Figure 11.12 are the safest, although they are less requested and used.

11.8.2

Decentralized Equipment

The system is said to be decentralized when the equipment to prepare and pressurize the cleaning solution is sited where the cleaning is carried out (Figure 11.13).

Although the decentralized systems are less safe (concentrated caustics and acids close to personnel), they are more popular because they enable the consumption of detergent to be monitored. The performance of the personnel and the overall functionality of the equipment can be deduced from the consumption of detergent.

Pressure can change as a function of the type of equipment installed. Table 11.2 shows the pressure generated by each type of equipment.

Complexity, high cost, and general unreliability have led to unpopularity of multi-pressure equipment.

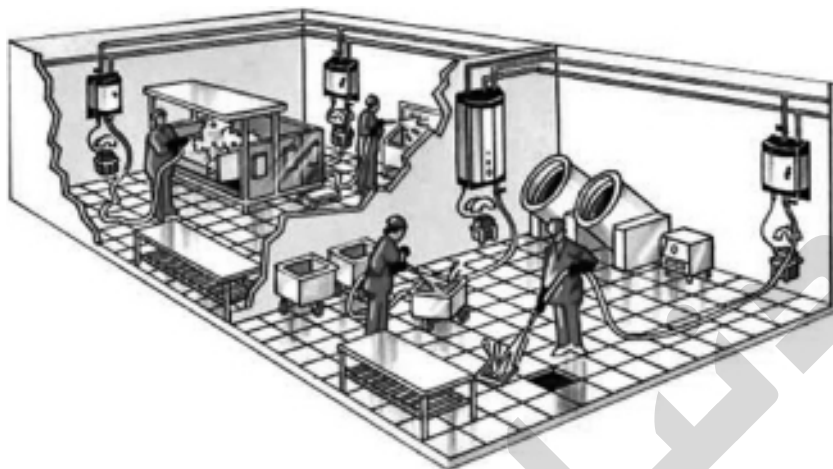


Figure 11.13 Decentralized equipment (courtesy of JohnsonDiversey).

Table 11.2 Equipment classification by pressure.

	Pressure (bar)
Low-pressure equipment	20–40
Medium-pressure equipment	40–80
High-pressure equipment	>80

One of the most interesting questions is what pressure to use for open plant cleaning. Several considerations point to the conclusion that low-pressure systems are the least problematical and the most cost-effective.

11.8.3 Loss in Pressure

As Figure 11.14 shows, the force of impact (in newtons) decreases with the distance from the nozzle. The cleaning efficacy is directly proportional to this. High, medium, and low pressures give the same force of impact roughly 0.30 m from the surface.

11.8.4 Loss in Temperature

Temperature drops as a function of the distance from the nozzle. Figure 11.15 illustrates this loss of temperature. With high pressure systems, one meter of distance causes the temperature to decrease by a factor of 2.

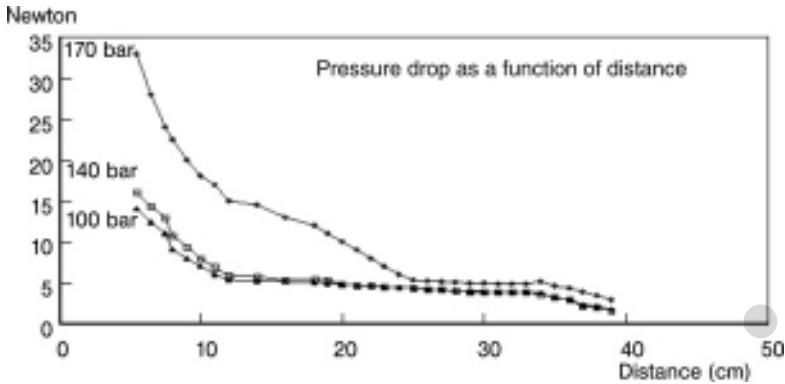


Figure 11.14 Force of impact as a function of distance from nozzle (courtesy of JohnsonDiversey).

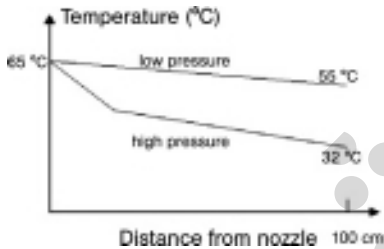


Figure 11.15 Temperature as a function of distance from nozzle (courtesy of JohnsonDiversey).

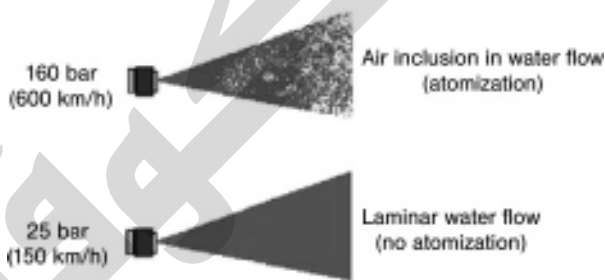


Figure 11.16 Effect of air in water flow (courtesy of JohnsonDiversey).

Why do pressure and temperature collapse? The answer is that the liquid is atomized between the nozzle and the surface, and the air in the liquid reduces the impact force and makes temperature decrease rapidly, as shown schematically in Figure 11.16. Atomized liquid can also be associated with redistribution of dirt and microbes, as described below.

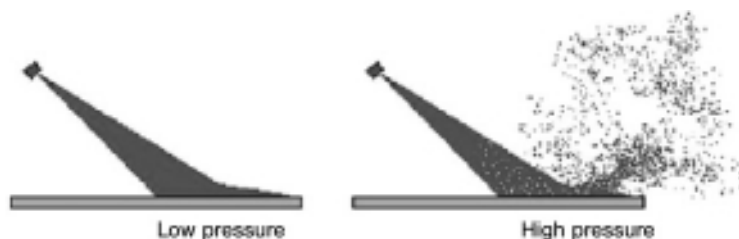


Figure 11.17 Aerosol produced from high-pressure system.

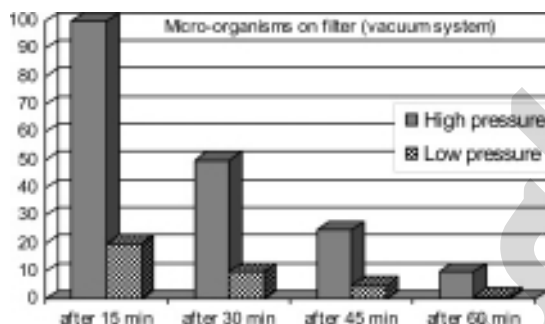


Figure 11.18 Spread of microorganisms by high- and low-pressure systems (courtesy of JohnsonDiversey).

11.8.5

Generation of Aerosol

High pressure impact causes a heavy aerosol to remain suspended for a long time. Aerosol means that water, steam, dirt, and microbes are dispersed. In practice, high pressure takes soil and microbes from one place and propels them to another (Figure 11.17). Figure 11.18 shows the significant difference between the spread of microbes at high pressure and that at low pressure.

It follows that low pressure gives superior cleaning and safety benefits in comparison with high pressure.

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12

Membrane Cleaning (Crossflow Filtration)

One of the most remarkable improvements in quality in industrial technology was achieved through the implementation of separation systems based on cross-flow (tangential) filtration. These require less energy (no phase change for water), are compact and modular, run at room temperature, and treat food without damaging its physical, chemical, and organoleptic properties. Crossflow filtration provides critical separations with plain solution (bacteria, antibiotics, colloids, pyrogen-free water, blood, proteins, salts ...) and can be readily tailored to existing applications. In these terms, crossflow filtration is considered the mild evolution of the traditional press-filters, terminal filters, evaporators, and centrifuges.

The prevalent technologies for food industrial processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) or per-filtration. These differ with respect to the average pore size. Figure 12.1 relates the type of filtration to the dimensions of the substances and the pore size.

The major innovation inherent in crossflow filtration is that the fouling of the filtering membranes is considerably delayed. While the traditional technology forces the whole solution to cross the membrane (dead-end), tangential filtration only separates those particles in the liquid layer in contact with the permeable barrier [4]. Solids are continuously kept moving and their concentration on the membrane (polarization) is delayed. Thus, filtration is longer performed (prolonged productivity), as simply illustrated in Figure 12.2.

A schematic representation of the flow in both types of filtration is given in Figure 12.3.

Microfiltration differs from UF, NF, and RO since it can perform both crossflow filtration (e.g., wine, milk) and the dead-end process (e.g., water sterilization, fruit juice filtration). Examples are given in Figure 12.4.

Nanofiltration is very close to reverse osmosis and operates at a lower pressure. Therefore, nanofiltration can supply a cheaper alternative to several processes such as industrial water recovery [5] and purification of detergent solutions.

Crossflow filtration delays the concentration of solids on the membrane but does not prevent eventual fouling. The more solvent crosses the membrane, the more a gradient of solutes grows and fouls the membrane (concentration polarization) (Figure 12.5). Fouling reduces the permeability of the membrane, and this

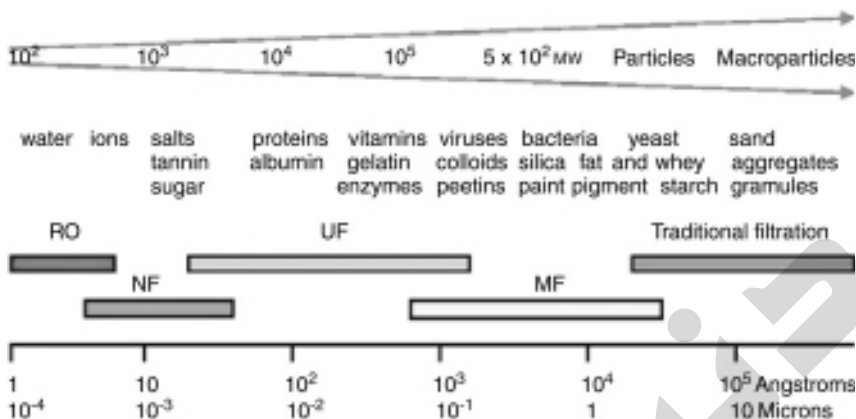


Figure 12.1 Types of filtration and pore size (adapted from Refs [1–3]).

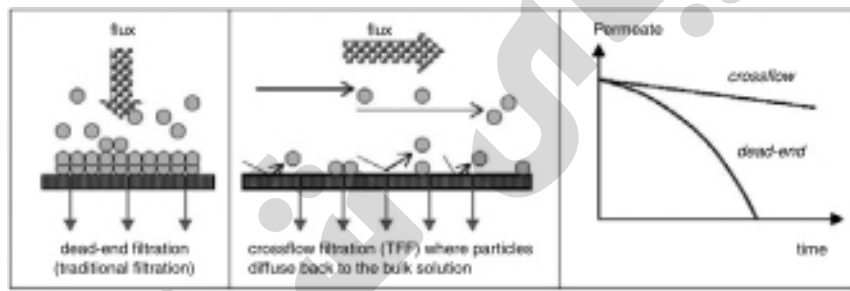


Figure 12.2 Comparison between traditional and crossflow filtration.

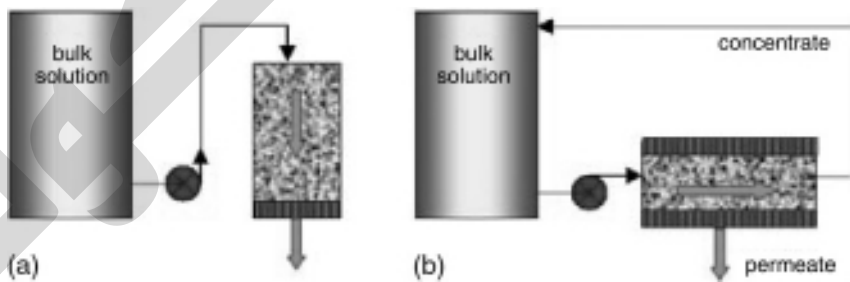


Figure 12.3 (a) Dead-end filtration and (b) crossflow filtration.

is measured by rate of flow of permeate and the associated rise in transmembrane pressure.

In order to minimize the influence of the concentration polarization, flow turbulence (recycle speed) and temperature can be used. Membranes actually

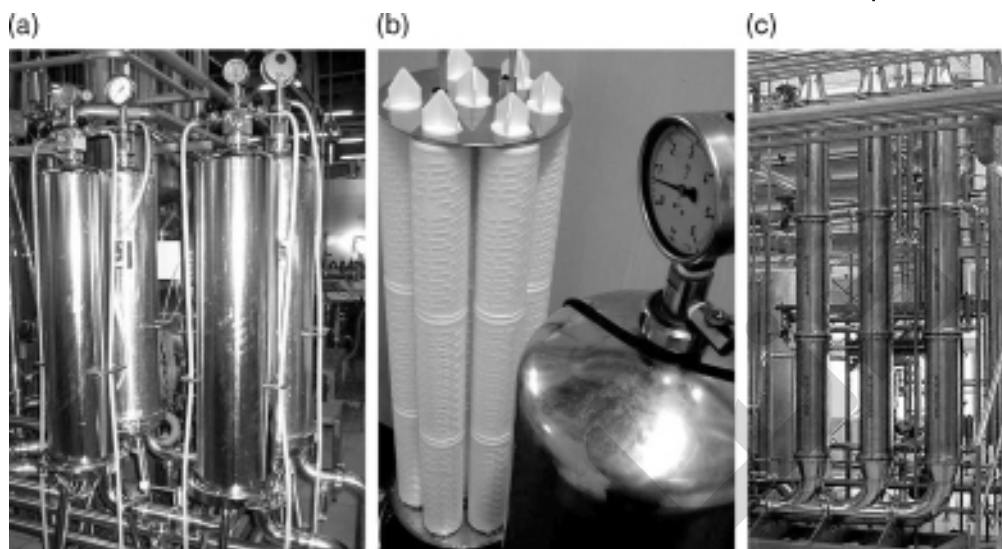


Figure 12.4 Examples of (a) water dead-end MF, (b) its membranes, and (c) crossflow MF in a brewery.

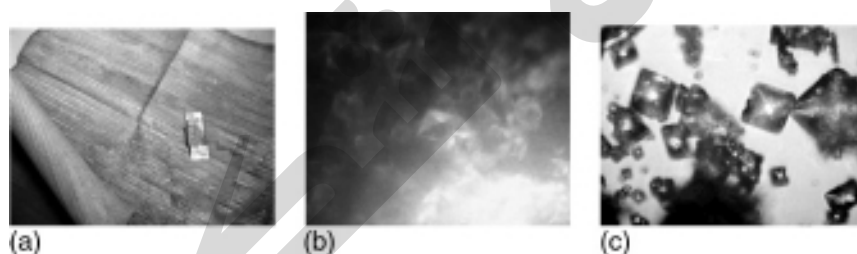


Figure 12.5 (a) Calcium oxalate fouling an NF membrane in tannin concentration and (b) the same under a microscope.

decrease in permeability in the course of time independently from the forced variation of flow. When the volume of permeate goes below a pre-established limit, only cleaning will recover permeability. The cleaning itself is not able to restore 100% of the permeate flow rate. Thus, the concentration polarization is only partially reversible (Figure 12.6). The negligibly small remaining fouling affects the membrane life until the loss in productivity makes its replacement essential (months or years, depending on the process) [5].

Membranes are required to concentrate (or separate) in a definite time and with a definite selectivity. Every deviation from steady conditions indicates changes in performance (clogging or damage). The Table 12.1 gives some definitions of terms describing to the steady state of a plant [6]:

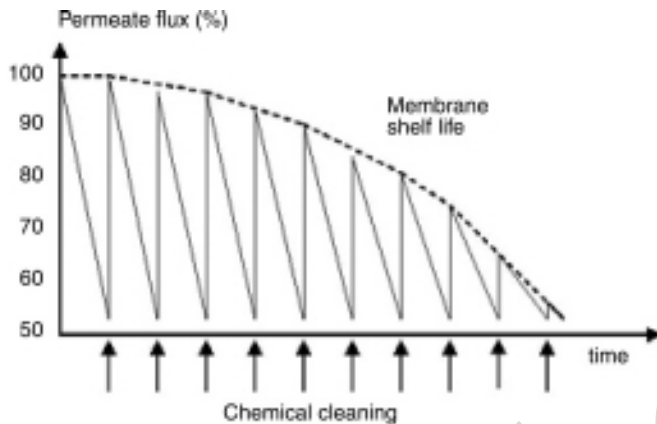


Figure 12.6 Loss in productivity of a membrane with time.

Table 12.1 Definition of terms.

Factor of concentration = $\frac{\text{initial volume of feed}}{\text{final volume of concentrate}}$	Loop or stage = course of continuous recycling in a module with pump
Flux rate = $\frac{\text{Volume of permeate}}{\text{Surface of membrane}}$	Feed and bleed = equilibrium of process given by adding product and withdrawing concentrate
Trans Membrane Pressure (TMP) = pressure drop across the membrane surface that drives the actual filtration process	Flux Rate = permeate rate crossing the membrane pores (alternatively known as the permeation rate)
Step = concentrate obtained in one or more loops (batch or continuous)	Plant capacity = volume of permeate/hour

12.1
Membrane

Membranes differ in the average size of pores. They can separate substances from 10^2 to 10^6 molecular weight, including colloids and viscous gelatinous materials [7]. Pervaporation and electrodialysis membranes are not widespread, although they find applications in industrial fields such as ethanol dehydration, fragrance concentration (pervaporation), purification of brackish waters, serum, and sugar, desalinization of proteins, and stabilization of juice and wine (electrodialysis) [8]. Figure 12.7 shows fouling of UF and RO membranes.

Using to the standard schematic representation, Figure 12.8 shows crossflow filtration applied to various systems.

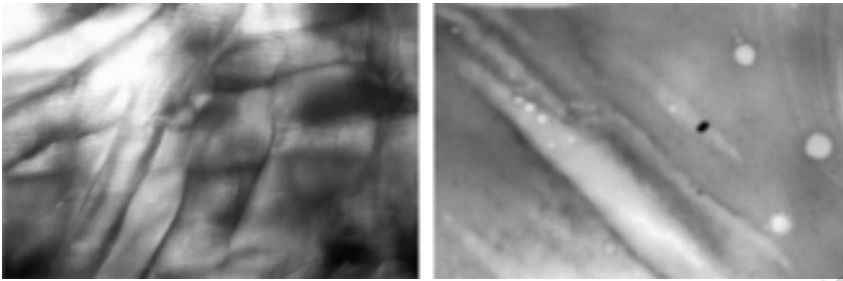


Figure 12.7 UF polysulfone membrane with trace of fouling and RO polyamide membrane (photomicrograph).

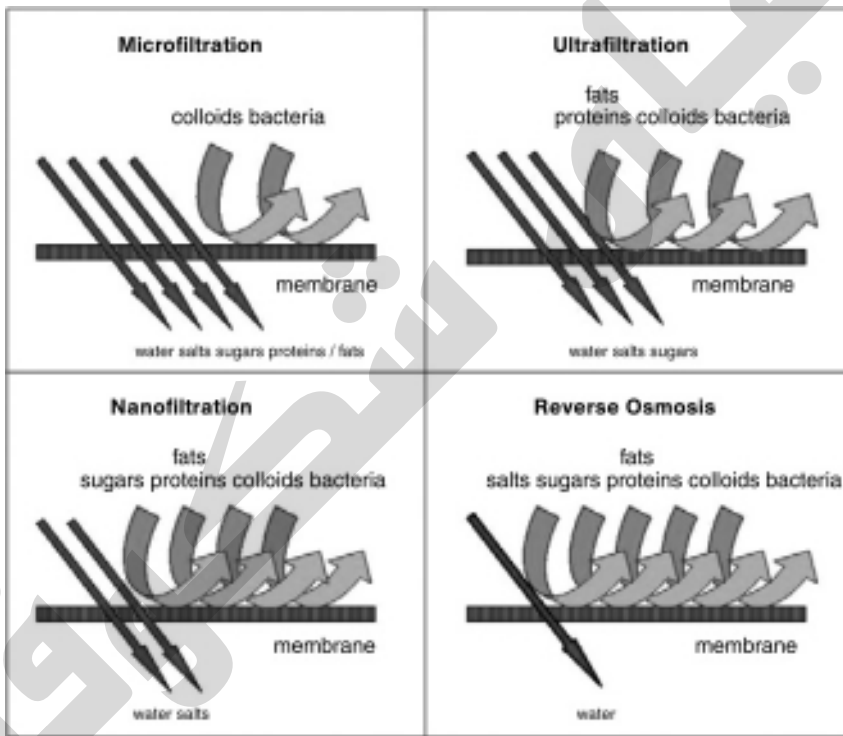


Figure 12.8 Crossflow filtration applied to various systems.

Pores differ in size because of diverse techniques in manufacturing. The same class of membranes may give a retention differing from one manufacturer to another [8]. Therefore, membranes are assigned a nominal cut-off (limits of filtration or selectivity). Berbenni and Nurizzo [9] report examples of selectivity (cut off) in Table 12.2.

Table 12.2 Examples of cut off.

Compound	Removal (%)		
	UF	NF	RO
NaCl	45	80	98
CaCl ₂	70	95	99
MgSO ₄	85	98	99
Glucose	88	98	98
Dye	90–95	90–95	95
Total Hardness	85–90	85–90	95
TOC	80–85	80–85	90

Table 12.3 Chemical structures of current membranes.

Polysulfone (PS)	$[-O-C_6H_6-C(CH_3)_2-C_6H_6-O-C_6H_6-SO_2-C_6H_6-]$
Polyethersulfone (PES)	$[-C_6H_6-SO_2-C_6H_6-O-]$
Polyphenylsulfone (PPS)	$[-C_6H_6-SO_2-C_6H_6-O-C_6H_6-C_6H_6-O-]$
Polyvinylidene fluoride (PVDF)	$[-CH_2-CF_2-]$
Polytetrafluoroethylene (PTFE)	$[-CF_2-CF_2-]$
Aromatic polyamide (PA _{ar})	$[-NH-C_6H_6-NH-CO-C_6H_6-CO-]$
Aliphatic polyamide (PA _{al})	$[-NH-(CH_2)_5-NH-]$
Acrylonitrile (ACN)	$[-CH_2-CH(CN)-]$
Ceramics (CE)	Al ₂ O ₃ /Al ₂ O ₃ coated with ZrO ₂ /TiO ₂
Polypropylene (PP)	$[-CH_2-CH(CH_3)-]$
Polyester (PES)	$[-O-(CH_2)_2-O-CO-(CH_2)_2-CO-]$

The concept of pores suits MF, UF, and NF. RO should be regarded as a non-porous membrane as permeate crosses the RO membrane through empty spaces of the polymeric molecules [5] according to various mechanisms proposed such as solution-diffusion, molecular sieve, steam pressure, preferential absorption-desorption, hydrogen bond and dielectric exclusion [8].

Great progress was made when the first cellulose acetate membrane, which was extremely sensitive to chemicals, was replaced by the current ones based on polymers able to tolerate larger variations of pH and temperature (polysulfone, fluoropolymer, polyamide, acrylonitrile, nylon, and spacers in polypropylene and polyester). The third-generation membranes were ceramic materials (aluminum and zirconium oxides). Ceramic MF accepts pH 0–13 and can even be sterilized with steam [8]. The latest generation is manufactured from carbon and silicon fibers. Table 12.3 gives the chemical structures of the current filtration membranes.

Each manufacturer supplying membranes states their chemical and physical tolerance, usually recommending limits for pH and temperature, as listed in Table 12.4.

Table 12.4 pH limits of current membranes.

Membrane material	pH	Temperature °C
CE	1–13	0–100
PS	1–12.5	0–65
PES	1–12.5	0–65
PVDF	1–12	0–60
CAN	2–10	0–55
RCA (regenerated cellulose acetate)	2–11.5	0–50
CA (cellulose acetate)	3–8.5	0–35
PS coated with PA, spacer PP (TFC) ^{a)}	1–11.5	0–60
PS coated with PA, spacer PE (TFC) ^{a)}	2–11.5	0–50

a) TFC = thin film composite.

Table 12.5 Current applications of various fibers.

	Spiral Wound	Plate & Frame	Ceramics	Tubular	Hollow Fiber	Pleated	Dead end
CA		X		X			
PS	X	X		X	X	X	
PES	X	X		X	X	X	
TFC	X	X		X		X	
Al ₂ O ₃			X				
RCA		X		X			
ACN				X			
PVDF		X					
Nylon						X	X

Table 12.5 gives the chemical structures of various types of membrane.

Membranes are expensive. Current developments are moving toward improvement of their resistance to chemical attack in order to give prolonged shelf life. In spite of this, the permeable membrane still remains the most vulnerable part of the cleaning treatment. The cleaning procedure must therefore carefully comply with the technical recommendations of the manufacturer (OEM). OEMs indicate chemical restrictions and pH limits. Detergents and procedures can be implemented only in compliance with these limits..

Membranes undergo poisoning. Iron, manganese, silicate, and colloids are usually found in raw water. These precipitate inert oxides, clays, and sulfides. As these are inert to chemical attack, the membrane life dramatically shortens in their presence. Raw waters from lakes, rivers, and marshes, for instance, include such substances and require careful pre-treatments (e.g., pre-filters, iron and manganese scavenging). Some limits are listed in Table 12.6 [9].

Table 12.6 Limits of acceptability of the commonest membrane poisons.

All membranes		NF and RO	
Iron	≤ 0.05 ppm	Conductivity	$< 5 \mu\text{S}/\text{cm}$
Manganese	≤ 0.02 ppm	Turbidity	< 1 NTU
Silicon dioxide (SiO_2)	≤ 5 ppm	Hardness	< 30 ppm
Suspended solid (colloids)	Nil	Particle size	$< 10 \mu$

**Figure 12.9** UF spiral wound membrane blistered by hot whey feeding.

Sensitive membranes (NF and RO) require more restrictive conditions. Permeate itself is normally used as dilution water to clean RO plants.

Temperature is another factor related to the durability of a membrane. As the filtering polymer is made of a plastic material, high inlet temperatures harm the membrane, and blisters are formed, irreversibly ruining the pore size, as Figure 12.9 shows.

12.2 Module

The semipermeable layer is the core of the filtering system. Spacers, supports, and housing decide its shape. These elements constitute a module, the structure of which supplies the highest possible density of filtering surface packed in the smallest body. The most common modules are described below.

12.2.1

Plate and Frame

The module represents the first type assembled and conceptually derives from the filter press. It uses flat membranes (flat sheet), and spacers (circular, elliptical,

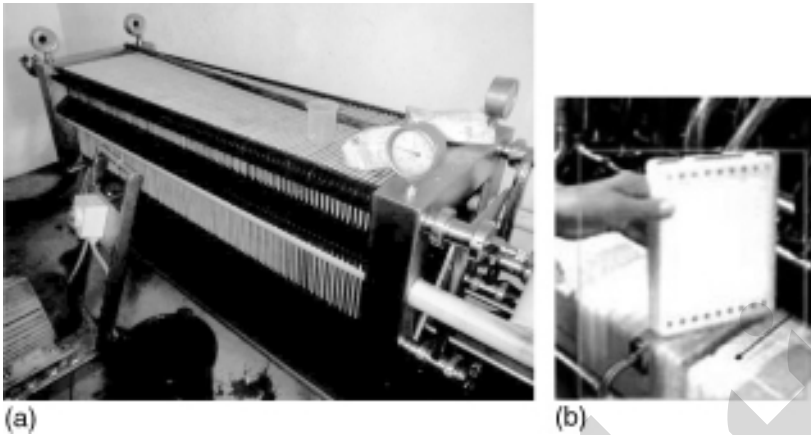


Figure 12.10 (a) conceptually derived from the traditional press-filter. (b) single plate and frame module (courtesy of Sartorius).

and rectangular) mounted in sandwich fashion and held together by bolts (see Figure 12.10).

The large number of gaskets, the tendency to rapid fouling, and the relatively expensive equipment result in the plate and frame module now being recommended for medium-to-small applications and laboratory equipment only.

12.2.2

Hollow Fibers

Two types of modules belong to the group:

- **Packed hollow micro-fibers**, where flow crosses from the outside to the inside. Flow is laminar. The microstructure exacerbates the occurrence of fouling. Fouling, difficulty of regeneration, and frequent breaking of fibers make this module restricted to treating clean liquids such as water for the electronics industry, pyrogen-free water for the pharmaceuticals industry, and gas purification [10].
- **Packed hollow capillary fibers** have a larger diameter than the hollow micro-fibers. Flow crosses from the inside to the outside. Fouling is less critical because back flushing can be applied. In spite of this, the module is mainly suitable for almost pure fluids (e.g., wine), removal of microbes, and gas purification [7].

Several hollow fibers are packed in one module. The integrity test can determine those damaged. Instead of changing the entire module, these fibers are isolated by blocking them with a plug. The Figure 12.11 shows plugged fibers with stainless steel stoppers.

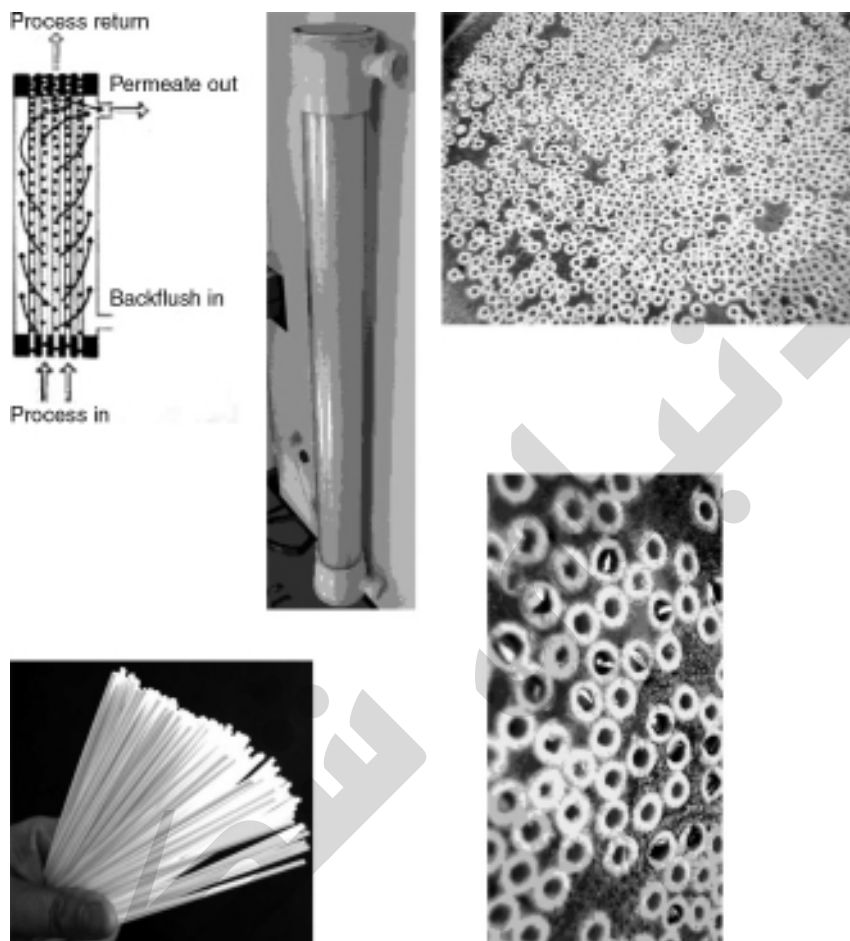


Figure 12.11 Hollow-fiber membranes.

12.2.3 Tubular

The tubular membranes are regarded as a development of the capillary ones. Their larger inner diameter makes them suitable to filter fluids rich in suspended solids and fouling substances. Fouling tendency is low and regeneration easy. The ceramic membranes belong to this group. Ceramics resist chemicals and temperature so they tolerate aggressive cleaning solutions and disinfection (inclusive of steam). Examples of tubular membranes are shown in Figure 12.12.

The phosphoric ion poisons a ceramic filter (phosphoric acid and its polymers when hydrolyzed to monomer). Thus, the use of phosphoric acid is not permitted.



Figure 12.12 APV structure of a ceramic module and types of membranes (courtesy of GEA Filtration).



Figure 12.13 Axial path of the SW membrane.

12.2.4

Spiral Wound (SW)

All the elements are wrapped around a central tube. Feed and concentrate are axial. Permeate follows a spiral path toward the central tube (Figure 12.13). Large filtering area, low fouling, low cost in initial investment, and cheap operation make this module the most interesting in the food industry.

The fully fitted module is a variant of the normal SW membrane. Larger spacers are set between the filtering membranes so as to facilitate the filtration of viscous solutions and highly concentrated solutions of solids. The modules vary and can assume behavior similar to that of the tubular membrane [10]. Figure 12.14 show possible arrangements of spacers.

SW membrane may suffer the ‘telescoping’ effect as shown in Figure 12.15. This twisted modification affects the flow characteristics through the spiral path and endangers the filtration performance.

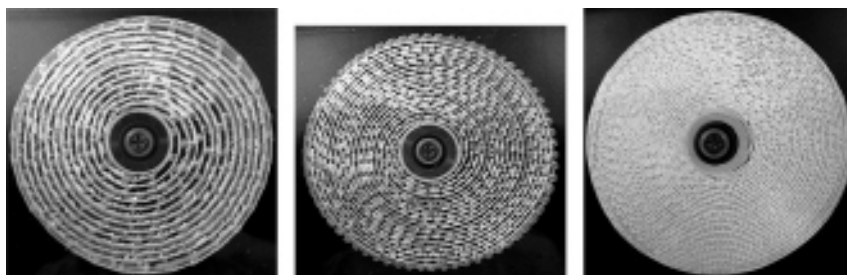


Figure 12.14 Various spacers.

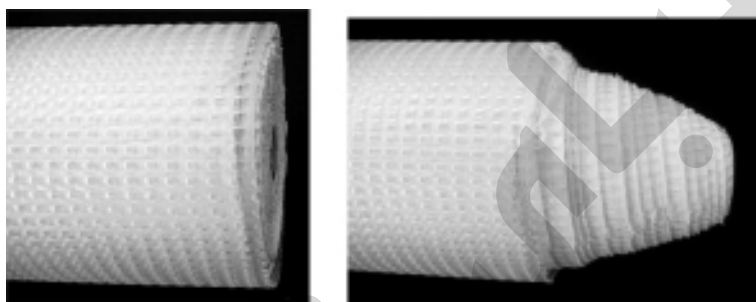


Figure 12.15 Telescoping effect.

In order to prevent deformations, an anti-telescoping device (ATD) is inserted at the end of each membrane, examples of which are shown in Figure 12.16.

12.2.5

Pleated

Instead of being wrapped, membranes are pleated (Figure 12.17). They undergo rapid fouling since the pleated configuration is based on dead-end filtration (Figure 12.17).

All the membranes described use filtration technologies determined by the pore size. Pores determine the exercise pressure (transmembrane pressure). The smaller the size, the greater the pressure. The Table 12.7 shows the average exercise pressure for different processes.

12.2.6

Modules

The membranes are housed and enter the process arranged in modules. Modules form different loops according to the needs of the process. The schemes shown in Figure 12.18 are commonly used.

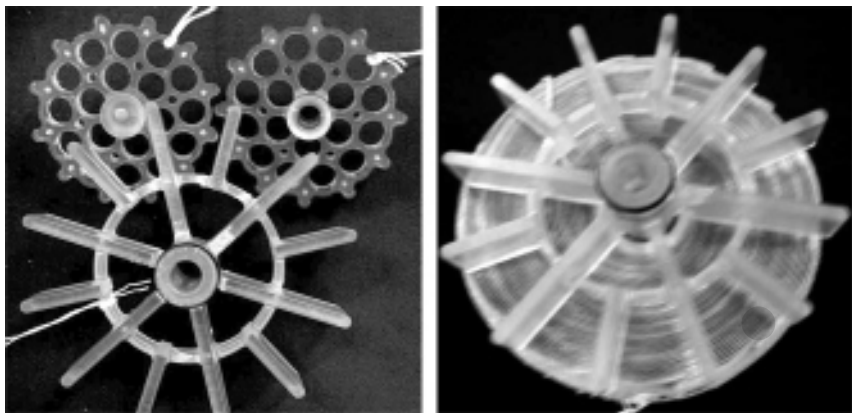


Figure 12.16 Anti-telescoping devices.

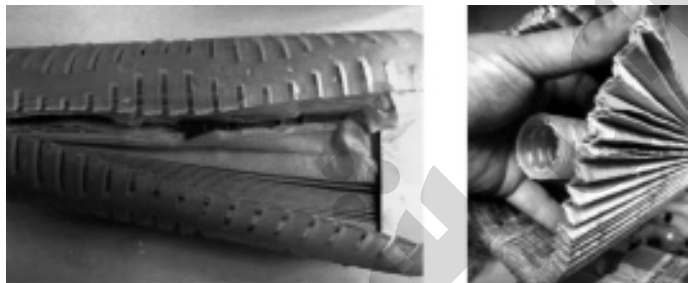


Figure 12.17 MF pleated membranes (dead end).

Table 12.7 Exercise pressures used in various filtration technologies (adapted from Ref. [9]).

Technology	Exercise pressure (bar)
Microfiltration	1–5
Ultrafiltration	1–10
Nanofiltration	5–20
Reverse Osmosis	10–70

The three graphs in Figure 12.19 show the influence of time, transmembrane pressure, and crossflow velocity on the filtration efficiency (permeate flux, $\text{Lm}^{-2}\text{h}^{-1}$). The trend has a minimum or a maximum (flattening). Thus, time, pressure, and velocity cannot be over-forced to enhance productivity. The steady condition is defined by correct values of pressure, velocity, and temperature. Cleaning must be performed when these deviate from prescribed values.

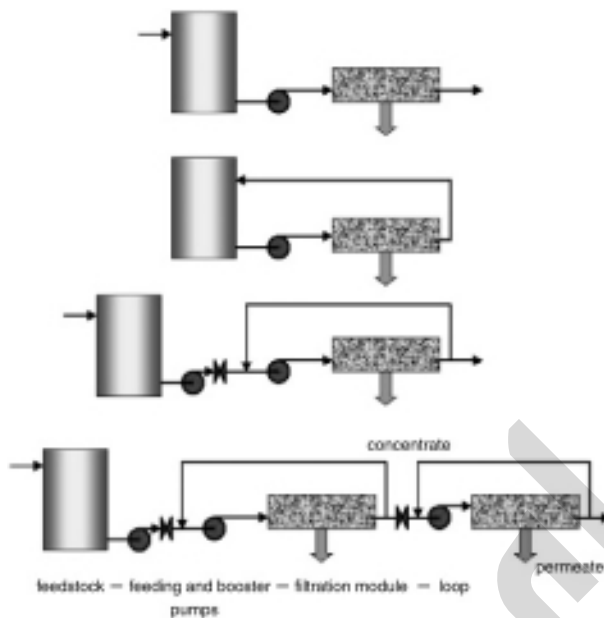


Figure 12.18 Examples of flow arrangements.

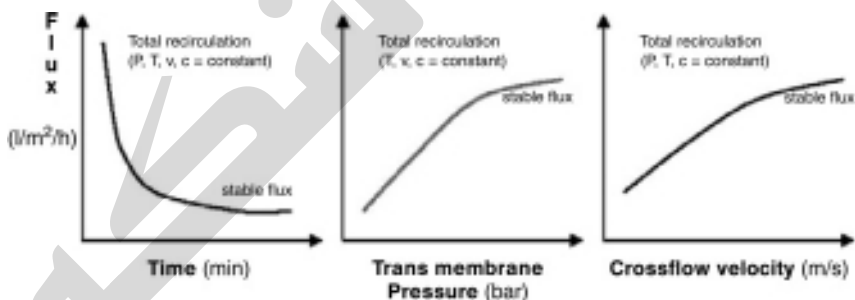


Figure 12.19 Time, transmembrane pressure, and crossflow velocity.

12.3

Diafiltration and Chromatography

Diafiltration is tangential flow filtration (TFF) usually performed in combination with any of the other categories of separation to enhance either productivity or purity. In processes where the product is in the retentate, diafiltration washes components out of the product pool into the filtrate, reducing the concentration of undesirable species. When the product is in the filtrate, diafiltration washes it

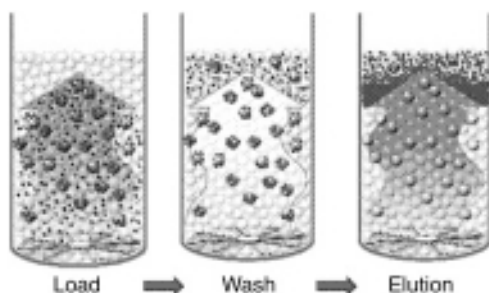


Figure 12.20 Target molecules are retained, unwanted material is washed away, and target molecules are released (courtesy of UpFront Chromatography AS).

through the membrane into a collection vessel. Since diafiltration is considered to be an ancillary process, the first step is to define what the process must achieve and what goals must be met:

- final product concentration
- feed volume reduction
- contaminant removal specification.

Diafiltration is frequently connected to UF to make the whey proteins concentration more effective (WPC). Whey contains less than 1% of proteins, together with lactose, salts, and a trace of fats. However, its proteins have the highest biological value of any known proteins. Diafiltration, added to the UF process, can increase WPC output by up to 80%. Reduction or elimination of fat and salts yields purified proteins (WPI). WPI are the start point of many other derivatives such as immunoglobulins, bovine serum albumin (BSA), glycomacropptides, beta-lactoglobulin, alpha-lactoalbumin, lactoperoxidase, and lactoferrin [11].

Proteins from WPC are a commodity. The added value consists just in their purification and separation of their components. Expanded bed adsorption chromatography (EBA) is successfully applied for large scale fractionation, purification, and isolation of proteins [12]. Ionic exchange chromatography separates proteins by exploiting their different isoelectric points. Proteins have groups positively or negatively ionizable as a function of pH. Acting on this property, an appropriate ion exchange resin can separate the components. For instance, since pH 9.0–9.5 includes the isoelectric points of lactoferrin and lactoperoxidase, these have a positive charge in the original whey (pH 6.2–6.6). Therefore, they can easily be separated from beta-lactoglobulin, alpha-lactoalbumin, and bovine serum albumins (negatively charged) by a proper adsorbing bed. Afterwards, suitable eluents selectively remove proteins from the resin and separate a highly purified protein [12]. The principles of the process are schematically represented in Figure 12.20 [13].

12.4

Electrodialysis

The stabilization of wine benefits from the electrodialysis process (ED). Stabilization of tartaric acid is conventionally obtained by cooling (bitartrate crystallization) and adding metatartaric acid (crystal growth inhibition). However, the bitartrate crystallization also causes unwanted modifications in the wine such as precipitation of colloidal and coloring substances. One of the less conventional processes for wine stabilization makes use of selective membranes combined with an electric field. The process forces specific ions to migrate into a discriminating flux of molecules that are separated from the wine bulk by charged membranes. This is the essential concept governing electrodialysis. A schematic representation of the ED concept is given in Figure 12.21 [14].

The cationic membranes, namely the membranes permeable to anion (mpa), have an anionic charge from sulfonic or carboxylic groups, and the anionic membranes (mpc) have a cationic charge from ternary or quaternary nitrogen. A difference in potential between two electrodes makes anions migrate to the cathode and the cations to the anode. Thus, two membranes of opposite charge select and concentrate ions into zone 2 (see Figure 12.21).

Wine cannot be standardized. Each wine is checked using an instability test (cooling and conductivity variance). The result of the test decides how the electrodialysis process should be set [14], that is, how many cations and anions will be removed. Potassium, calcium, and tartrate ions are subjects of wine chemical stabilization. Electrodialysis simplifies the process and makes it friendly to the quality of wine. However, electrodialysis is usually carried out on low valued wines intended for rapid consumption. High-quality wines require several months or years of natural ageing (generally in wood) and undergo negligible or no improvement from the electrodialysis technique.

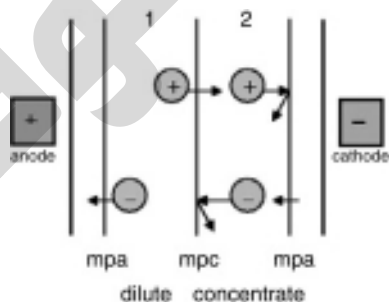


Figure 12.21 Electrodialysis: 1 = dilute zone (wine), 2 = concentrate zone, mpa = membrane permeable to anions, mpc = membrane permeable to cations (adapted from Ferrarini [14]).

12.5

Ultrasound Applied to Membrane Processings

The filtration process concentrates solids. Their agglomeration at the membrane interface causes loss in productivity (decrease in permeate). Plant stoppage and cleaning are periodically applied to restore the steady condition. The combination of crossflow filtration and an ultrasonic device helps to keep membranes performing longer. Ultrasound provides the system with vibration energy sufficient to force particles to remain suspended and generate preferred channels that favor the elution of the liquid. Adjustable ultrasound probes and an 18–27 kHz generator coupled to crossflow filtration assist in prolonging the performance of the membrane in [15].

A particular synergistic application, for instance, is found in fresh food preparation, where microfiltration is implemented to purify and re-use the process water, and ultrasound supports the cleaning and detachment of macroorganisms from vegetables (insects, larvae, and nematodes).

12.6

Fields of Application

Crossflow technology is expected to improve quality and productivity, reduce costs, save space and personnel, and increase profitability. Thus, crossflow filtration has extended into every type of industry. The following list includes only a few out of the huge number of its applications [7].

Food and beverage

- clarifying of fruit juices, beer, and musts
- stabilization of wine
- removal of alcohol from beer and wine
- cold sterilization of beer
- concentration of fruit juices
- concentration of proteins in jellies
- concentration and purification of whole egg and albumen
- recovery of proteins from manufacturing waste from cereals, starches, yeasts, and enzymes
- removal of microorganisms
- separation and re-assembling of milk
- energy saving from concentration processes.

Dairy

- concentration of milk proteins
- recovery and concentration of whey proteins
- separation of whey proteins and desalination
- continuous production of fresh cheese

- concentration of lactose before evaporation
- water recovery

Pharmaceuticals and bio-technology

- concentration and purification of enzymes, antibiotics, proteins, bacteria, and yeasts
- production of pyrogen-free water and glucose solutions.

Primary and wasted water

- sea water desalination
- removal of colloids, bacteria, virus, dyes, and suspended solids
- cost reduction and better quality of ultra-pure water for electronics
- better efficiency and cost reduction in removing oils, metals, and detergents
- recovery and concentration of latex, inks, pigments, paints, tannins, resins

Primary and wasted gas

- carbon dioxide separation from methane in anaerobic processes and methane fields
- air enrichment in oxygen for burners
- hydrogen recovery from chemical processes.

Waste water treatment

- sludge concentration
- water recovery.

12.7

Cleaning

Fouling is an obvious consequence of the filtration process even in the crossflow system, as the membranes in Figure 12.22 show.

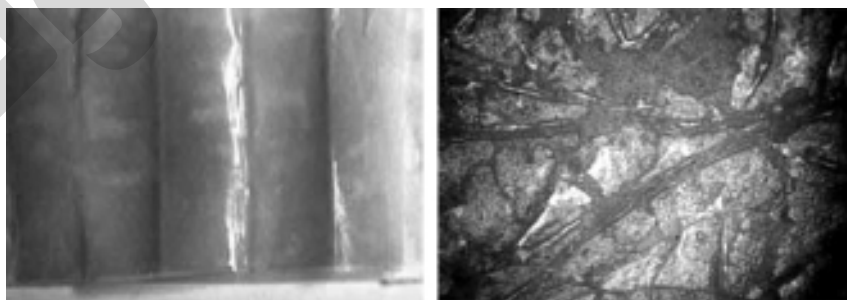


Figure 12.22 Fouling on pleated MF membrane of apple essence water. The same membrane under a microscope reveals fouling resembling a glassy layer.

Diminished or blocked permeation is restored by cleaning procedures. Although the stability of the permeable layer toward chemicals has been substantially improved in the current generation of membranes, the permeable layer still remains the vulnerable point of the cleaning treatments. RO and NF have pores with a smaller margin of tolerance, so that these membranes are even more critical. Therefore, manufacturers supply technical data for these membranes that include compatibility and limits of pH and temperature. Cleaning procedures are tailored according to these specifications. Only approved detergents comply with the required limits of alkalinity, surfactants, solvents, percentage in-use, and pH.

Statements from OEMs about the restrictions that apply to the use of detergents can be summarized in five points:

- Aggressive detergents are only approved on membranes freely tolerating alkalinity and acidity (pH 1–13). Detergents are applied in concentrations usually not exceeding 2% of pure alkalinity and acidity. Ceramic membranes belong to this group.
- pH governs detergent application on membranes sensitive to causticity and acidity (pH usually below 12 and above 1).
- More sensitive membranes (e.g., RO and NF polyamide membranes) need a pH buffered within a smaller range (below 11 and above 1). Cleaning is often achieved using enzymatic detergents. Cellulose acetate membranes require pH values closer to neutrality.
- Membranes developing a (partially) charged surface cannot come into contact with surfactants. Surfactant-free detergents are mandatory on these membranes.
- Phosphate ion (phosphoric acid and, less compulsorily, its polymers) damages the ceramic membranes. Phosphate and phosphoric acid-free detergents are therefore recommended for cleaning these.

Detergents have to deal with porous surfaces, but these encourage the growth of fouling inside the membrane frame. Consequently, detergents are formulated with agents having carrier and anti-redeposition effects. The former remove soil from the inside and the latter prevent its redeposition. EDTA, phosphonates, and hydrogen peroxide constitute detergent builders, which with ancillary additives achieve thorough and rapid cleaning.

If plant does not immediately start running again after cleaning, suitable preservatives should be added to prevent the growth of biofouling (microorganisms). Sulfur dioxide (SO_2), from acidified bisulfite, is an effective solution applicable to every membrane.

12.7.1

Alkalinity

Of the alkalis, caustic soda and potash have the small ions Na^+ , K^+ and OH^- , and are suitable for all the membranes and, as they cross from concentrate to

permeate, are effective for cleaning in depth. The comparison between caustic soda and potash has been already discussed (Section 5.2). Sodium forms more rigid structures than potassium at room temperature. Flexible compounds of potassium (e.g., soaps) are more readily pulled out of the pores than sodium ones.

Polysulfone, fluoropolymers, and polyethylene even resist high percentages of alkalinity. Conversely, sensitive membranes (Section 12.1) can only resist low concentration of caustics. However, builders (sequestrants and surfactants) must always be kept in a high enough concentration to achieve cleaning. Hence, a decrease in concentration when using a caustic detergent is not the best way to comply with the pH limits. It is more efficient to change the detergent and move to mildly alkaline products rich in builders.

Pectins, gums (e.g., xanthan and carrageenan), gelatin (e.g., fish glue), typical natural or added components to fruit and wine processes, prove particularly resistant to cleaning. In these cases, oxidizing agents provide detergents with the ability to detach soil. Hydrogen peroxide added to an alkaline detergent is an eco-friendly and effective alternative to chlorine.

12.7.2

Sequestrants

Filtration clogs membranes with dirt, and this is protected by the surface morphology. As well as alkalinity, the ability of sequestrants to keep polyvalent cations in solution and re-solubilize them if they are precipitated is a key factor in achieving a successful cleaning (Figure 12.23).

Figure 12.23 shows a water deionization RO membrane damaged by the growth of calcium carbonate and calcium sulfate crystals, which cause stressing and thinning of the filtering polymer. The damage visible in the form of points of light.

Sequestrants weaken the deposit through carrier, suspending, dispersing, and anti-redeposition ability. Combinations of stoichiometric (carrier) and threshold (anti-redeposition) sequestrants are also required to protect the membrane during the infinite dilution of the rinsing step. EDTA, the best carrier agent, is always

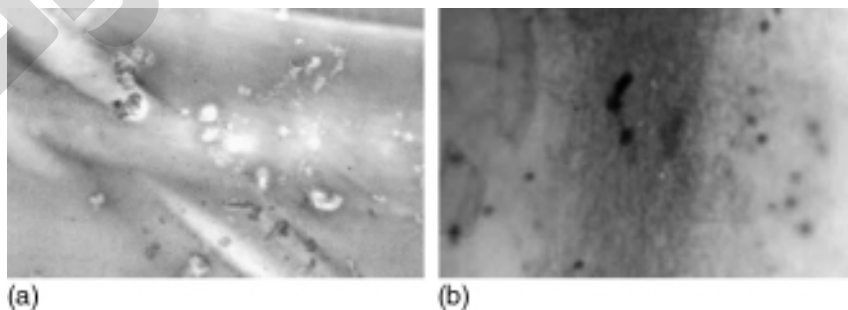


Figure 12.23 (a) Inorganic crystals on RO membrane (water demineralization) and (b) gums on MF membrane (wine clarification) under a microscope.

included in detergents if permitted. Otherwise, NTA and IDS can satisfactorily replace it. Phosphonates (e.g., ATMP and PBTC) and STP are co-formulated to develop anti-redeposition. Since EDTA, NTA and IDS are unstable to chlorine, STP and PBTC are mandatory in chlorinated detergents.

Polyphosphates (hexameta, pyro, and tripolyphosphate) and monophosphates form the basic buffer for enzymatic detergents.

Phosphoric ion poisons ceramic membranes, so phosphate-free detergents and acids are specifically formulated for cleaning these.

12.7.3

Surfactants

Suitable surfactants have been identified to clean polymeric porous structures and prevent stress cracking and selective adsorption. The properties of the full range of surfactants are briefly summarized below.

- Surfactants wet and clean fatty substances. They are usually needed.
- EO and PO condensed nonionic surfactants are responsible for chemical stress cracking.
- Noncondensed anionic and amphoteric surfactants are stress cracking free.
- Amphoteric surfactants give high foam and low detergency.
- Cationic surfactants are adsorbed. They irreversibly damage the filtering area.
- Specific nonionic surfactants are effective against foam (defoamers). However, there is no need to depress foam in membrane cleaning.
- The morphology of membranes makes rinsing of surfactants difficult.

Anionic surfactants are effective against fats and preserve the integrity of membranes, and are therefore to be preferred. Dodecylbenzenesulfonate, alkanesulfonates, and α -olefinsulfonates are usually found in formulated detergents and boosting additives.

12.7.4

Enzymatic Systems

The enzymatic detergents were developed to meet the cleaning needs in RO and NF processes (polyamide coated). Enzymes lose their activity soon after contact with water. An aqueous medium destabilizes them. Therefore, enzymes were incorporated in powder detergents at an early stage. Liquid detergents are prevalent now (automatic CIP). In order to keep enzymes effective, liquid detergents are split into two parts: the enzyme and the buffered builders.

The enzyme is preserved in components containing little or no water, such as surfactants and glycols. As most of the food deposits include proteins, protease is the preferred enzyme. Lipase frequently synergizes with protease to remove fatty matter as well. Other specific enzymes are available such as amylase, cellulase, and enzymes for egg (see Section 8.6).

Builders and buffering salts are included in the usual aqueous product. A suitable combination of monomeric and polymeric phosphates to give a mild pH

buffer (~10) together with sequestration, suspension, and dispersion (phosphonates) was produced, this being the formulation of the builder components. Since mild alkalinity decreases the cleaning efficiency, enzymes compensate for the absence of chemical strength.

Enzymatic cleaning is currently considered to be an all-purposes procedure able to restore the functionality of a filtering plant. Over-use leading to exhausted membranes makes the fouling impossible to remove with the usual cleaning products. Such membranes, soaked in enzymatic detergent for several hours (even overnight), regain their functionality and often have extended lifetimes. The concentration of whey proteins in RO is an example. The daily procedure is based on alkaline cleaning ($\text{pH} < 11$) reinforced with EDTA, anionic surfactant and, sometimes, hydrogen peroxide, followed by the acid and another alkaline step. Nevertheless, an enzymatic soak is included once a week to restore the normal flow of permeate.

12.7.5

Acids

The acidic step normally follows the alkaline and chlorinated alkaline cleaning in order to complete the removal of soil, mainly the inorganic deposit. In some cases, when there is a considerable amount of phosphate (e.g., whey), the first (acidic) step prevents precipitation of calcium phosphate. It is difficult to keep calcium phosphate soluble in caustic solutions. Its re-solubilization from the inside of pores is difficult. The early acidic step removes most of phosphate (no precipitation in acid). As an alternative, the first contact with a highly sequestered low-alkaline detergent ($\text{pH} 10$) can be used to prevent precipitation and remove phosphate. Examples of calcium phosphate precipitation on membrane are shown in Figure 12.24.

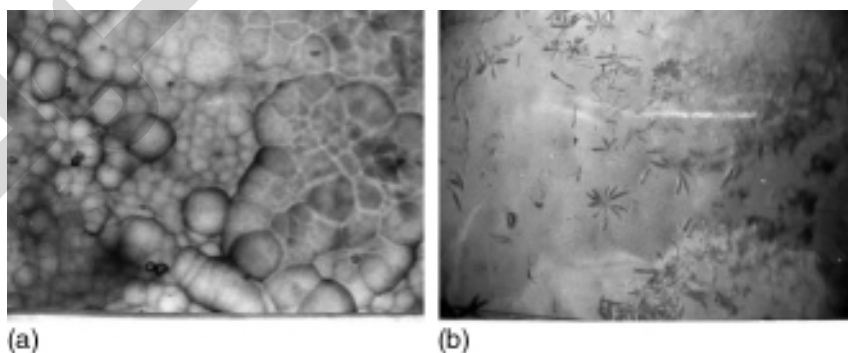


Figure 12.24 (a) Calcium phosphate/casein deposit in milk concentration UF membrane and (b) Calcium phosphate crystals on brine purification UF membrane in cheese hardening (photomicrograph).

Nitric is the only acid able to resolubilize calcium phosphate. Phosphoric acid is effective in removing proteic deposits. Thus, nitric and phosphoric acids form the best blends to descale membranes.

Blends of citric, lactic, and glycolic acids are specific products aimed at solving problems of iron and manganese deposits.

As already mentioned, phosphoric acid harms ceramic membranes. Phosphoric acid-free detergents are mandatory for this application.

12.8 Cleaning Procedures

Although each filtration plant has its own procedure, cleaning methods can be grouped into a few basic procedures from which all the others derive as local variants. The basic concepts are described as follows:

- The general procedure needs two steps of washing at least: the alkaline followed by the acidic one.
- When the risk of phosphate precipitation is high, the acidic step comes first. An alkaline and another acidic step follow the first. Mildly alkaline detergents (pH < 10) rich in sequestrants may alternatively be used as the first step.
- When an intense cleaning is required, the procedure also includes either alkaline chlorinated detergents or hydrogen peroxide added to alkaline detergent. For very intense cleaning and sanitation, the chlorinated detergent can follow the acidic step. Chlorine is only permitted on MF and UF. It damages NF and RO membranes.
- When raw waters are being treated, an acidic wash only may be sufficient. A periodic complete cleaning, inclusive of an alkaline step, is required to remove biofouling metabolites.
- As well as their typical use on reverse osmosis, enzymatic detergents are widely exploited on every type of membrane (usually soak technology).
- Every procedure can end with a disinfecting step.
- During a plant shut-down, membranes are preserved from the microbial pollution by keeping a few ppm of compatible disinfectant inside (e.g., sulfur dioxide).

A summary is given in Table 12.8.

All tailored procedures are considered to be variations of the general methods described above. Approved products and their concentrations are selected for each membrane depending on their compatibility and the type of soil. It is usually recognized that

- The best reproducibility of the flow of permeate is obtained by ending the procedure with an alkaline step.

Table 12.8 Basic cleaning procedures.

General cleaning	Risk of phosphate precipitation		Deep cleaning and disinfection		Raw water filtration	Enzymatic detergent	
Rinse	Rinse	Rinse	Rinse	Rinse	Rinse	Rinse	Rinse
Alkaline	Acid	Enzyme or mild alkaline	Alkaline	Enzyme	Acid	Enzyme	Mild alkaline
Rinse	Rinse	Rinse	Rinse	Rinse	Rinse	Rinse	Rinse
Acid	Alkaline	Acid	Acid	Acid	Disinfection	Acid	Acid
Rinse	Rinse	Rinse	Rinse	Rinse	Rinse	Rinse	Rinse
Alkaline	Acid	Alkaline	Chlorinate	Chlorinate	(Alkaline step suggested)	Enzyme step	Enzyme step
Rinse	Rinse	Rinse	Rinse	Rinse		(or alkaline)	(overnight
		Acid				Rinse	soaking)
		Rinse					Rinse
Disinfection step in every procedure, if required							
Preservative treatment after cleaning, if the plant rests							

- Proteic deposits need cleaning with enzyme and/or oxidizing detergent (chlorine or hydrogen peroxide, if permitted).
- Carbohydrate deposits (starch, gums, pectin, xanthan, carrageenan) need cleaning with addition of hydrogen peroxide to the alkaline step.
- A correct blend of carrier and threshold sequestrants plays a significant role in achieving good cleaning (e.g., EDTA, NTA, IDS, MGDA phosphonate and tripolyphosphate).
- Anionic surfactants are added as ancillary additives to clean fats.
- EDTA is added as an ancillary additive to solubilize crystalline deposits (e.g., phosphate and oxalate).

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13

Milk Production

Most industrial and handcrafted foods make use of milk, one of the main products of farming.

Breeding, growing, nourishing, and preserving animals requires hard work and great care to obtain the highest volume of milk of the best quality. Quantity and especially quality also depend on the provisions of the law. Nevertheless, one of the universal rules relates the quality of milk to the net profit obtainable while minimizing the microbial charge and the quantity of somatic cells accumulated during milking. Bacteria and somatic cells are directly proportional to each other and are connected through the typical disease known as mastitis in clinical and sub-clinical form. Microbial charge and somatic cells in raw milk depend on

- animal care before milking
- cleanliness of the milking equipment and refrigerated bulk milk tank
- mechanical condition of the milking equipment
- health of the cattle
- environmental conditions, on which cattle health largely depends
- appropriate cooling of the bulk milk tank
- performance of the milking operative.

Several of the aforementioned parameters depend on the milking operative, whose performance, including looking after the cows and the milking, determines the level of microbiological charge and somatic cells in the milk. Figure 13.1 shows the two ways that cows live.

13.1

Mastitis

As already mentioned, bacteria and somatic cells are interconnected through the typical disease known as mastitis in its clinical and sub-clinical form. Mastitis is the result of a defense against microbial infections whereby the cow releases white globules and flaking tissue cells that enter the milk. The milk quality depends on the level of the bacterial population and the amount of somatic cells, the limits of which are governed by domestic and international agreements.



Figure 13.1 (a) Freely grazing cows and (b) intensive cattle farm.

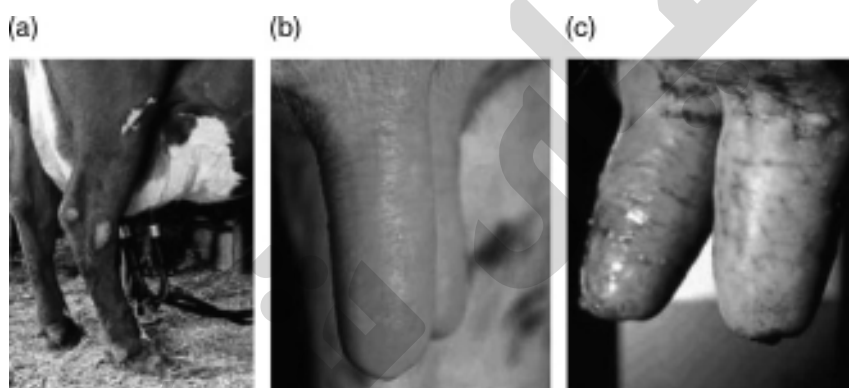


Figure 13.2 Milking unit (a), sound (b), and infected (c) teats (courtesy of Diversey Co. Agri Department).

Bacteria responsible for mastitis originate from various sources and are generally divided into two groups:

- **Infective bacteria**, living on teats and responsible for spreading infection from animal to animal through the milking unit. *Staphylococcus aureus* and *Streptococcus agalactiae* are typical bacteria of this group. They cause intense and long-lasting mastitis.
- **Environmental bacteria**, living on litter and cow's hair. They cause intense but brief mastitis and mainly include *Streptococcus uberis*, *Streptococcus dysgalactiae*, and *Escherichia coli*. A simple milking unit and sound and infected teats are shown in Figure 13.2.

Mastitis lowers milk quality and dairy productivity by causing composition changes affecting proteins, fat, and minerals (Table 13.1).

The farmer loses his quality award and suffers a reduced volume of milk and increased veterinary expenditure.

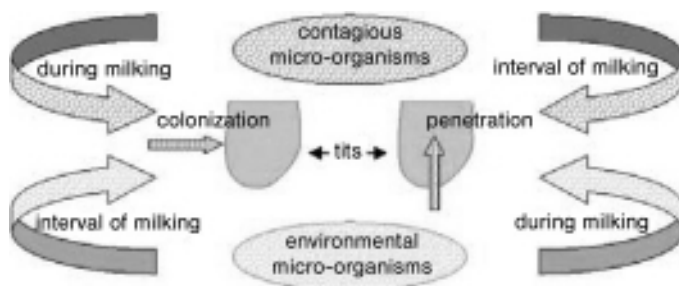


Figure 13.3 Microorganisms colonize and penetrate teats in different ways and at different times.

The animal, the environment, and the farm worker interact to keep bacteria controlled (Figure 13.3). Intensive cattle farms make optimum use of animals (4–5 calvings) but generate conditions of stressed and short-lived cows in comparison with animals living in an open environment. What is lost because of an intensive life should be restored through animal and environmental care (feeding, handling, and disinfection). Disinfection is achieved by the application of ready-to-use disinfectants to the skin. They are formulated with

- chlorexidine, benzyl alcohol, polybiguanide, and iodine as disinfectants
- lactic acid and sodium lactate as co-disinfectants with buffering activity
- essential oils as long-lasting antiseptic agents on the skin
- allantoin as a healing component
- glycerol, propylene glycol, and sorbitol as emollients

Disinfectants can be free-flowing liquids to spray on teats or thick liquids to be used in dipping. Examples of the use of thick disinfectants for dipping are shown in JohnsonDiversey's technical brochures (Figure 13.4).

13.2 Cow and Milk

A healthy herd of cattle is the treasure of a farm. It is attainable through years of selective breeding aimed at producing a herd specifically for quality and quantity either of milk or meat. As far as milk is concerned, cows can be directed to produce milk rich in fats or proteins according to the long-term planning. Table 13.2 gives approximate average compositions of milk from different species.

It is obvious that any change in strategy is slowly achievable. A modification of planning forced by sudden legislative directives causes damage and confusion to the overall agricultural industry. This is more understandable after looking at the life cycle of an average cow as set out in Figure 13.5.

In terms of detergency, the chemistry of proteins, fats, phosphate, calcium, and magnesium have already been extensively discussed. Fortunately, raw milk does

Table 13.1 Composition changes caused by mastitis (courtesy of JohnsonDiversey).

Milk	Cow	Buffalo	Ewe	Mastitic milk
Water (%)	87.5	81–85	81.5	Increase
Protein (%)	3.2	4.2–5.0	6.2	Invariable
Whey proteins	0.6	0.8–1.4	1.0	Increase
Casein	2.6	2.8–4.2	5.2	Decrease
Fat (%)	3.5	7–9	5.8	Decrease
Calcium (%)	0.12			Decrease
Minerals (Na, Cl, K) (%)	0.9		0.8	
Lactose (%)	4.9	4.5–4.8	4.5	Decrease
Cryoscopy point	–0.520°	–0.560–0.590		Invariable
Somatic cells	<200 000	<500 000	<1000 000	Up to 15×10^6
Total bacteria count	10–20 000 (<100 000)	<500 000	<500 000	Uncountable



Figure 13.4 Use of thick disinfectants (iodine and clorexidine based) for dipping (courtesy of JohnsonDiversey Agriculture Technical Centre).

Table 13.2 Approximate average compositions of milk from different species (wt%).

Species	Total solids	Fats	Proteins	Lactose	Minerals/water soluble vitamins
Cow	12.6	3.7	3.6	4.6	0.7
Sow	20	8	6	5.2	0.8
Ewe	17	5.8	6.2	4.5	0.8
Rabbit	35	18.3	14	2	0.7
Human	12.4	3.8	1	7	0.6

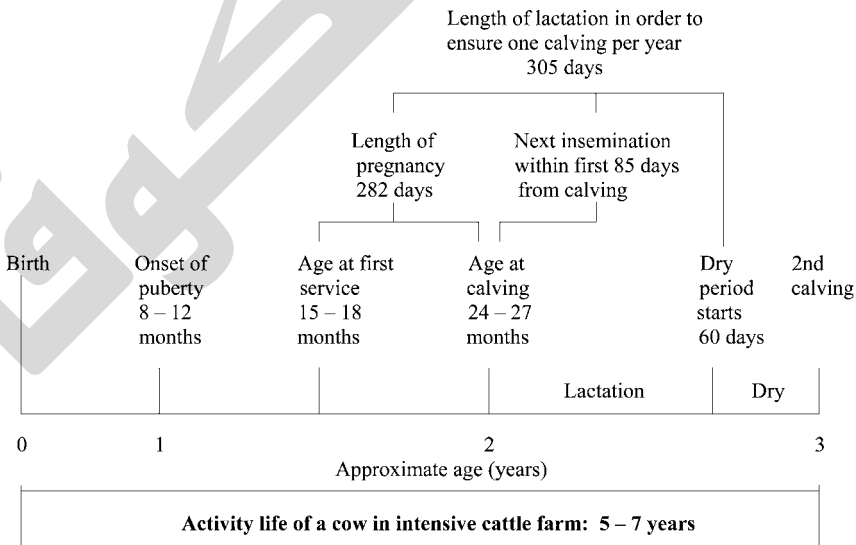


Figure 13.5 Life cycle of an average cow.

not undergo heat treatment on the farm, so all the constituents retain their original structure. Milk is only cooled before being collected in order to restrict the growth of the microbial charge. Two groups of equipment are involved in milking and are subjected to thorough cleaning: the milking machinery and the bulk milk cooling tank.

13.3 Milking CIP

The milking system requires a fairly complex CIP, consisting of vacuum lines, peristaltic pump, milking cluster, and filter, also pipelines and pumps for milk collection and transport to the bulk tank. The equipment consists of various materials such as stainless steel, galvanized steel, glass, and rubber, and is situated in a room which can simultaneously serve from 2 to 32 milking places arranged abreast or in single tandem, double tandem, herringbone, or rotary tandem as schematized in Figures 13.6 and 13.7.

As well as the equipment described, milking by robot is interesting because it can be carried out without human aid. The robot is arranged as a completely automatic milking station for which cows are trained for some weeks. After training, cows spontaneously enter the robot for milking, whenever they like, with no

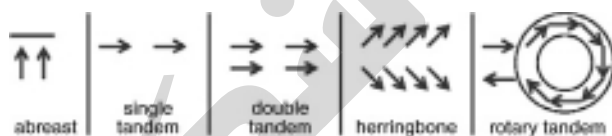


Figure 13.6 Geometrical positioning of cows.



Figure 13.7 Twelve milking places in the herringbone arrangement.

human presence. One robot performs all the operations before, during, and after milking for roughly 70–80 animals. It guarantees an increase in milk production and a saving in manpower cost.

The paths of milking and CIP coincide. A balance tank is added to deliver the cleaning solution and rinsing water. Figure 13.8 shows the balance tank and associated ancillary equipment.

Milkstone is the typical contamination of milking equipment. The composition of milkstone depends on the water hardness, temperature of cleaning, type of detergent and procedure, type of animal, and layout of equipment. The constituents of milkstone are listed in Table 13.3, which also indicates the composition range for each constituent.

Molds are always detected in the microbiological analysis of milkstone grown in milking equipment. Together with the fat, proteins, calcium, phosphate, and generic micro-organisms, molds take a leading role in starting up and promoting the contamination of milking equipment. Since there is no heat exchange, alkaline detergents should readily remove the organic and inorganic dirt. However, if only an alkaline detergent is applied, whitish grains appear inside the milk header (Figure 13.9) even though this detergent includes a high concentration of powerful sequestrants such as EDTA, tripolyphosphate, and phosphonates.

The yellow-whitish grains multiply after each milking until, within a few weeks from starting, they cover the entire surface with a compact deposit. This layered soil is known as milking milkstone, the origin of which is different from that of the heat milkstone found in the pasteurizer and sterilizer. Viewed through a



Figure 13.8 Example of cleaning equipment.

Table 13.3 Composition of milkstone in milking equipment (wt%).

Water	25–50	Proteins and organics	10–34	Minerals	2–17
Fat	6–28	Lactose	trace	Molds and bacteria	



Figure 13.9 Jars and their valves showing milkstone formation due to unsuitable cleaning.

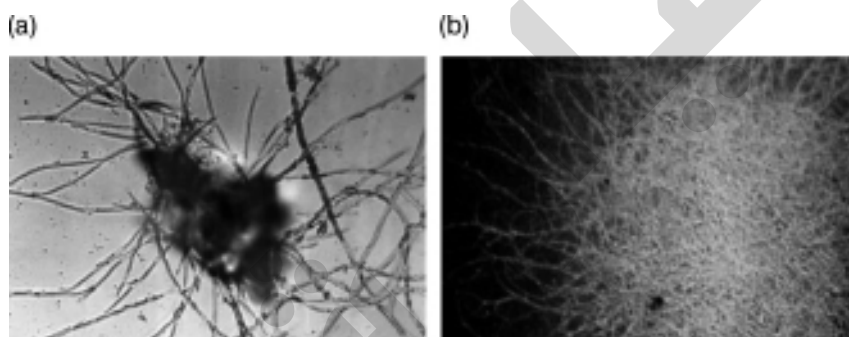


Figure 13.10 (a) Mold colony, and (b) spreading viewed under a microscope (courtesy of Diversey Co. [1]).



Figure 13.11 Dry milkstone.

microscope, the starting contamination (single grain) is seen to be made up of a mold colony sited under a gelatinous coat in which bacteria move around. Figure 13.10 shows the structure and typical spreading behavior of the starting mold.

This spreading process contaminates the whole surface, as shown in Figure 13.11.

It is known that molds bind themselves to the surface through glycol-protein materials cemented by metals [1]. Cleaning is effective if the detergent succeeds in detaching molds by destroying their links with the surface. Chlorine proves to be the most effective and rapid agent for removing milkstone and preventing its growth. The higher the concentration of chlorine, the more effective and rapid is the removal. Thus, the best detergents for CIP of milking equipment develop more than 4% of free chlorine, the key to a good cleaning operation.

The presence or absence of molds inside the milking equipment depends on the final draining after rinsing, which is accompanied by some minutes of forced recirculation of the environmental air. The farm environment is full of spores, as illustrated schematically in Figure 13.12.

The environmental spores are carried with the air inside the equipment, remain trapped, and have time to sprout and grow from one milking to the next. Only a detergent (e.g., chlorine) able to detach molds at their first stage of growth enables effective cleaning of the milking equipment to be performed.

Chlorinating chemicals are unstable to light and high temperatures (summer), so that large amounts cannot be stocked on a farm. Hence, small canisters are usually supplied, and this increases the amount of plastic to be disposed of. Therefore, chlorine-free detergents were investigated in order to provide farms with a stable detergent in re-usable larger containers. The result of the investigation has simply confirmed that removing milkstone without the help of chlorine is difficult. However, if cleaning is carried out using alkaline and acidic detergents on alternate days, the result will still be satisfactory.

The chlorinating chemical used is sodium hypochlorite, a compound stable in alkaline detergents. Thus, the alkaline detergents based on hypochlorite include a little sequestrant to prevent scale and a minimum of caustic soda to just neutralize the acidic sequestrants during the manufacture of the detergent. A few sequestrants are stable to the strong oxidizing action of chlorine. These include PBTC, acrylic homopolymers, phosphonoacrylates, and phosphinoacrylates. Tri-polyphosphate still remains an excellent alternative to the phosphono-phosphino-polyacrylate technology.

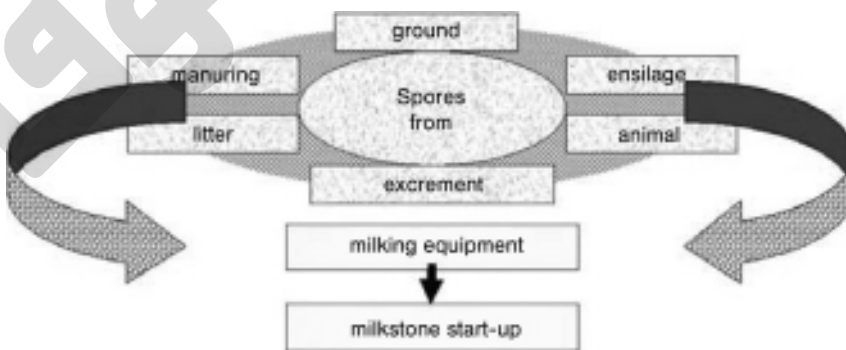


Figure 13.12 Various routes taken by spores entering the milking machine.

13.4

Bulk Milk Tanks

The bulk milk tank collects and cools milk at 4°C in order to keep the microbial charge at its initial level for as long as possible (Figure 13.13). The inside of the cooling tank is fairly complex, incorporating components such as a milk agitator, a dipstick rod and holder, a thermostat and a thermometer shaft. These help to control cooling but prove to be an obstacle to a smooth wash. Cleaning is carried out manually or through centralized CIP. It meets with same requirements and uses the same detergents as the milking equipment. A weekly check of the cleaning efficacy and daily control of the cooling function confirms that all is well and gives peace of mind.

It is calculated that of the total bacterial count in the raw milk 25% comes from the inside of udders (mastitis), 50% from the outside (state of cleanliness), and 25% from the milking equipment. When cattle are healthy and cleaning is consistent, the main contributor to the microbial charge is teat soil. This is mainly influenced by rainy weather and wet and dirty floors (see Figure 13.14).



Figure 13.13 Bulk milk tank.



Figure 13.14 A cow in dirty, wet ambient conditions (courtesy of Diversey Co.).

It is found that each milking operative (milker) unconsciously establishes his own level of microbial charge as a function of his method of working. The microbial count in milk usually increases or decreases only on changing the milker. The bacterial charge depends on the care taken in preparing the cow for milking, that is, on how the milker deals with the teat soil and performs the cleaning and disinfection.

13.5

Raw Milk Quality Standards

Professional cleaning and sanitizing specialists to the dairy industry must be able to anticipate dairy product quality problems and communicate these problems and their possible causes and solutions to plant management.

A fluid milk plant could have product returns amounting to 1% of the processed volume. Improving the raw milk quality standards reduces the product returns. The annual savings could mean the difference between profitability and failure. A major source of information on product quality is the dairy laboratory report. This document should give the following information:

- **Standard plate count** indicates the total bacterial population. It is known that if the milk received at a plant contains more than 200 000 colonies per mL it would be extremely difficult to produce finished products with long shelf life. A desired total bacteria count is below 50 000 per mL. This level is reasonable and attainable by employing good sanitation practices on the farm. In addition to enabling products with a long shelf life to be manufactured, the benefit to the farmer increases as the bacterial population decreases (rewards per quality).
- **Thermoduric count** indicates the presence in the milk supply of heat resistant bacteria (e.g., mastitic bacteria). These bacteria are significant since they are capable of surviving pasteurization and then causing flavor and texture degradation in the finished product. An acceptable thermoduric count is below 300 colonies per mL. Counts higher than this indicate the need for more work on quality on the farm.
- **Coliform count** indicates the sanitary conditions on the farm. Coliforms are found in most raw milk supplies. Raw milk coliforms level above 200 per mL should serve as an indication of possible problem areas on the farm.
- **Raw milk flavor:** The occurrence of weed, feed, cooked and other non-microbially induced off-flavors as well as microbially induced flavors can be found in products throughout the market place. Some degree of flavor deficiency is frequent in milk available at the retail level. All farm bulk tank loads of raw milk should be evaluated by trained personnel for both aroma and off-flavors.

- **Raw milk temperature:** Loads of raw milk having temperatures above 4°C should be regarded as suspect, and should be subjected to close surveillance if they are received.

The dairy industry is extremely complex. Numerous conditions can cause high bacteria counts and diminish the shelf life of the finished product. It would be impossible to list all possible causes of the problems. However, experience teaches that care in cleaning and sanitizing on the farm prevents many problems in the dairy and helps to produce high quality products with long shelf life.

Reference

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14

Biofilm

The presence of biofilm on a surface means risk to food preservation and consumer safety. Analysis reveals the complex structure and the composition of this sort of bacterial slime which aggregates, grows, and protects itself in a thin film forming a layer on the surface. This glycoproteic slime is an organic soil in every respect. Therefore, the organic film generated by microorganisms (biofouling) and in which they live has to be tackled by detergency rather than disinfection. In-depth knowledge, cleaning experience, and proper sanitation enable the latent problems caused by biofilm to be identified, removed, and effectively prevented.

14.1

Microbiological Background

Since the object of any disinfectant process is the elimination of the entire population of the infecting and spoiling agents, a short reminder of the elements of microbiology is appropriate to obtain a proper appreciation of the fascinating and fearful world of microorganisms. An understanding of the structure and various functions of bacteria, fungi, viruses, parasites, and growth factors, as well as the formation of biofilm, its structure and removal, constitutes that basic knowledge essential to an understanding of what we are doing and why we must do it.

Microorganisms are the smallest form of life (Figure 14.1). They are ubiquitous and behave in different ways depending on whether they are bacteria, fungi (yeasts and molds), algae, protozoa, viruses, or spores.

They can be

- **Beneficial:** Millions of healthy flora exist in the human body (bacteria in the intestine help digestion), in the manufacture of food products (e.g., yoghurt, cheeses, vinegar, buttermilk, bread), and for drug production (e.g., production of penicillin).
- **Spoilage organisms:** These cause spoilage of foods and drinks.
- **Pathogens:** These cause disease in humans and animals.

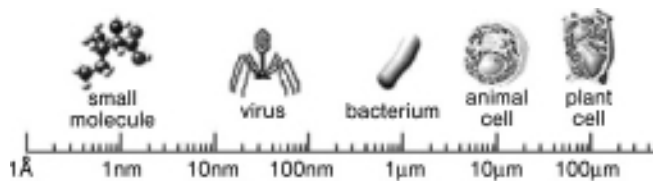


Figure 14.1 Size range of microorganisms (courtesy of Department of Biochemistry and Molecular Biophysics of the University of Arizona).

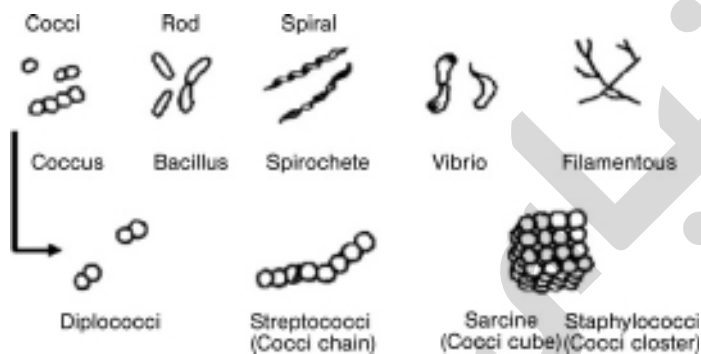


Figure 14.2 Characteristic cell structures and arrangements.

Bacteria exhibit three basic shapes: cocci (spherical), bacilli (rods), and spirula (curved), each of which may appear in various arrangements, as shown in Figure 14.2. Rods can likewise arrange themselves into *Diplobacilli* and *Streptobacilli* (Bacillus chain).

Spores represent a reproductive form of several microorganisms in a dormant and highly resistant early stage of their life. They are very resistant to heat, drying, cold, and chemicals and may lie dormant for long periods of time, germinating when favorable conditions return.

Fungi include yeasts and molds. Microbiologists prefer to differentiate yeasts, unicellular microorganisms, from branching filamentous molds, and to speak of a colony only for unicellular organisms. One mold can cover several square meters of surface!

Viruses are infectious particles of genetic material surrounded by a protein coat called a capsid, helical or polyhedral in shape. Viruses that infect bacteria are called bacteriophages or phages. Cheese-making bacteria can be infected, thereby causing loss of productivity.

Algae convert the sun's energy into cellular energy (photosynthesis). Unicellular, filamentous, colony-forming, or plant-like structures take on green, red, or brown colors depending on the amount of chlorophyll and carotenoids in their system. They are typical organisms inhabiting water systems exposed to light (e.g., cooling towers and swimming pools).

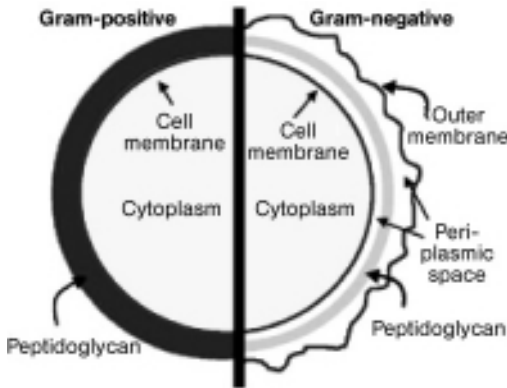


Figure 14.3 Different structures and membrane colors of gram+ and gram– bacteria (courtesy of JohnsonDiversey).

Protozoa are unicellular and motile in a free-living or parasitic form. Protozoa of importance in the food industry because of their responsibility for serious illness include *Toxoplasma gondii* (toxoplasmosis) and *Giardia lamblia* (dysentery).

One important characteristic of bacteria is their reaction to the Gram stain. The type of color retention divides most bacteria into two major groups, gram positive (gram+) and gram negative (gram–), depending on their reaction with crystal violet and dilute iodine solution followed by decolorization with ethanol and counter staining with safranin. The bacteria that retain the blue-purple stain are gram positive. Those that lose the blue-purple complex and become stained red are gram negative (Figure 14.3).

Pseudomonas fluorescens, *Salmonella typhimurium* and *Yersinia enterocolitica* are examples of gram– bacteria, while *Staphylococcus aureus* and *Listeria monocytogenes* belong to the gram+ group.

Bacteria need nutrients for growth, metabolizing and converting foods either by enhancing quality or destroying the organoleptic body or poisoning (toxins).

Bacteria need nutrients for growth, metabolizing and converting foods. This may have a very wide range of consequences, for example (i) the food quality could be enhanced, (ii) its organoleptic properties could be destroyed, or (iii) the food could become poisonous.

Bacteria reproduce by cellular fission, forming two daughter cells, each of which divides again and then again, giving a continual increase in the number of cells. Under certain conditions, bacteria may also reproduce sexually, donating genetic material from one cell to another. Other bacteria reproduce by spores. The classical graph of replication is given in Figure 14.4 (a).

Yeasts and molds do not multiply by binary scission, but by the budding method [Figure 14.4 (b)]. A small knob or bud forms on the parent cell, grows, and finally separates to become a new yeast cell. Molds multiply by producing clusters of dry

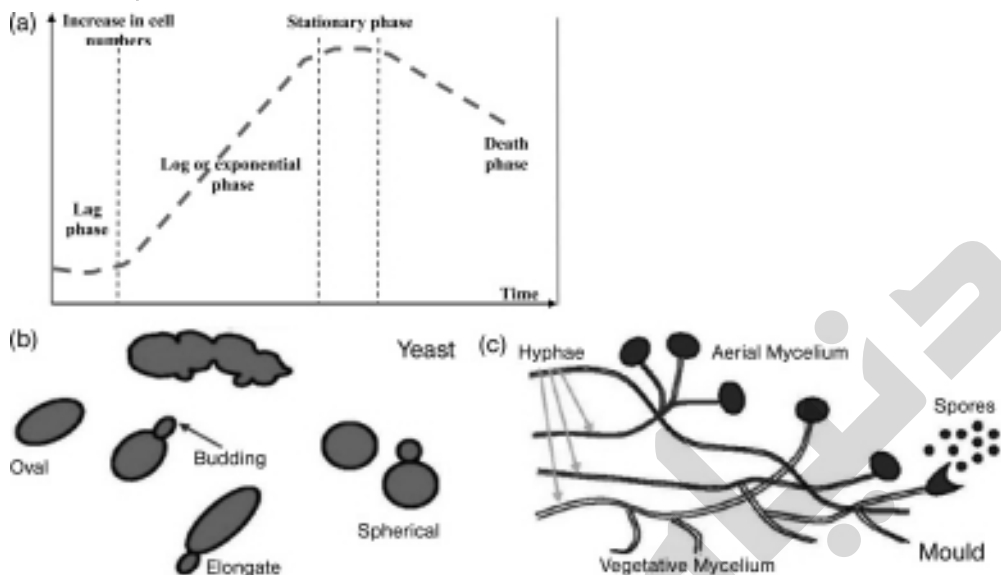


Figure 14.4 (a) Adaptation, growth, survival, and death of microorganisms. Reproduction through (b) budding (yeasts) and (c) spores (molds).

spores which are blown by the air like seeds [Figure 14.4 (c)]. As well as reproducing by spore production, some molds can reproduce by fragmentation of hyphae.

The debate on prions continues. These consist of protein only. Their small proteinaceous structure is not yet well understood. Although they cannot theoretically be living things they are implicated in a number of diseases, causing scrapie, kuru, BSE (bovine spongiform encephalopathy), Creutzfeldt-Jakob Disease (CJD), and Gerstmann-Sträussler-Scheinker syndrome. Prion is the most resistant form of contaminant. It has been found to remain infective after heating at 360°C for 1 h or even after incineration.

In ideal conditions, the duplication of microorganisms can take place within 20 min. Thus, billions of bacteria can develop from one cell in a few replications. The ideal condition changes depending on the nutrient (carbon-nitrogen-phosphorus), temperature, and pH.

Microorganisms are classified by their ability to grow and reproduce at different temperatures:

- Psychrophilic bacteria grow well in cold temperatures, e.g., refrigeration at temperatures below 10°C. They are responsible for many types of spoilage in refrigerated foods, such as slime formation on meats and ropiness in milk, beer, and wine.
- Mesophilic bacteria grow only at moderate temperatures, i.e. 10–43°C. They include most of those which cause disease and food poisoning.
- Thermophilic bacteria grow well at temperatures between 43°C and 60°C. They can cause spoilage in under-processed canned foods.

Table 14.1 pH range for microbial growth.

General microbial growth pH range	
Most types of bacteria	6.5–10.5
Lactic acid bacteria	3.5–7.5
Acid-tolerant bacteria	2.4–7.0
Yeasts	3.0–8.0
Molds	2.0–10.0

The pH is defined by the free hydrogen ion concentration in a medium, and can be acidic (0–6), neutral (6–8), or alkaline (8–14). Life cannot exist at extreme pH values, as shown in Table 14.1.

Pickling and acidification have been used for many centuries to reduce or retard spoilage. Acidification below pH 4 markedly reduces most microbial spoilage.

Microbes, like all living organisms, require water for their metabolic functions. The presence of unbound water is measured as the water activity (a_w). Most bacteria require a range of 0.90–0.99 in order to function. Below this range, a few microorganisms can survive but do not grow. Reduction in a_w is achieved by binding free water (addition of salt and sugar) and drying or curing (e.g., smoking).

Microbes can also be grouped into aerobic and anaerobic, obligate, and facultative organisms. Therefore, food spoilage can be reduced by modifying the level of carbon dioxide, nitrogen, and oxygen in the packaging. However, the repression of aerobic microbes can enhance the growth of others (e.g., *Clostridium botulinum*). Thus, modified atmospheres help to improve the preservation of food if the previous operations have been correctly carried out. Conversely, modified atmospheres can eliminate spoilage microbes but permit pathogens to grow.

14.2

Formation and Growth of Biofilm

Investigations aimed at understanding the formation and growth of biofilm reveal the complexity of the biolayer [1]. The polymeric substances produced by several species of microorganisms protect the colonies and promote suitable environments for growth. Observations by scanning laser microscopy [2] reveal a configuration resembling a city, in which colonies of bacteria rise up from a layer of polysaccharides, alginic, and glycoproteic polymers. The layer of metabolites clings to the surface [3], enveloping the bacterial colonies and forming conical or fungiform shapes as shown in Figure 14.5.

The space between these structures forms a network of channels through which nutrients, oxygen, and substances necessary for the microbial metabolism flow. Small parts of these conical structures of microorganisms are randomly released, and these rapidly colonize the whole plant. Biofilms appear to vary dynamically, and their extracellular matrix composition can clearly change with time.



Figure 14.5 Schematic representation of the biofilm structure on a surface.

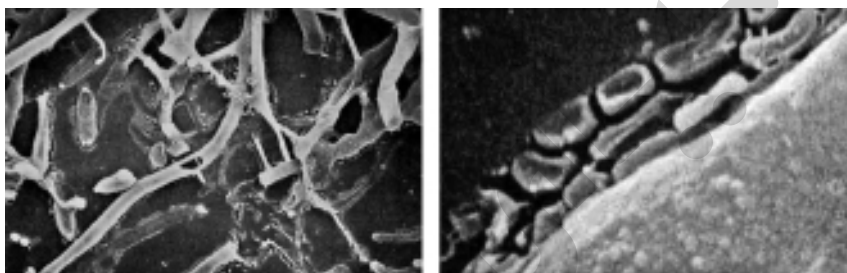


Figure 14.6 Mold hyphae inside metabolic organic polymers magnified near a dried hypha (courtesy of Diversey Microbiology Department [3]).

Biologists have discovered that a cell behaves in a different way when alone (planktonic state as in solution or airborne) compared with when it feels others on a surface. Microbes start growing on a surface in very small aggregates (microcolonies) and exchange signals even with the aid of volatile compounds. When they feel the presence of other microorganisms (quorum sensing), specific genes become active and induce bacteria to synthesize new specific proteins. Some proteins exchange information among bacteria, stimulating the build-up of a gelatinous extracellular matrix [2, 3]. It is reported that *Pseudomonas aeruginosa* takes 15 minutes to activate these genes [2]. As the concentration of organic excretion increases, so the cellular activity is further aroused. Cells can also produce enzymes able to destroy a disinfecting agent before spreading inside the biofilm. Organic materials and enzymes can succeed in inactivating even strong disinfectants such as chlorine, quaternary ammonium chloride, amphoters, and peracids. For this reason, what is active against suspended cells in laboratory cultures could be absolutely ineffective against cells protected in a biofilm (Figure 14.6). The experimental conditions do not correspond to the environment in which bacteria really live. The laboratory decides whether a chemical kills or fails to kill bacteria. Field experimentation establishes how the killing strategy is to be accomplished.

Surface condition and environmental physico-chemical properties affect the formation and growth of biofilm.

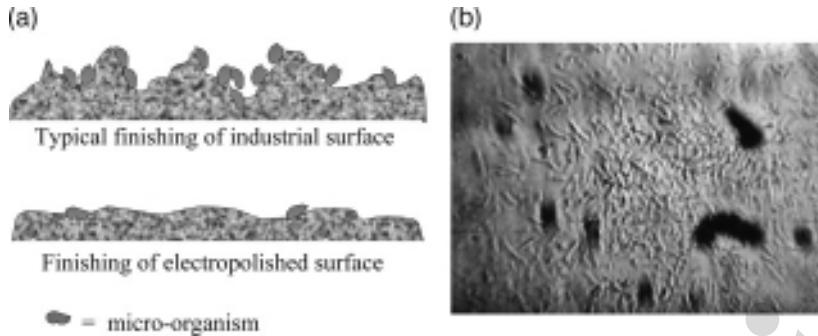


Figure 14.7 (a) Schematic representation of surface finish and (b) *Lactobacillus* from brewery tank biofilm.

Table 14.2 Surface finishes and processes used in achieving them.

EN	ASTM	Finishing	Work cycle
1D	1	Coarse and dull	Hot-rolled, heat treated, pickled
2E	1	Coarse and dull	Cold-rolled, heat treated, mechanically descaled, pickled
2D	2D	Smooth	Cold-rolled, heat treated, pickled
2B	2B	Smooth	Cold-rolled, heat treated pickled, skin passed
2R	BA	Smooth, shiny and reflecting	Cold-rolled, bright annealed
2H	TR	Shiny	Work hardened

14.2.1

Surface Condition

The Table 14.2 gives the ASTM and EN standards for surface finish as a function of the surface treatment process.

Roughness and smoothness do not significantly influence the potential quantity of biofilm developing on the surface. A smooth surface only delays the initial phase of bacterial adhesion in comparison with a rough one on which depressions and peaks trap microorganisms more readily. For instance, a stainless steel surface, modified by the deposition of polyethylene glycol cross-linked by radio frequency plasma, gives a smoother morphology and a 81–96% decrease in the attachment of *Listeria monocytogenes* and the formation of biofilm [4]. In both cases, when the first microorganism clings to a point, the rate of the biofilm growth is independent of the surface finish (Figure 14.7).

It is generally accepted that the bacterial cell itself does not directly touch the substratum. Adsorption is mediated by extracellular structures capable of over-

coming the electrostatic repulsion effect [1]. Growth and reproduction of the primary colonizing bacteria modify the surface characteristics of the substratum, rendering it suitable for subsequent colonization by secondary organisms. The maturing biofilm incorporates not only secondary colonizing microorganisms but also inanimate materials including clay, colloids, and other minerals as well as organic detritus. The spatial differentiation generates niches for different physiological types of bacteria that form consortia with integrated metabolic processes [1].

Microbes adhere to stainless steels and plastics in a roughly similar manner. On the other hand, biofilm has more difficulty in clinging to galvanized steel. As the toxicity of zinc delays or prevents microorganisms from adhering, the incorporation of antimicrobial additives into plastic should be an interesting way to reduce microbial attachment. However, such a modification of the surface is impracticable since the chemical safety would be questionable in the food industry. Toxic surfaces cannot be used in food preparation and potable water systems.

The growth of biofilm takes place in static conditions (e.g., storage tanks, dead end points) and can even take place in turbulent flow along pipelines. Bacteria take advantage of the laminar flow, which can be static enough near the surface. Turbulence and the associated shear forces only limit the thickness of the bacterial slime. The greater the turbulence, the thinner the biofilm is on the surface. However, even though biofilm is reduced approximately to the thickness of the laminar layer as a function of the intensity of the flow rate, flushing will never be able to prevent its formation.

14.2.2

Environmental Conditions

Environmental conditions (pH, aerobic-anaerobic ambient) and nutrients level promote or limit bacterial growth. Neutral conditions encourage general growth even in high-purity systems. Microorganisms do not need high concentration of nutrients. They can extract organic carbon, nitrogen, phosphorus, and trace elements directly from water (organic colloids, nitrates, phosphates, sulfates...) and surfaces (cement, plastic, steel). Even under non-ideal conditions their initial growth follows a logarithmic trend, so that one cell could lead to a large enough number of microorganisms to cover the whole surface in very short time. The efficient adhesion of filament-forming organic matter gives an advantage to varieties of filamentous organisms. Typical examples of common biofilm are produced by bacteria (e.g., *Pseudomonas*), filamentous molds (e.g., *Mucor*, *Fusarium*), and yeasts (e.g., *Torula*, *Saccharomyces*) (Figure 14.8).

14.3

Practical Significance

A biofilm, even if it occurs in a limited area, is source of rapid deterioration of manufacturing conditions and water systems. The growth of biofilm beyond the

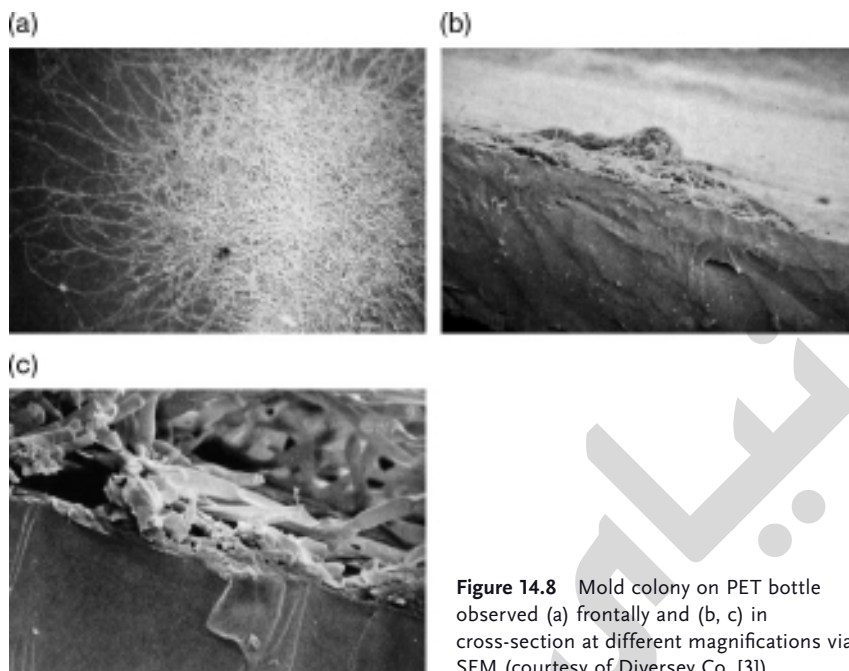


Figure 14.8 Mold colony on PET bottle observed (a) frontally and (b, c) in cross-section at different magnifications via SEM (courtesy of Diversey Co. [3]).

boundary layer allows the cells to be released and to colonize other areas of the plant. An indication of the presence of biofilm is the appearance of unexpectedly high figures in routine microbiological analysis. Fluctuations in total bacterial counts in a plant are a warning of a biofilm settlement somewhere. The growth of biofilm in static conditions (e.g., headspace of equipments and machines, dead pipelines, neglected surfaces) forms niches from where bacteria diffuse and contaminate everything in its surroundings. The addition of chlorine to disinfect the water is not always effective. What seems to be a contradiction is really a case of disinfectants positively tested in laboratory on planktonic microorganisms but unable to reach bacteria protected by biofilm. This explains why microbial contamination can be detected even when water contains chlorine. A low concentration of chlorine can kill dispersed bacteria but is ineffective against biofilm. Owing to their great production of slime, *Pseudomonas* bacteria are a prime example of such resistance [2].

Aerobic bacteria consume oxygen, can exhaust it inside a biofilm, and can create an undesirable anaerobic environment. This environment allows fermentation of carbohydrates and sulfate and the development of hydrogen gas and hydrogen sulfide, which diffuse into metals causing hydrogen embrittlement and underdeposit corrosion. The absence of oxygen destroys the protective film of passivation on stainless steel and generates ideal conditions for sulfate-reducing bacteria. The production of hydrogen sulfide leads to black deposits of iron sulfide. Corrosion, stench, and black deposits increase. Iron bacteria are shown

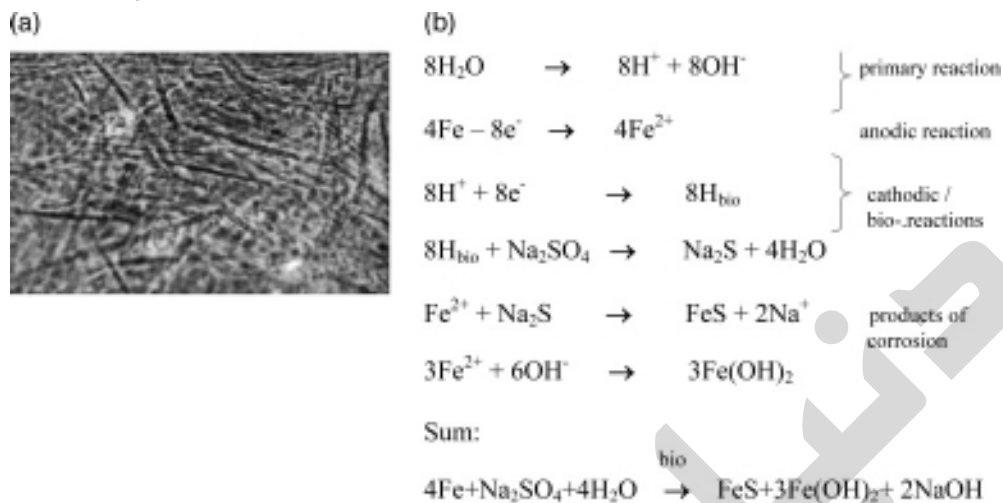
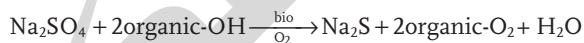


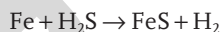
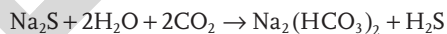
Figure 14.9 (a) Biofilm with corrosion by iron bacteria in progress in cooling water plant (photomicrograph) and (b) suggested mechanism.

and a suggested mechanism for biological corrosion in anaerobiosis is proposed in Figure 14.9 [5].

Organic soil is practically independent of bio-corrosion in anaerobic conditions. On the contrary, the first phase of aerobic bio-corrosion takes place from the decomposition of organic soil:



The actual process of corrosion occurs by the action of hydrogen sulfide on iron. There is no correlation between reduced sulfate and final concentration of iron sulfide. Carbonic acid, too, takes part in the reaction:



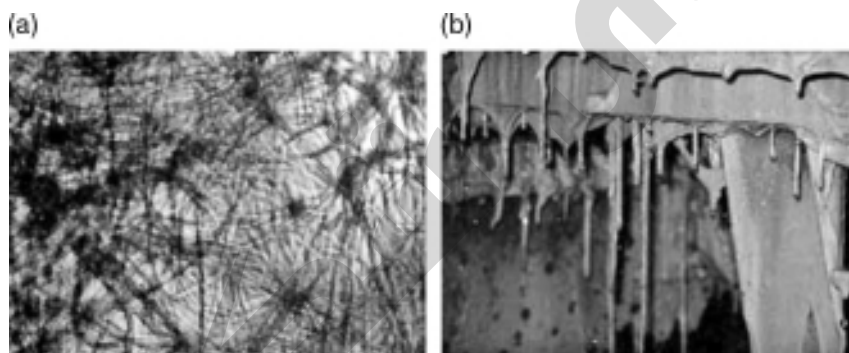
Some aerobic bacteria act as oxidants producing sulfate ion. Others oxidize ferrous and manganous ions to ferric and manganic, which promote tubercle formation. The Table 14.3 reports the main recognized bacteria involved in micro-biologically influenced corrosion (MIC) [6]:

MIC may occur everywhere water is used. In particular, it has been increasing so much as to be considered a form of corrosion usually affecting stainless steel [6].

As already stated, the correct approach to biofilm control primarily requires the removal of the polymeric organic metabolites before disinfecting. To maintain constant conditions, it is necessary to implement either procedures for cleaning before disinfecting or cleaning after a predetermined number of disinfection treatments.

Table 14.3 Bacteria and corresponding bioreactions leading to corrosion (from Inossidabile No. 167).

Bacteria	Metabolism	Bioreaction
<i>Desulfovibrio desulfuricans</i>	Anaerobic	Reduction of sulfate (SO_4^{2-}) to hydrogen sulfide (H_2S) and its salts (S^{2-})
<i>Desulfotomaculum nigrificans</i>	Anaerobic	Reduction of sulfate (SO_4^{2-}) to hydrogen sulfide (H_2S) and its salts (S^{2-})
<i>Thiobacillus thiooxidans</i>	Aerobic	Oxidation of sulfur and sulfides to H_2SO_4
<i>Thiobacillus ferro-oxidans</i>	Aerobic	Oxidation of ferrous (Fe^{2+}) to ferric ion (Fe^{3+})
<i>Gallionella</i> and <i>Sphaerotilus</i>	Aerobic	Oxidation of ferrous and manganous ion to ferric and manganic

**Figure 14.10** Biofilm in (a) cooling tower and (b) tunnel pasteurizer.

14.4 Cleaning and Disinfection

Being an organic contamination in which microorganisms live, biofilm has to be cleaned and disinfected. In practice, disinfectants (with the exception of chlorine at high concentration) do not clean effectively enough to remove biofilm. Thus, there is a high probability that disinfection alone can fail to provide sanitation. The best result is attained by the application of cleaning and sanitation individually and consecutively. Disinfectants are specifically targeted against living matter, but soil disturbs the effectiveness of disinfectant. Thus, before disinfecting, biofilm must be removed by a cleaning step usually based on alkaline and chlorinated-alkaline detergents. It is obviously impossible to disinfect biofilm-covered surfaces like those pictured in Figure 14.10 without a previous cleaning operation.

14.4.1

Alkaline Cleaning

Carbohydrates and glycoproteic polymers, which form the biofilm substrate, are starches and proteins, whose chemistry has been discussed in Sections 1.3.1 and 1.3.2. To attack the gel and to absorb multivalent metals it is necessary to provide

- caustics to dissolve and solubilize protein and starch derivatives
- carrier and threshold sequestrants, for example, EDTA, NTA, ATMP, and polyacrylates
- PBTC and STP, which are useful in chlorinated detergents
- wetting agents (surfactants in chlorine-free detergents).

Chlorine (hypochlorite) added to caustics enhances cleaning and detaching capacity. Chlorine itself positively performs as a biofilm remover when at high concentration (several hundred ppm). Although chlorine has disinfecting properties, its primary function is in cleaning (detaching). The chlorine solution provides disinfection only if free chlorine is still detectable at the end of the cleaning step, which takes at least 20 min.

Hydrogen peroxide in an alkaline medium behaves like chlorine. It has strong detaching ability and gives good control of microorganisms without causing corrosion and off-odors typical of chlorine derivatives (e.g., chlorophenols and chloramines). The small size of its molecules enables hydrogen peroxide to pass through the filtration membranes. Hence, added to the alkaline step, hydrogen peroxide provides the filtering system with enhanced biofilm removal and disinfection even in the permeate zone. This benefit is notable in reverse osmosis. However, chemicals used in crossflow filtration need the approval of the membrane manufacturer. Hydrogen peroxide is therefore applicable in NF and RO provided that OEM endorsement is obtained.

14.4.2

Acidic Cleaning

Acidic cleaning is usually used for systems processing raw water. In time, hard water leaves porous deposits of inorganic salts (limestone) even at low temperatures, and these deposits constitute an ideal substrate where microorganisms can protect themselves and readily grow. Acids remove limestone and the biofilm living inside. Acidic cleaning is applied periodically together with alkaline cleaning to be sure to prevent unpredictable problems.

14.4.3

Disinfection

Disinfectants can be broadly classified into two groups based on their physical behavior and biocidal activity:

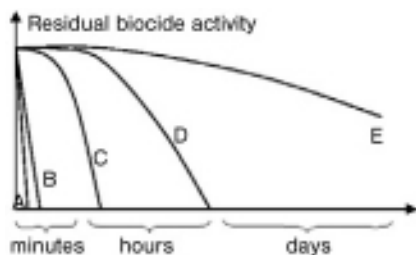


Figure 14.11 Durability of various disinfectants: A = peroxides; B = halogens; C = monomeric QAC; D = polymeric QAC; E = alkylpolyamines and amphoteric alkylpolyamines.

- the first contains one or more nitrogen groups in the molecular structure
- the second includes all the remaining disinfectants (redox and metals).

Nitrogen compounds decrease the zeta potential, are absorbed, and a thin layer on the surface persists even after a good rinse. This behavior is very valuable since it keeps the surface disinfected longer. On the other hand, nitrogen-free disinfectants follow Coulombic-Born repulsion, perform faster, and are completely removed by rinsing, after which the bare surface is no longer protected. Slow-acting nitrogen derivatives (mainly fatty and amphoteric polymers) prove to be more tolerant of dirt. The concept of durability and soil compatibility differentiates the application of disinfectants. Nitrogen compounds are preferred on open surfaces. The remaining categories find ideal application in CIP and aqueous systems. A comparison of the durability of disinfectants is roughly indicated in Figure 14.11.

Rapidity and durability are inversely proportional characteristics. The complete spectrum of action (inclusive of spores and viruses), bacteriostaticity and adaptation depends on the specific biocide molecule.

The organic matter forming biofilm inactivates peroxides, anhydrides, aldehydes, chlorine dioxide, ozone, and low levels of chlorine. Nitrogen compounds remain adsorbed on the contamination where they slowly lose efficacy. Both groups neither succeed in killing the microorganisms living under the biofilm nor in removing the biofilm. Therefore, once again cleaning before disinfecting is the best approach to the biofilm control. When the surface is clean, disinfectants conclude the treatment. Disinfectants applicable in the food industry are listed below:

a) CIP treatment (closed systems)

- **Halogens:** complete spectrum, rapid action, easily rinsable and sensitive to soil.

Chlorine donors: several chemicals can be formulated in alkaline medium.

- **Sodium hypochlorite:** the main agent for cleaning and disinfecting.
- **Chloramine T:** 25% chlorine available, slowly released
- **Sodium di or tri-chloroisocyanurate:** 55% chlorine available (powder)
- **Sodium chlorophosphate:** 3.5% chlorine available (powder)
- **Calcium hypochlorite:** 65% chlorine available (powder)

The chlorine demand is a parameter that characterizes colloids, humic and fulvic acids, and sulfides in raw water. It is to take precaution at a remarkably low dosage (water chlorination, ppm).

AOX (adsorbed organic halogen), NPOX (non-purgable organic halogen) and THM (trihalomethane) represent organic derivatives of chlorine connected to aftertastes and destruction of the protective ozone layer in atmosphere. Medicine aftertaste of the reaction with polyphenols and cork aftertaste with anisole (di- and trichloroanisole) are perceptible at ppb concentration. This is particularly feared in the brewery, winery and vegetable (fresh-cut produce) industries. Carbon tetrachloride, chloroform, and dichloroethane are typical by-products.

Iodine donors: chemicals effective in acidic medium, technically known as iodophors.

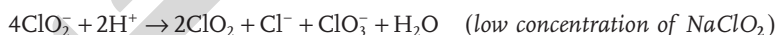
- iodine stabilized on surfactants in strong acids
- iodine stabilized on polyvinylpyrrolidone in mild acids
- iodine stabilized as iodine chloride in strong acids free of surfactants

Iodine is highly corrosive on steel and adsorbed on plastics, leaving a yellow-brown color. It loses biocidal activity in alkaline media.

- **Peroxides:** complete spectrum, rapid action, easily rinsable and sensitive to soil.
 - **Hydrogen peroxide.** Effective activity at relative high concentration (above 1%). The cleaning activity increases in alkaline media (lower concentration needed)
 - **Peracetic acid.** Extremely active even at low concentration (below 0.3%). Volatile with a pungent odor.
 - **Hydrogen peroxide in citric acid**, also known as *percitric acid*. Active at higher concentration than peracetic acid. Free of pungent odor, percitric acid is a very interesting food treatment agent.
 - **Percarbonate, persulfate, and perborate.** Powders slowly releasing oxygen.
 - **Peroctanoic and phthalimidoperhexanoic acids.** Very rapid disinfecting action. Stench and doubts about health safety (phthalates) limit their application.
- **Aldehydes:** complete spectrum, rapid action, easily rinsable, sensitive to nitrogenated soil.
 - **Formaldehyde.** Effective at low concentrations at every pH. Ammonia and its derivatives reduce its activity. With suspected carcinogenic properties, it is usable only as a preservative and in specific controlled

applications, for example, in pharmaceuticals, hospitals, laboratories, and in hoof care on the farm.

- **Glutaraldehyde.** Effective only within a restricted pH range (7–9), glutaraldehyde is negatively affected by the presence of ammonia and nitrogen derivatives. Easily polymerizable, it is stabilized in a mildly acidic medium.
- **Organic acids:** substances active in acidic pH. They constitute a group of disinfectants and preservatives that provide the acidic detergents with disinfecting action. Benzoic, salicylic, lactic, octenylsuccinic acids, short-chain fatty acids (C_8 – C_{10}), and ethoxy(1EO)carboxylate fatty alcohols are examples of this category.
- **Anhydride:** *sulfur dioxide* is exploited at $pH < 6$ as a disinfectant and preservative. Wineries and crossflow filtration are the main users.
- **Alcohols:** *ethyl and isopropyl alcohols*, active when at concentrations above 60%, are utilized as ‘dry cleaners’. Disinfection is accomplished when they are kept in an enclosed space or when synergized with QAC, biguanide, or amphoteric fatty polyamine compounds. *Benzyl alcohol* is effective at concentration $>2\%$. Owing to its skin compatibility, benzyl alcohol is formulated in ready-to-use products (e.g., prevention of mastitis on the farm).
- **Chlorine dioxide:** terminal disinfectant added to aqueous systems. It is generated on the spot. Active at very low concentrations in gaseous form, chlorine dioxide is produced in different ways, for example, from the reaction between hydrochloric acid and sodium chlorite or from hypochlorous acid on a platinum catalyst. Typical reactions are:



Chlorine dioxide slowly hydrolyzes to chlorite and chlorate (disproportionation):



Chlorite, besides being a corrosive agent, affects human health. Hence, its concentration in drinking water is subject to restriction (≤ 200 ppb).

- **Ozone:** used on aqueous systems and for terminal disinfection. It is generated on the spot with suitable ozonizers and acts in gaseous form. The oxidizing effect of ozone is superior to that of peracids but it has much lower surface disinfecting power. An unstable and toxic molecule, it must be environmentally controlled.

- **Potassium permanganate:** one of the strongest oxidants. Although it is active against most microorganisms, it is only used for special applications because of its black-violet color and especially its environmental impact. One of its applications is in wineries, where it is used for disinfecting the wooden barrels. (control of *Brettanomyces* and *Acetobacters*).
- **Silver and hydrogen peroxide:** blend approved specifically against *Legionella* pollution. It is used in hospital service waters as a terminal disinfectant and in soak application. Chloride ion inactivates silver, which precipitates as chloride.
- **Zinc chloride and copper sulfate:** used in hoof care on the farm and for the prevention of algal growth in recycling water and swimming pools.

b) Treatment of open surfaces

- **Quaternary Ammonium Compounds (QACs):** These fall into two groups:
 - **Monomers:** foaming agent with one nitrogen group in the molecule.
 - **Polymers,** nonfoaming agent having more than one charge in the molecule.

Polymerization slows the biocide activity. The claimed resistance of the gram- microorganisms (e.g., *Pseudomonas*) toward QACs means that higher concentrations are needed to kill them. QACs in acidic medium (phosphoric acid) are particularly effective against *Listeria monocytogenes*.

- **Chlorhexidine**, also known as 'biguanide', is a nontoxic, nonirritant agent suitable for hospital, veterinary and cosmetic applications. Active at relative high concentration (above 1%), it is widely used as an antimastitis disinfectant (cow) and in hygienic hand cleaners.
- **Polybiguanide** is a nonfoaming and noncorrosive compound. Its superior activity to that of chlorhexidine and QACs makes it more sensitive to soil.
- **Fatty alkylpolyamines:** Two and three nitrogen groups in a fatty chain provide a nonfoaming molecule with slow activity and prolonged durability, also in contact with soiled surfaces. Being also lubricants, they are applied on bottling tracks.
- **Amphoteric (glycine) fatty alkylpolyamines:** more rapid biocide activity than fatty alkylpolyamines makes them less resistance in contact with soil. The amphoterization adds foaming behavior to the structure.

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15

Environmental Sanitation

Hygienists do not like enclosed spaces where microbes can concentrate, putting people and goods at risk. Not only hospitals, but every industry where indoor air carries any type of environmental and manufacturing pollution needs to be assessed from the point of view of hygiene. Food, pharmaceutical, cosmetic, and catering industries as well as clinics, hospitals, aero-space, and electronics are examples of sensitive environments in which the prevention of infections is a fundamental requirement. However, when cleaning and disinfection are discussed, these are usually thought of in terms of being directed at hard surfaces, equipment, and floors. Only exceptionally is enclosed air considered to be so important to a manufacturing process that air sanitation is performed routinely. On the other hand, environmental sanitation cannot be the only method of preventing infection in the area. Molds on walls and ceilings, for instance, have to be removed by suitable cleaning and disinfection procedures (Figure 15.1). They certainly cannot be prevented by a simple air treatment directed at moving particles and microorganisms. A microbiologically controlled environment prevents most infections from harming goods and personnel.

Microbiological prevention does not merely mean applying a disinfectant. Prevention involves a global plan of procedures such as the use of nonturbulent fans, removal of hazardous materials, installation of extraction systems to drive polluted air outside, and keeping the enclosed space as dry as possible. Prevention also means knowledge of the historical condition of the work areas. Such knowledge, obtained through systematic microbiological tests of the enclosed environment in the course of manufacturing, should be documented. Environmental care is as important as the microbiological analysis performed on work tables, equipment, and surfaces in contact with food.

15.1

Environmental Particles

In every work zone under normal conditions, it has been estimated that the number particles of size 0.5 microns or greater in unfiltered air can reach 10^8 per cubic meter [1]. Most of these particles consist of amorphous matter (dust).

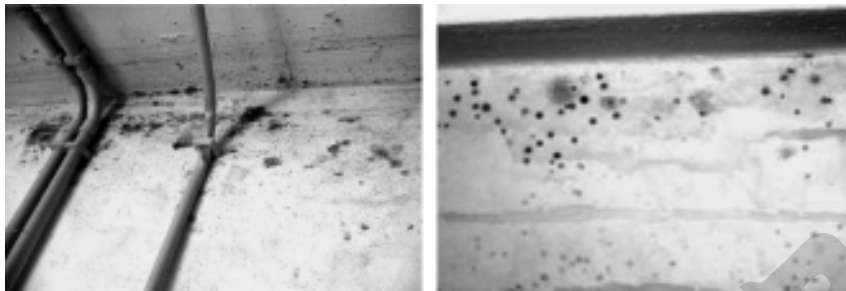


Figure 15.1 Freely growing molds in uncontrolled environment.

However, bacteria, yeasts, molds, mites, viruses, spores, and allergenic matter (e.g., pollen) account for a significant proportion of the organic constituents. The size of the particles is strictly related to their mechanism of formation. For instance, particles from fabrics have sizes typical of fibers, whereas flour particles are smaller than 100 microns. Aside from what is produced inside the enclosed environment by fork lift trucks, engines, and goods handling, a large number of particles come from exogenous sources and are carried in the air through doors and windows and by fans that bring the air in from the outside. Granules of size $>10\mu$ tend to be deposited, while atmospheric turbulence keeps smaller particles suspended indefinitely. Particles have a relatively enormous surface, which is responsible for their capacity for adhesion. The smaller the particles, the higher is the adhesion [2]. Particles absorb and carry steam, which can also contain chemicals (acids, alkalis, and hydrocarbons) and can promote reactions by catalysis by metallic oxides and by typical cations of work stations, namely those of Fe, Al, Pb, Zn, and Mn. As well as moving matter, the atmosphere also moves energy in thermal form. Sensible heat (measurable by thermometer) and latent heat (stored in steam) induce continuous turbulent movements that absorb and deposit material. Although air does not prove to be an ideal medium for the growth of microorganisms, it is an ideal means of spreading them wherever they are attached to particles [3].

People are sources of foreign materials as well being an important means for their prevention. Problems can be unintentionally caused by thoughtless actions, absence of clear rules to do the job correctly the first time, absence of self-discipline, and lack of supervision to ensure that the rules are obeyed [1]. People in enclosed air environments release bacteria and viruses in droplet and aerosol form from the respiratory tract or attached to solid particles detached from skin and hair. These become active agents of pollution in an environment enclosed within walls. Human activity is responsible of producing 10^4 to $5 \cdot 10^6$ particles per minute, of size 0.3μ [4]. Since people frequently are asymptomatic carriers of pathogens, human contamination is generally hazardous because of the impossibility of identifying the incubation period.

The suspension time of solid and liquid particles depends on air turbulences and degree of humidity. Transfers of steam from manufacturing to the packaging

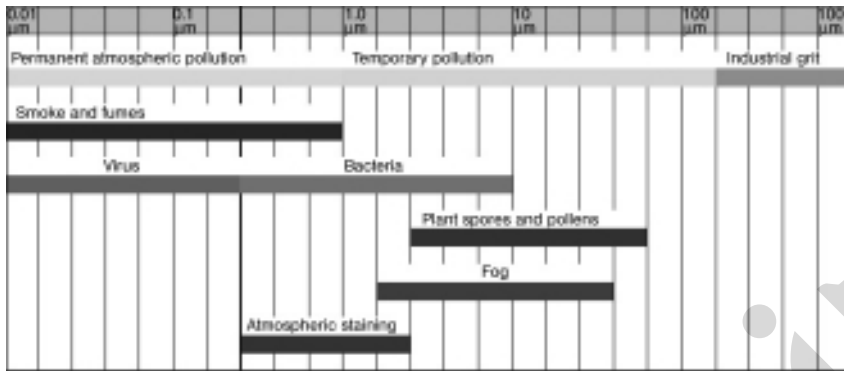


Figure 15.2 Sizes of particulates (courtesy of JohnsonDiversey).

and storage zone spread humidity and turbulence and increase microbial growth and fouling. Whatever happens, particles yield pollution which continuously varies in quantity and quality. Moreover, 97% of particles are invisible to the naked eye. Hence, the first difficulty derives from having no certain evidence about the true condition of the environment. By the time a bacterial colony makes itself visible, a billion bacteria will have already grown and irreversible damage could have already occurred [1]. The effect of a polluting agent increases as a function of its concentration. Three different concepts of pollutant dose are reported in the literature [4]:

- **environmental dose:** the overall amount of pollutants available. It is also known as the exposure factor and is obtained from the average concentration of pollutants multiplied by the exposure time [$P = C_a \cdot t$].
- **absorbed dose:** the amount of pollutants absorbed on a surface. It is a measured by the increase in absorbed pollutants in the course of the exposure [$\Delta P = K \cdot C_a \cdot t$].
- **effective dose:** amount of pollutants actually able to affect the physico-chemical state of the food [$\Delta P_e = (K C_a - K_i C_{ai}) \cdot t$]

[Where 'a' means average, 'e' means effective, 'i' means inert matter, and K = accumulation constant]

Microorganisms are the real agents of pollution. As well as causing organoleptic modifications to the manufactured food, they transmit diseases by direct contact. Therefore, the number of microorganisms assumes the value of the effective dose (ΔP_e). Examples of particulates and size are given in Figure 15.2.

The environmental microbiology is considered the point of reference for enclosed spaces. As living matter immediately starts growing, it follows that a neglected dose of microorganisms absorbed from the environment rapidly harms the food. In ideal conditions microorganisms roughly double their number every 20 minutes.

15.2

Physical Control

The prevention of polluting agents in manufacturing environments is physically carried out by means of air filtration and ultraviolet radiation.

15.2.1

Air Filtration and Clean Rooms

The air filtration is modulated according to the needs of the manufacturing site in order to block the organic and inorganic airborne particles and ensure a flow of pure air. It achieves excellent results of lasting sterility and provides enclosed spaces with hygienic protection. The premises have to be sealed. The sealed environment is then kept at over-pressure (>5 Pascal) in order to establish an air flow from the inside to the outside (from clean to dirty areas). The technology is ideally exploited in a clean room, also known as a white chamber (see Section 6.9). Inside this segregated environments the particulate concentration is kept within definite limits even in the presence of variations in temperature, humidity, and pressure, parameters that affect the concentration and behavior of the particles. The removal of particles is carried out by absolute (HEPA) filters (High Efficiency Particulate Airfilter) (Figure 15.3). The efficiency of HEPA filters covers different needs, from 95% of 0.3μ to 99.99996% of 0.12μ particulates. The latter prevents the ingress of all airborne microorganisms [5].

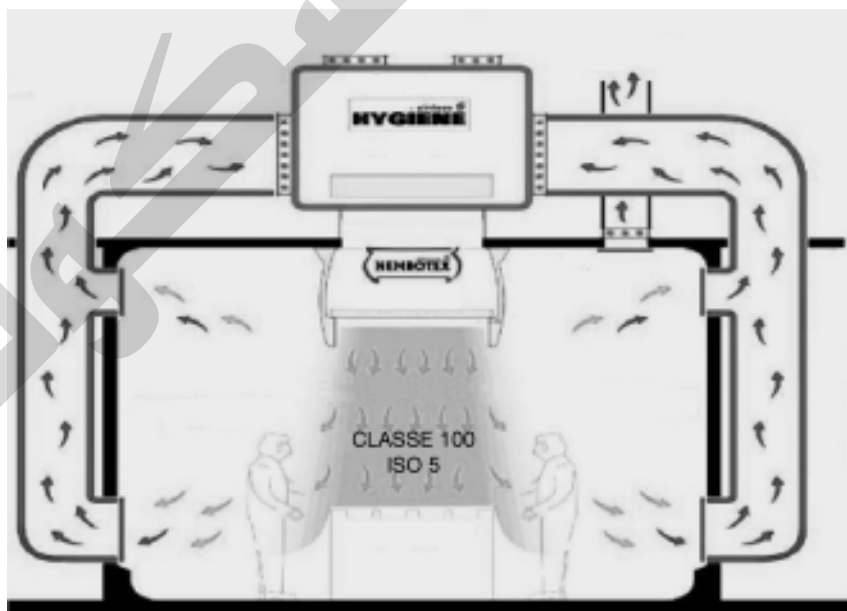


Figure 15.3 Schematic representation of HEPA filters air flux (courtesy of Sinteco).

Table 15.1 Clean room classification.

ISO Number	FS 209E class	Maximum concentration permitted for particles $\geq$ to those indicated in the table (particles/m ³ of air)					
		0.1 μ	0.2 μ	0.3 μ	0.5 μ	1 μ	5 μ
ISO 1		10	2				
ISO 2		100	24	10	4		
ISO 3	class 1	1000	237	102	35	8	
ISO 4	class 10	10000	2370	1020	352	83	
ISO 5	class 10 ²	100000	23700	10200	3520	832	29
ISO 6	class 10 ³	1000000	237000	102000	35200	8320	293
ISO 7	class 10 ⁴				352000	83200	2930
ISO 8	class 10 ⁵				3520000	832000	29300
ISO 9					35200000	8320000	293000

Federal Standard 209E and ISO 14644 classify clean rooms as a function of how much air purification is used, which refers to the filtering efficiency (e.g., FS 209E class 100000, 10000, 1000, 100, 10, 1). The FS class number indicates the maximum number of particles with a size greater than or equal to 0.5 μ per cubic foot of sampled air. Class 100000 indicates the dirtiest room, and Class 1 the cleanest. European ISO 14644 extends the number of classes to 9 and includes the FS 209E classification, as given in Table 15.1.

Clean rooms devoted to the preparation of ham are examples of a different hazard analysis: cooked ham is sliced in a class 100 environment whereas class 10000 is accepted for Parma ham and salami. The reason is that cooked ham is sterile whereas the other products already contain their own microbial charge (up to 10⁴–10⁶ colonies per gram in salami), which makes the sterility of the environment less essential. Table 15.1, adapted from Ferrari [4], gives the ISO 14644 and FS 209E classifications for a clean room.

Critical clean rooms require strict procedures of admission of personnel and chemicals, for example, two personnel air locks, materials air locks, cloth change, personnel and materials disinfection, packs of disinfectants sterilized by gamma rays (Figures 15.4 and 15.5). Isolators are an example of absolute sterility in which no particle is permitted.

Clean rooms require automatic cleaning and disinfection (fillers, tracks, work tables, floors, and walls) with OPC, CIP, and SIP products, at the end of and even during the manufacturing process, and after accidental events. The cleaning of dismantled parts is accomplished outside the enclosed space.

The unquestionable advantages of air filtration for enclosed environments are excellent hygiene, no dependence on chemicals, and the possibility to stay inside the manufacturing process. However, the investment for each room and the



Figure 15.4 ISO 5 (class 100) clean room (courtesy of Sinteco).

Layout with cleanroom classes

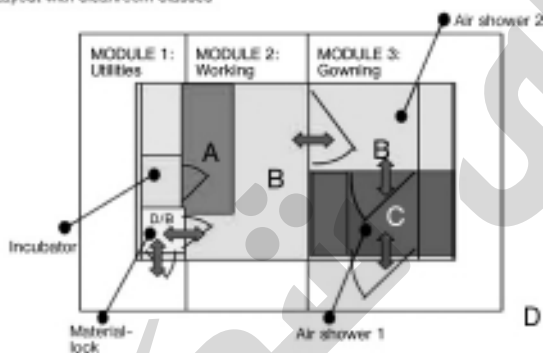


Figure 15.5 Clean room to the incubator (isolator) (courtesy of JohnsonDiversey).

operating costs are considerable. It is quite impossible to benefit from advanced filtration in a general manufacturing operation of large size. Hence, clean rooms involve small-to-medium areas in hospitals, pharmaceuticals manufacture, electronics, food laboratories, and high-quality food processes (ready-to-eat foods).

15.2.2

Ultraviolet Radiation

Electromagnetic radiation is characterized by the relationship between frequency (ν), wavelength (λ), and energy (E), which are connected by two equations:

$$\nu = c \cdot \lambda^{-1} \quad \text{and} \quad E = h \cdot \nu = h \cdot c \cdot \lambda^{-1} \quad \begin{array}{l} (c = \text{velocity of radiation,} \\ h = \text{Planck's constant}) \end{array}$$

Electromagnetic radiation falls into five main groups:

- ionizing λ <10 nm (X and gamma rays)
- ultraviolet 100> λ <400 nm (UV)

• visible	400>	λ	<800nm (light)
• infrared	0.7>	λ	<1000 μ m (IR)
• radio	0.03>	λ	m

Ultraviolet rays are further divided into three frequency bands:

• UV-A	$315 > \lambda < 400 \text{ nm}$	(tanning property)
• UV-B	$280 > \lambda < 315 \text{ nm}$	(therapeutic property, vitamin D synthesis)
• UV-C	$100 > \lambda < 280 \text{ nm}$	(biocide property)

UV-C are sterilizing nonionizing rays, usually at 253.7 nm radiation, obtained from mercury vapor by low-pressure discharge in quartz lamps, an application of which is shown in the Figure 15.6.

UV radiation is effective in killing unprotected microorganisms suspended in air. However, the intensity decreases as a function of the distance from the source [1]. Different protections developed by microorganisms offer different resistance to the UV radiation. The Table 15.2 [6] reports the approximate lowest dose (J m^{-2}) of UV radiation at 253.7 nm to kill 90% of various microorganism populations.

Both direct and reflected UV radiation are effective when they strike microorganisms. UV rays are free of any residual effect and have no efficacy in dead points (in shadow). As intensity and killing capacity decrease as a function of the distance and reflection, several lamps are installed together with suitable reflectors such as walls coated with highly reflecting material (e.g., stainless steel and anodized aluminum, which reflects as much as 80% of the radiation) [6].

UV rays acting on the cellular DNA of microorganisms do not immediately kill them, so that this kind of disinfection needs time. This is a problem in air-conditioning systems and inside crossing spaces of protected premises. Therefore, the air rate (m^3/min) per $\text{UV}_{253.7\text{nm}}$ watt must be carefully calculated in order to reach the required degree of sterilization. The best result is achieved by coupling UV radiation with high efficient air filters.



Figure 15.6 Example of conveyor protected by UV lamps before filler. UV rays are reflected inside a stainless steel tunnel which covers the track.

Table 15.2 The lowest dose in J m^{-2} necessary to kill 90% of various microorganisms (table adapted from Ref. [6]).

Bacteria		Molds	
<i>Bacillus anthracis</i>	45	<i>Aspergillus niger</i>	1320
<i>B. megatherium</i> (veg.)	11	<i>Aspergillus amstelodami</i>	661
<i>B. megatherium</i> (spore)	27	<i>Aspergillus flavus</i>	600
<i>B. paratyphosus</i>	32	<i>Aspergillus glaucus</i>	440
<i>B. subtilis</i> (veg.)	70	<i>Cladosporium herbarum</i>	600
<i>B. subtilis</i> (spore)	120	<i>Mucor mucedo</i>	650
<i>Clostridium tetani</i>	130	<i>Mucor racemosus</i>	120
<i>Corynebact. diphtheriae</i>	34	<i>Oospora lactis</i>	50
<i>Eberhella typhosa</i>	21	<i>Penicillium digitarum</i>	440
<i>Escherichia coli</i>	30	<i>Penicillium expansum</i>	130
<i>Leptospira spp</i>	32	<i>Penicillium chrysogenum</i>	500
<i>Micrococcus candidus</i>	61	<i>Penicillium roqueforti</i>	130
<i>Mycobact. Tuberculosis</i>	62	<i>Rhizopus nigricans</i>	1110
<i>Phytomonas tumefaciens</i>	44	<i>Scopulriopsis brevicaulis</i>	800
<i>Proteus vulgaris</i>	26		
<i>Pseudomonas aeruginosa</i>	55		
<i>Salmonella enteritis</i>	40	Yeasts	
<i>S. typhosa</i> – Typhoid fever	22	<i>Saccharomyces ellipsoideus</i>	60
<i>S. paratyphi</i> – Enteric fever	32	<i>Saccharomyces cerevisiae</i>	60
<i>S. typhimurium</i>	80	<i>Torula sphaerica</i>	23
<i>Sarcina lutea</i>	197		
<i>Serratia marcescens</i>	24		
<i>Shigella dysenteriae</i>	22		
<i>Spirillum rubrum</i>	44		
<i>Staphylococcus aureus</i>	26	Algae	
<i>Streptococcus hemolyticus</i>	22	Diatomeae	3600–6000
<i>Streptococcus lactis</i>	62	Green algae	3600–6000
<i>Streptococcus viridans</i>	20		
<i>Mycobacterium tubercoli</i>	100		
<i>Vibrio comma</i> -Cholera	34		

UV lamps prove to be very useful in air ducts and store rooms for seasoning, chilling, and drying when foods cannot be removed (e.g., cheese, salami, Parma ham). Air is disinfected without contaminating the foods. UV radiation prevents unwanted green-gray molds from growing and leaves the white ones to compete better on salami, lowers the bacterial charge in cold-storage rooms, reduces waste during meat trimming, and promote the smooth maturing of cheese by controlling wild yeasts and color-forming bacteria.

The output of ultraviolet lamps drops below an acceptable level in the course of time. Thus, time of use is monitored, and lamps are replaced at the end of their life, usually after 85% loss in activity (roughly 5–8000 hours of running). UV rays injure eyes (severe irritation) and skin (inflammation). Suitable shields prevent personnel from being directly affected by radiation.

15.3

Control by Chemicals

The treatment of enclosed spaces with chemicals is accomplished by applying dry bactericidal systems (at temperature above the condensation point, e.g., dry gases such as ethylene oxide and dry formaldehyde) or wet systems (e.g., atomization and aerosolization of disinfectants).

The use of dry gases is a specialized and hazardous application. Licensed experts carry out the treatments in carefully prepared premises (sealed) and under well-controlled running conditions. Fumigation by dry aerosols belongs to this technology [7].

Wet systems characterize the application of traditional chemicals aimed at obtaining clean rooms and disinfecting critical enclosed spaces. A wet treatment is based on disinfectants diluted in water and spread in air. Suitable equipment converts them into very small particles able to keep the enclosed spaces saturated for a long time.

15.3.1

Atomization and Aerosolization

Atomization, also known as nebulization, differs from aerosolization in the drop-lets size. Atomized micelles have a typical diameter greater than 30μ and are significantly larger than those of aerosols, which do not exceed 5μ . Large size causes low retention time in air, yields undesirable moistened surfaces, and decreases disinfecting activity. However, particles whose diameter is within the range $0.5\text{--}5\mu$ give the disinfectant a more dry effect (non-wetted surfaces) and longer suspension times. A small size is not only responsible for a persistent saturation but also for an electric charge on the generated micelles as a consequence of rubbing and friction during the aerosolization. Small size, electric charge, and vibration contribute to the suspension stability and prolong the disinfecting activity. The disinfection mechanism is summarized in the following steps and is illustrated in Figure 15.7.

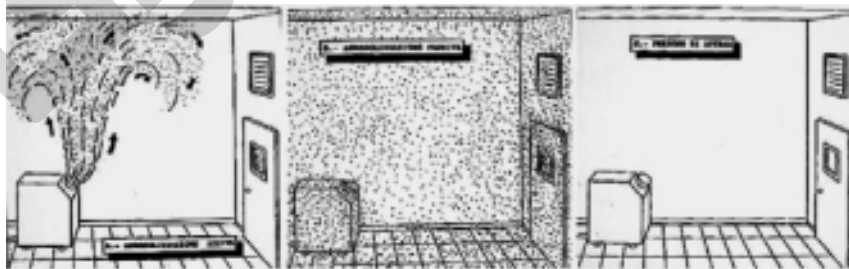


Figure 15.7 Aerosolization, saturation, and sanitation (courtesy of Crivello-Bavagnoli [8]).

- ❑ fill the fogging units
- ❑ 5-10 minutes fogging
- ❑ 15 minutes pause
- ❑ new cycle of fogging lasting 5-10 minutes
- ❑ 15 minutes pause
- ❑ new cycle of fogging lasting 5-10 minutes
- ❑ rinse the fogging units

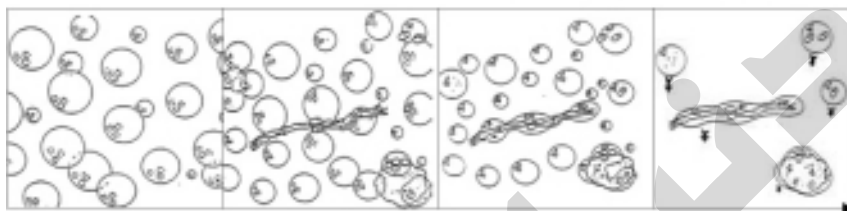


Figure 15.8 Fogging device and schematic mechanism of wrapping and sedimenting the airborne particles (courtesy of Crivello-Bavagnoli [8]).

- The disinfectant solution is aerosolized. The aerosol structure is also enhanced with suitable smoke or fog promoters. Promoters are additives based on glycols and glycol ethers able to make the disinfecting micelles smaller.
- Aerosols come into contact with, absorb, and coat the polluting particles with a layer in which the biocidal activity starts.
- The coated particles become heavier and precipitate out.
- The disinfection is complete.
- The inertized particles are removed when the floor and surfaces are cleaned.

It is evident that the success of the treatment depends on the ability of the equipment to saturate the environment. Fogging is performed in rooms free of personnel. Nobody must enter the saturated area. After settling, personnel cannot enter the room before at least 5 changes of the air volume. The typical cycle shown in Figure 15.8 is usually practiced.

Checking nozzles for clogging and gaskets for integrity are obvious steps to take before proceeding.

The concentration of disinfectant per cubic meter varies as a function of the type of the disinfecting molecule. Disinfectant are assessed according to their lowest lethal concentration. This is usually within the range $0.5\text{--}5\text{ g m}^{-3}$ of pure disinfectant.

15.3.2

Chemicals

A relatively long list of disinfectants is theoretically available. However, restrictions due to toxicity, corrosion, persistent odors, and foam difficulties, the number becomes limited to the following classes:

15.3.2.1 Aldehydes

Glutaraldehyde is one of the best chemicals, being able to interact with the whole spectrum of microorganisms. The action mechanism is based on the ability of the functional group to react with the proteic nitrogen. Glutaraldehyde is used alone or in combination with quaternary ammonium and amphoteric compounds, the activity of which is to complement (killing spores) and synergize (acting faster). There are no residual effects when glutaraldehyde (a volatile compound) is applied alone. Hence, it is also suitable for treatment of air recycling systems, including the filtering system. Its characteristically pungent odor is a useful signal revealing the presence of the compound at very low concentrations. The sense of smell warns personnel not to enter the enclosed space before the chemicals have been thoroughly evacuated.

15.3.2.2 Nitrogen Derivatives

The presence of the nitrogen group characterizes these chemicals and provides them with a long-lasting effect for the following reason. Nitrogen is strongly absorbed onto the surface and, even after rinsing, a layer of molecules still remains adsorbed. This residue, though only a trace, keeps surfaces disinfected longer. The cellular membrane is affected by this adsorbed layer and its vital exchanges are blocked. The vegetative microorganisms are killed and its spores are prevented from germinating. The condensation of the particulate into larger droplets enhances this effect as well promoting precipitation. Absence of odor, no corrosion, and low toxicity make this group of chemicals particularly suitable for treating enclosed spaces. Typical members of the group include

- monomeric and polymeric quaternary ammonium compounds (QACs)
- fatty polyamines
- amphoteric fatty polyamines
- polybiguanide.

They are atomized alone or in combination with glutaraldehyde, nonionic surfactants, and sequestrants such as EDTA, which is able to synergize the QAC disinfecting activity. The choice of nitrogen derivatives depends on whether filters are included in the air cycle or not. Filters adsorb and do not release the nitrogenated disinfectants. Thus, if the disinfection procedure is also applied to a filtering barrier, nitrogen compounds cannot be applied (clogging of filters). HEPA filters usually are not disinfected but disposed of when they lose activity.

15.4

Mold Control and Prevention

Mold growth is one of the most common and troublesome problems in the food industry. Although molds grow on dead organic matter everywhere in nature, their presence is only visible to the unaided eye when mold colonies grow. A mold colony does not comprise discrete organisms, but an interconnected network of hyphae known as mycelium. Closed environments, humidity and temperature

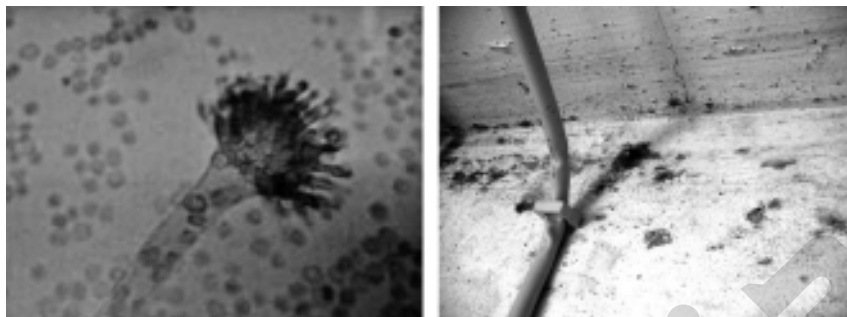


Figure 15.9 Spores release (courtesy of Oxoid) and growth of molds on wall.

are often stable enough to foster the growth of mold colonies. Thus, buildings, being stable environments, enable mold proliferation to occur. Some molds can grow at temperature as low as 2°C. When conditions do not enable them to grow, molds remain alive in a dormant state within a large range of temperatures before they die. This explains how molds survive harsh conditions such as containers in refrigerators or inside building structure cavities.

Some mycotoxins from mold metabolism are harmful to everyone. Others induce immune system responses that vary depending on the individuals.

Molds reproduce through small spores (Figure 15.9). A spore is even more resistant to adverse conditions than the vegetative form. Spores can be allergenic or, when inhaled, can germinate along the respiratory tract causing infections and death. Airborne spores contaminate food, modifying its organoleptic properties and reducing its shelf life.

The control of molds is often carried out with an unsuitable choice of disinfectants and procedures. In order to understand the reason for the failure of several active agents, it is necessary to know how the disinfectant performs. Disinfectants are divided into two main groups:

- oxidants (redox activity)
- nitrogen group derivatives (cationic and partially cationic activity).

Redox chemicals are characterized by a rapid killing action but a lack of any residual activity. Chlorine, iodine, bromine, peracids, hydrogen peroxide, chlorine dioxide, sulfur dioxide, glutaraldehyde, and ozone belong to this group.

Cationic compounds are less sensitive to dirt (depending on the type of molecule) and give prolonged surface protection after rinsing. According to the zeta potential theory, a layer of cationic molecules is not removable, remaining on the surface even after a vigorous rinse. The residual layer goes on protecting the surface from the airborne fall-out. Monomeric and polymeric cationics, chlorexidine, polybiguanide, imidazoline derivatives, fatty polyamines and amphoteric polyamines belong to this group.

Because of their behavior in enveloping and clinging to the surface for a long time, cationics kill the vegetative form and prevent spores from growing by

coating them. Thus, cationic derivatives provide good control and prevention of growth of molds on open surfaces.

Chlorine is commonly used against molds on walls. In practice, chlorine only shows a bleaching action. After treatment with chlorine, molds soon start growing again. Therefore, chlorine can be used as first step to clean and bleach. After washing with chlorine, covering the surface with 1% cationics solution (no rinse) prevents molds from further growth. By repeating the treatment with QAC once a year, the problem of mold growth is permanently solved.

Quaternary ammonium compounds and fatty (amphoteric) polyamines should also be sprayed onto walls before and after whitewashing. Thus, the complete procedure for preventing the mold growth is as follows:

- 1) Clean wall with chlorine.
- 2) Rinse chlorine off.
- 3) Spread 1% QAC solution without rinsing.
- 4) Apply whitewash.
- 5) Spread 1% QAC solution after the whitewash has dried without rinsing.
- 6) Repeat the QAC application at least once a year.

A simplified procedure is:

- 1) Clean wall with chlorine.
- 2) Rinse chlorine.
- 3) Spread 1% QAC solution without rinsing.

Then, although the cationic compounds cannot be defined as sporicides according to the correct definition of the term, in practice they behave as spores controllers by preventing them from sprouting. The final result of the sanitation is just the same as far as the food industry is concerned.

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دینی جای
مکتبہ

16

Ultrasound Cleaning

Simple basic concepts of detergency based on high frequency sounds are briefly discussed with the emphasis on understanding chemicals and equipment. Ultrasounds are waves whose frequencies are above the limit of human audibility (Figure 16.1).

Frequencies above $16 \cdot 10^3$ cycles per second or 16 kilohertz (kHz) do not affect the human ear (ultrasound) and are suitable to be used for cleaning. In particular, sounds with frequencies within the range 18–40 kHz are used in cleaning technology [1]. High-frequency vibrations generate cavitation, agitation, and implosion of hydrostatic pressure. In nonelastic media, such as aqueous solutions, compression and rarefaction are responsible for bubble creation (rarefaction and cavitation) and violent collapse (compression and implosion), which cause shock waves to radiate from the site of the collapse [2]. In other words, the cavitation bubbles produced by rarefaction implode during compression, resulting in the production of highly intense shock waves as shown in Figure 16.2.

Magnetostrictive or piezoelectric oscillators produce ultrasonic waves. Vibrations are produced by a resonance device when an alternating current is applied. It is estimated that micro-pressures higher than 200 bar are generated. A further increase in pressure occurs when ultrasonic waves spread through a liquid. In this case, the hydrostatic pressure reaches a few thousand bars immediately prior to the annihilation [1]. The mechanical force of high frequency sounds is considered to be responsible for dissolving soluble soil and displacing insoluble soil. This is especially beneficial when irregular surfaces, crevices, and internal zones are cleaned.

Equipment varies, according to the industrial application, from the simplest heated tank to more sophisticated systems including rinsing and hot-air dryers, and finally to large installations using immersible ultrasonic transducers mounted on the sides or bottom of the cleaning tanks [2]. Detergents dedicated to ultrasonic cleaning are formulated to supplement the mechanical pressure with chemical strength, sequestration, and wettability, according to the nature of both the contamination and the surface. Particular care is taken in order to obtain ultrasonic waves with the best conductivity.

The approach to ultrasonic cleaning is summarized in the following points:



Figure 16.1 Approximate frequency ranges with a rough guide to some applications (Wikipedia, CC-BY-SA-2.5).

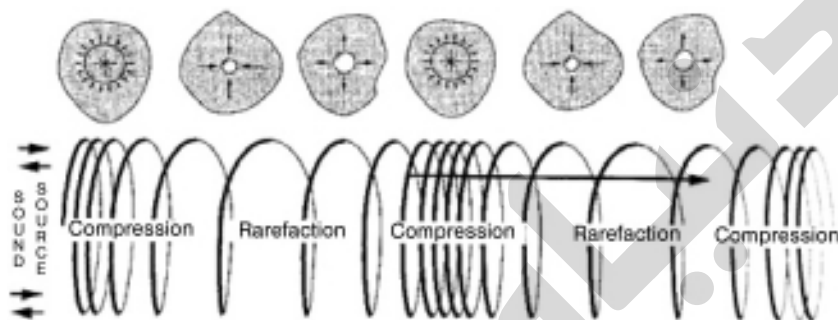


Figure 16.2 Cavitation bubbles are created during rarefaction and violently collapse by implosion during compression (adapted from F.J. Fuchs [2]).

- 1) Ultrasonic equipment is designed according to the type of contamination and the shape of the items to be cleaned. Ultrasonic waves are unidirectional and are focused like a light beam. They concentrate in a limited area, so that the remote side of the bodies usually receives less energy because the mechanical force is usually less intense than claimed. For this reason, the ultrasonic sources (transducers) are set not only along one side of the tank but also in multidirectional positions.
- 2) Ultrasonic waves tend to form standing waves at roughly 2 cm intervals consisting of alternating peaks and troughs of energy (Figure 16.3). Differences in energy lead to poor detergency and leave stripes of contaminants. Therefore, besides maximizing the cavitation of the cleaning liquid, the ultrasonic apparatus is designed to provide a slow movement of the pieces (rotation) in order to enable the peaks of energy to cover the whole area (set-up of cleaning).
- 3) The cleaning solution should provide the ultrasonic waves with good transmissibility rather than aiming at high concentrations and temperatures. Although increase in temperature improves traditional cleaning, ultrasonic cleaning reaches its highest efficiency at an intermediate temperature [1]. Change in temperature means change in viscosity and solubility of the gas in the liquid. Viscosity and gas decrease the intensity of cavitation.

If efficiency and temperature are compared in a graph, each solution reveals an optimal narrow range of warm temperature where cavitation and cleaning are at their best. Increase in causticity (viscosity) leads to less effective cavitation. The cavitation effect is maximized by rising temperature up to the steady point

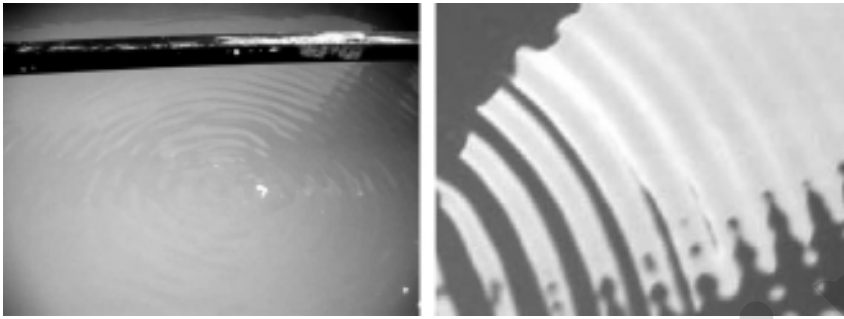


Figure 16.3 Waves induced by high-frequency vibrations (compression and rarefaction).

of viscosity. Best practice is to use a detergent at its maximum recommended temperature, preferably within the range 50–70 °C but not exceeding 85 °C [2].

The mechanical force of the ultrasonic waves is achieved by implosion against the surface and is maintained by the transmissibility of the waves. Thus no chemical agent or physical hindrance (micro-foam) should diminish the implosion energy. For effective cavitation, the cleaning liquid should contain as little dissolved gas as possible because the cavitation phase releases the dissolved gas. This release diminishes the power of the implosion and leads to less efficient cleaning [2]. Strong chemicals and high temperatures could be less effective than good wave transmissibility. Preliminary laboratory tests are carried out to define the most effective narrow interval of concentration and temperature.

- 4) Listening to the sound of the equipment can roughly reveal the status of efficiency (when they reach the peak or leave it).
- 5) As far as the conductivity of the ultrasonic waves is concerned, it has been verified that:
 - the inorganic components of the detergent (caustic soda/potash, mineral acids, sequestrants, inorganic builders. ...) do not allow the ultrasonic waves to reach their optimum strength.
 - caustic soda and inorganic builders achieve maximum cleaning only when they are formulated together with wetting surfactants. Then, specific surfactants have to be investigated for the ultrasonic application. In spite of what is claimed about the benefits of preventing gas formation inside the solution, the benefit of wetting surfactants in preventing premature cavitation is so great that the negative effects of a few gases generated inside (micro-foam) are negligible in comparison with the cleaning efficacy.
- 6) Soft bodies (plastics, cotton) are difficult to clean. According to the theory, implosion is partially absorbed by the flexible elastic materials. For this reason, the use of soft walls for tanks is not recommended. When plastics and other



Figure 16.4 Laboratory ultrasound equipment.

soft materials are involved in cleaning, particular care in matching the ultrasonic equipment and detergent solution is even more necessary. Overloading (mainly with small parts) can sometimes result in ultrasonic energy being preferentially absorbed and attenuated. Cleaning cannot be expected in remote areas.

- 7) Cavitation can generate mechanical corrosion, especially when excessive power (watts per volume unit) is used. However, the short treatment time prevents metals from being attacked, so that cavitation in ultrasound technology does not induce significant corrosion. When corrosion occurs, it usually depends on the type of detergent and nature of the metal rather than on the mechanical strength of the cavitation pressure.
- 8) A planned cleaning procedure includes periodic removals of the accumulated bulk of soil in order to achieve a good time schedule and maximum cleaning efficiency. To minimize the amount of soil held in suspension, an amount of cleaning solution should be removed at regular intervals.
- 9) Before deciding on the most suitable detergent and working conditions, it is useful to investigate samples of soil and other relevant materials with laboratory pilot equipment (Figure 16.4).

Ultrasound technology does not yet play a significant part in the food industry. It first needs investment and more operating experience. However, ultrasonic aqueous cleaning can give results surpassing those achieved by the standard methods of detergency. Properly utilized, ultrasound can contribute to saving time and money, and can take cleanliness to a level that cannot be achieved by any other means.

References

- 1 Spring, S. (1974) *Industrial Cleaning*, Prism Press, Melbourne.
- 2 Fuchs, F.J. (1995) Ultrasonic cleaning: fundamental theory and application. *Precision Cleaning '95 Proceedings*, Rosemont, IL, May 15–17, pp. 334–346.

17

Corrosion and Corrosion Inhibition

In this chapter, we discuss the most frequent problems of corrosion resulting from the application of detergents and disinfectants in the operational complexity and environmental conditions of a food industry. One should be familiar with the elements of electrochemistry, metallography, chemistry of metals, chemistry of the components of formulations, the configuration of plants, and electromagnetism induced by motors and electrical conductors in order to succeed in identifying the causes and kinetics of corrosion.

The intensity of corrosion is expressed as the weight change per unit of surface (e.g., g/m²/year) and as the corrosion rate considered as penetration of the corrosive process into the metallic mass per unit of time (mm/year). Stainless steel (AISI 304, 316) and aluminium represent the most common reference materials in the food industry. Acids, caustics, chloride, and biofilm provide potentially corrosive environments, while oxidants (oxygen donors) affect the kinetics of corrosion in progress.

Corrosion is costly not only because of its sheer destruction of expensive equipment but also because of the possible contamination of finished foods by causing product instabilities (off-flavors and fragrance changes, appearance modification, shorter shelf-life) and health dangers. Therefore, it is always necessary to strike a balance between the cost of anticorrosion measures and their efficacy as illustrated in Figure 17.1.

Each industry defines its own degree of safety by a point (P) that gives the most profitable compromise. Equipment planning, materials selection, and periodic inspection (maintenance) enable corrosion to be prevented or kept under control. The types of corrosion, the resistance of materials to corrosion, and the corrosion potential of the various chemicals are exhaustively described in the literature (see, for example Refs [1–7]).

17.1

Calculation and Monitoring of Corrosion

The measurement of weight is the simplest method to obtain quantitative evidence of corrosion, but it only has a practical meaning if it refers to generalized

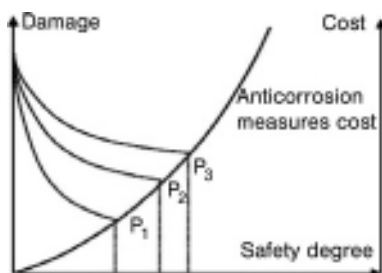


Figure 17.1 Cost of corrosion damage and anticorrosion measures as a function of the desired safety degree.

and uniform corrosion. The loss in weight does not give information about localized corrosion such as pitting on stainless steel. Electrochemical methods measure localized corrosion by changes in redox potential and give more useful information about corrosion in progress than loss in weight.

17.1.1

Intensity and Rate

The weight variation per unit of surface is defined as the corrosion intensity. The penetration of a corrosive process into the metal mass per unit of time indicates its rate. The following equation provides the relationship between the two parameters:

$$R(\text{mm y}^{-1}) = \frac{8760 \cdot \Delta w \cdot 10}{S \cdot d \cdot t}$$

where:

R = corrosion rate	mm y^{-1} = mm of penetration per year
8760 = number of hours in a year	Δw = weight loss in g cm^{-2}
S = exposed surface in cm^2	t = exposure time in hours
d = density of metal in g cm^{-3}	

The specific gravity of the metal (d) is essential in the calculation. Table 17.1 gives some values of this parameter [2].

The metallic coupon is carefully cleaned, abraded with inert powder, pickled, dried, and preserved in solvent (ethyl ether) before starting the contact with the corrosive solution to be tested. A weighing correct to four decimal places ensures that the loss in weight will be accurately measured. On the basis of price and corrosion data, Rice [2, 8] divides metals into three classes:

- **Class I:** silver, titanium, nickel-molybdenum alloys, nickel-molybdenum-chromium alloys, gold, platinum, tantalum, zirconium and their alloys
- **Class II:** aluminum, copper, bronzes, copper-nickel alloys, high-alloy steels, nickel, monel, nickel-chromium alloys
- **Class III:** iron, lead, brasses, zinc.

Corrosion ratings are given for each class and are reported in Table 17.2.

Table 17.1 Specific gravity of metals used in the calculation of corrosion intensity.

Cast iron	7.20	Nickel-chromium alloys	8.50
Mild steel	7.87	Lead	11.15
Steel	7.86	Molybdenum	10.20
Aluminum and its alloys	2.70	Hastelloy B	9.24
Brasses	8.60	Hastelloy C	8.94
Bronzes	8.70	Silver	10.50
Copper	8.94	Tantalum	16.60
Cr and Cr-Ni steels	7.85	Titanium	4.54
Nickel	8.90	Zirconium	6.50
Monel	8.84	Platinum	21.45

Table 17.2 Rating of corrosion.

Corrosion rate (mm/y)			Rating on the use of the detergent
Class I	Class II	Class III	
to 0.075	to 0.125	to 0.225	Fully satisfactory
to 0.150	to 0.300	to 0.750	Use with caution (observe carefully the suggested procedure)
to 0.250	to 0.500	to 1.380	Use only under special conditions for short exposure (use in extraordinary applications and under continuous control)
>0.250	>0.500	>1.380	Not to be used

Even though the above corrosion assessment is approximate, nevertheless it meets the operational standard. Predictions, extrapolated from the above table, are satisfactorily confirmed in practice.

17.1.2

Electrochemistry

Since pitting (Figure 17.2) is concentrated on a small localized area of the metal surface, loss in weight procedures are unsuitable to monitor this highly destructive form of corrosion. An effective measurement is inferred from electrochemical methods (Figure 17.3).

Corrosion consists in oxidizing the metal, which releases an electron stream. The intensity of the electron stream is directly correlated to the corrosion rate. Since reduction (reaction of the electrons) simultaneously occurs on the same metal, corrosion cannot be measured without an auxiliary device. The addition of an auxiliary electrode allows the electrons from the oxidation process to be

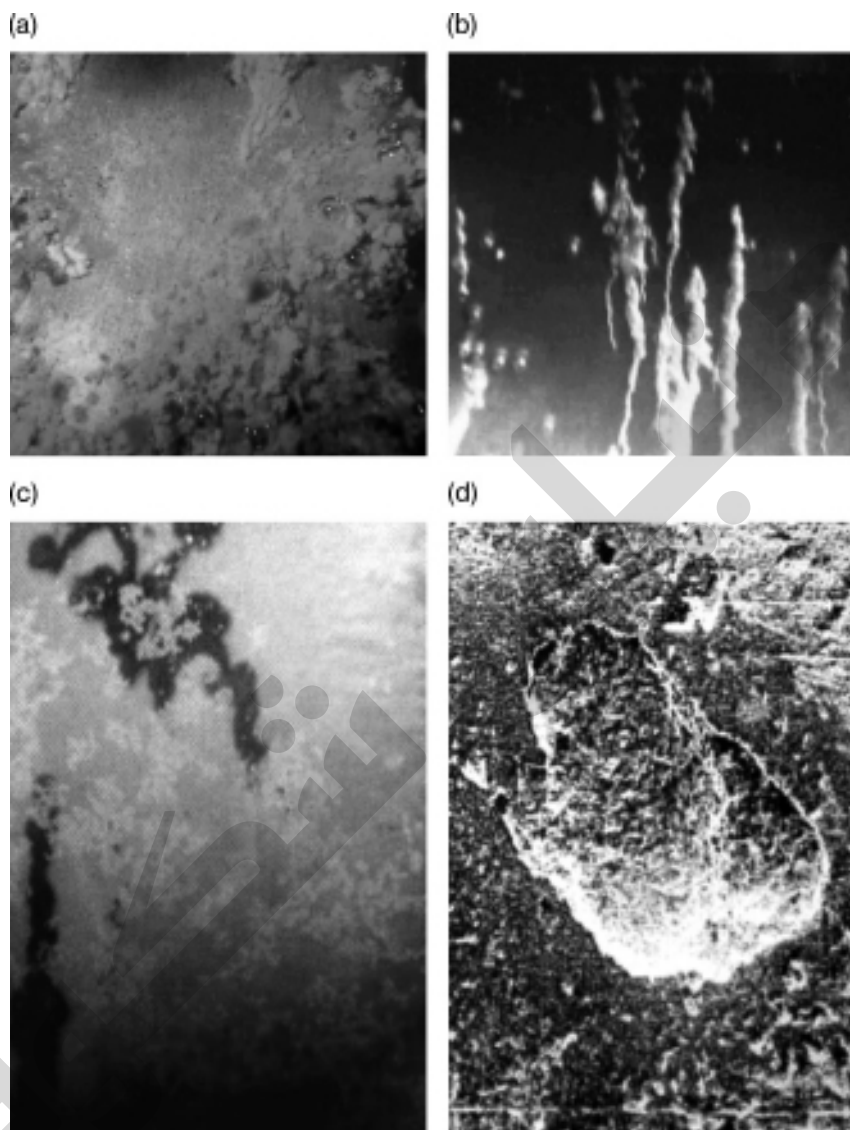


Figure 17.2 Pitting on different metals: (a) mild steel, (b) galvanized steel, (c) copper, and (d) stainless steel AISI 304 (microscope).

collected and a direct measurement of the intensity of the stream (corrosion) to be measured. Figure 17.3, adapted from Bearfield [20] explains the concept:

Oxidation and reduction create a voltage (potential E) on the metal. This potential, known as the rest potential (E_{rest}), is measurable with a voltmeter and a reference electrode. For each specific metal/solution system, a unique E_{rest} is established. If a potentiostat imposes onto the metal an external voltage more

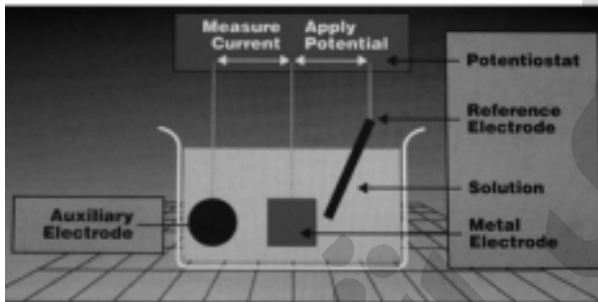
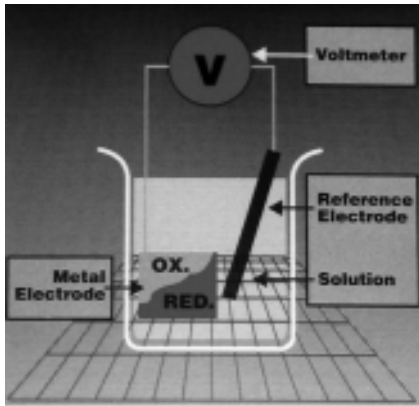


Figure 17.3 Measurement of rate of corrosion (courtesy of Diversey Co.).

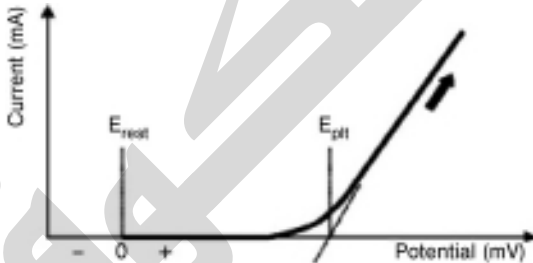


Figure 17.4 Pitting potential.

positive than E_{rest} (polarization) and an auxiliary electrode is introduced into the system to collect electrons, oxidation will predominate and the metal corrosion will be detected as a flow of electrons.

Polarization induces an increase in current. The potential at which the current sharply increases defines the pitting potential (E_{pit}) (Figure 17.4).

$(E_{pit} - E_{rest})$ gives the measure of the tenacity of the passivation film. Positive $(E_{pit} - E_{rest})$ values indicate a noncorrosive system. No current at E_{rest} reveals absence of corrosion. Negative values indicate pitting in progress.

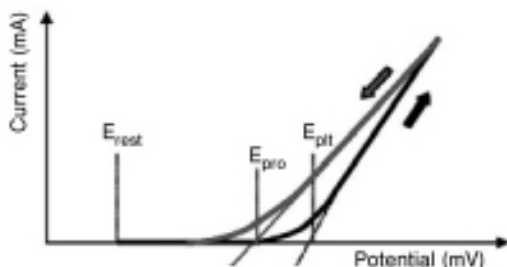


Figure 17.5 Protection potential.

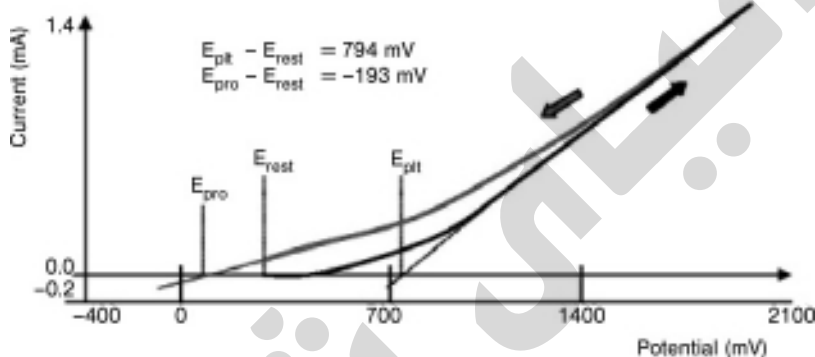


Figure 17.6 100 ppm available chlorine from sodium hypochlorite in distilled water (courtesy of JohnsonDiversey).

In order to measure the corrosion, after reaching the predetermined current polarization is stopped and the current decreases to its original value (cyclic polarization). The potential at which the current sharply decreases and intersects the zero-current axis is known as the protection potential (E_{pro}), where passivity is restored and corrosion stops (Figure 17.5).

($E_{pro} - E_{rest}$) indicates whether the metal restores passivity or pits will continue to grow. When E_{pro} is higher than E_{rest} , passivation is restored on the metal. When E_{pro} is lower than E_{rest} , the metal-solution system is unable to self-repair pits. Then, if a current is observed at the rest potential, pitting will be self-perpetuating and the system has an inherently corrosive nature. Sodium hypochlorite is the typical example, as shown in Figure 17.6.

The Figure 17.6 electrochemically demonstrates the well-known inherently corrosive nature of sodium hypochlorite on stainless steel. This conclusion is applicable to all chlorinated detergents/disinfectants. Statistically (16 replicates) no differences are observed for any product between 304 and 316 stainless steels.

Figure 17.7 shows the noncorrosive nature of peracetic acid and how corrosion starts in the presence of chloride.

Peracetic acid gives E_{pro} higher than E_{rest} , so that passivity is restored. The presence of chloride shifts E_{pro} to a negative value, and pitting is then in progress. Peracetic acid (and peroxides) does not corrode stainless steel at the usual con-

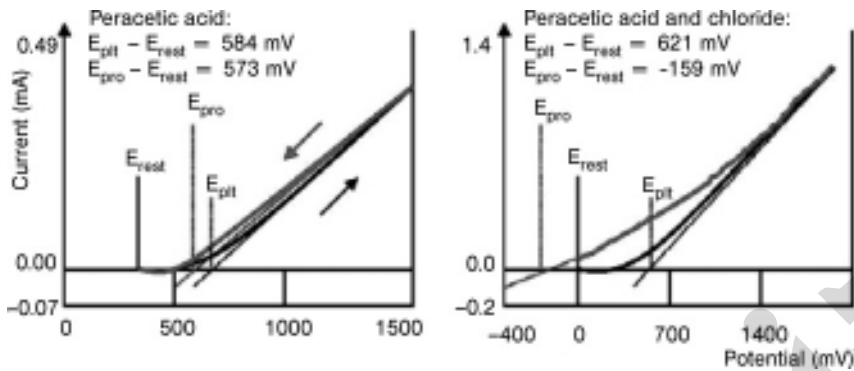


Figure 17.7 PAA 0.15% and PAA 0.15% + chloride 100 ppm in distilled water (courtesy of JohnsonDiversey).

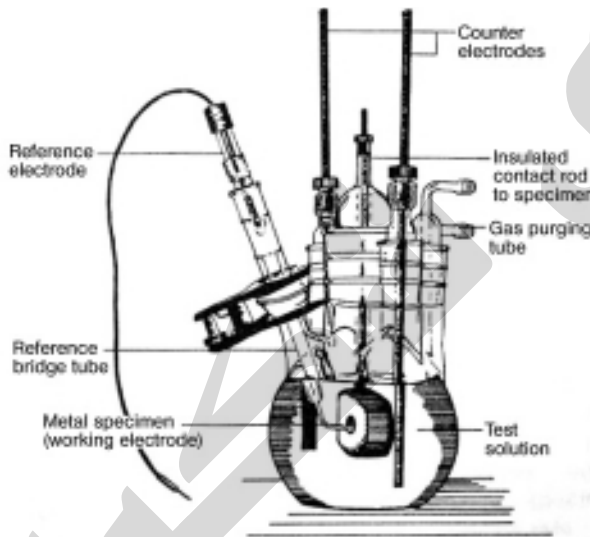


Figure 17.8 Example of electrochemical corrosion equipment (courtesy of EG&G Princeton Applied Research [9]).

centration. However, the presence of 50 ppm chloride causes the solution to corrode. A chloride content of 25 ppm gives erratic behavior. The results indicate that no corrosion will take place only if chloride levels are below 25 ppm. If chloride exceeds 25 ppm, peroxides take part in accelerating the corrosion kinetics (oxygen donors). Pitting without the presence of an external voltage needs time to start (inductive period). Thus, peroxides (peracetic acid) can be very useful in CIP and OPC disinfection (for short periods), but stainless steel cannot be soaked for long periods in the presence of chlorides (see Section 17.2).

A typical electrochemical corrosion test cell is shown in Figure 17.8 [9]. The test cell includes the metal specimen, the solution in which the specimen is

tested, the reference electrode, and two counter electrodes used to supply the current flowing at the metal specimen during the test.

In practice, although chlorinated products perform a considerable number of cleanings and disinfections, no problem of corrosion is observed. If certain rules are observed, such as using a short contact time, an alkaline/phosphate medium, and a chlorine concentration below 1000 ppm, chlorine can be used without generating pitting. Of these limitations, contact time and ppm of chlorine have an inverse relationship. Moreover, tolerance to pitting is proportional to increase in pH. The next paragraphs develop these relationships.

17.2

Stainless Steel and Chloride

Pitting corrosion is a highly localized form of attack characterized by a penetration in depth much greater than the superficial area involved. It is probably one of the most destructive forms of corrosion in spite of the relatively small amount of metal corroded. The formation and development of pits are associated with the migration of aggressive anions to localized anodic sites. Any protective films (passivation) are locally destroyed and corrosion starts [10]. The loss in passivation is mostly due to the presence of chlorides in the environment, as schematically shown in Figure 17.9.

Local falls in pH (hydrochloric acid formation) keep stainless steel from becoming re-passivated, accelerate the corrosion inside the pit nucleus, and set up an autocatalytic mechanism. Conventional theory ascribes the triggering of a pit to the condition of the surface. The surface film is heterogeneous because of chemical variations in the underlying metal (e.g., at segregated grain boundaries) and scratches, inclusions, and sheared edges, which are likely to produce internal stresses in the film. This means that the film has local weak spots where it is less thick, less resistant, and more permeable than elsewhere. Thus, metal starts dissolving at those points (Figure 17.10) [10].

The aggressive ions must penetrate the passive film to start up the corrosion. The time elapsing before the pitting starts is crucial because it permits the application of chlorinated detergents/disinfectants without causing corrosive events. The time of contact is the key to understanding randomly occurring corrosion. Under caustic chlorinated detergent solutions, the time to establish irreversible pitting corrosion varies from 1 to 3 hours of contact at room temperature, accord-

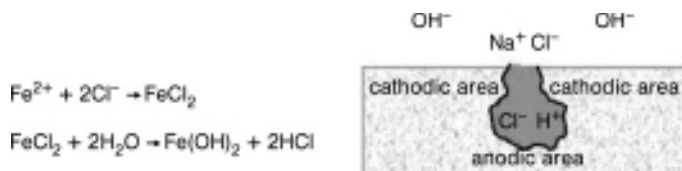


Figure 17.9 Formation and development of pits.

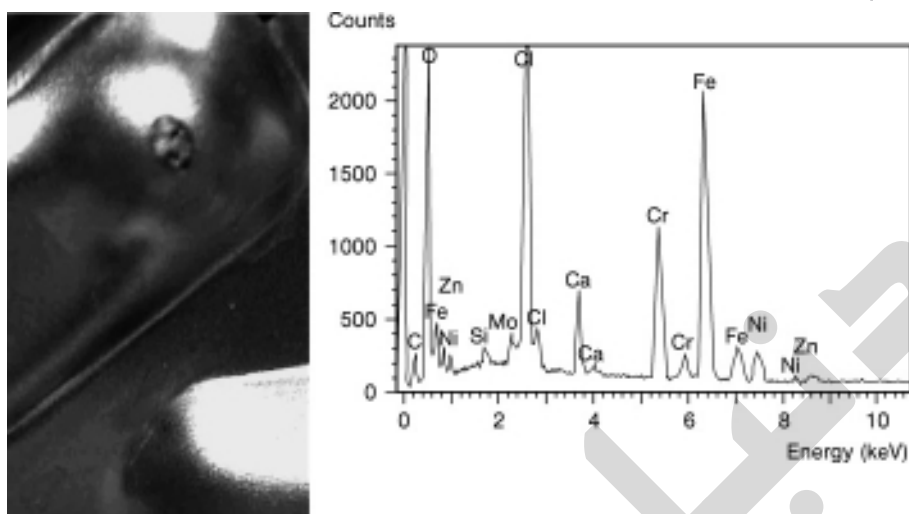


Figure 17.10 Pits on sterilizer plate of fruit juice and EDS analysis of its inside where the concentration of chloride is clearly obvious.

Table 17.3 Analysis of water causing pitting corrosion.

Component	Result				
	Test no.				
	1	2	3	4	5
1 Total suspended solids (mgL^{-1})	35.33	18.6	27.33	28.66	16.0
2 Conductivity ($\mu\Omega\text{cm}^{-1}$)	2650	2670	2760	2590	2680
3 pH	5.82	6.16	5.92	6.23	6.39
4 Iron (ppm)	0.131	0.020	0.021	0.045	0.015
5 Nickel (ppm)	nd	nd	nd	nd	nd
6 Chromium (ppm)	0.013	0.014	0.014	0.011	0.009
7 Chlorides (mg^{-1})	546.31	520.09	493.86	640.53	503.49

ing to the type of metal and concentration of chlorine. During this time, the metal is still able to self-repair and to restore passivation when the conditions change (e.g., rinse). Unfortunately, there are several sources of chloride, and raw water is one that is often ignored. Water sources close to sea and geological sedimentary deposits originating from the sea contain several ppm of chloride. Table 17.3 shows the analysis of water supplying a tunnel pasteurizer in Mexico, with chloride concentrations up to 600 ppm combined with acidic pH. This tunnel pasteurizer was operating in a very badly corroded state.

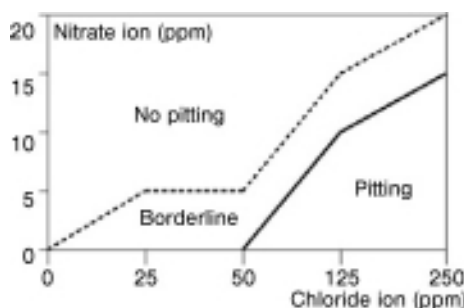


Figure 17.11 Pitting development in the presence of chloride.

The chloride content of raw waters is one of the most frequently neglected causes of corrosion. Rinsing a plant with water containing several ppm of chloride leads to the appearance of aggressive salinity after drying. It is sometimes difficult to make people understand that the water itself can originate pitting corrosion.

Bearfield [20] reports the relationship between chloride, nitrate, and pitting corrosion in Figure 17.11. Although nitrate is effective as a corrosion inhibitor, disposal restrictions make it increasingly unacceptable in food detergency.

Pitting corrosion is certainly expected with chloride levels ≥ 50 ppm in water, whereas corrosion does not occur below 25 ppm. In the borderline region from 25 to 50 ppm, pitting will occur randomly in the absence of corrosion inhibitors.

17.3

Chromium and Chemicals

Chromium plating is widely applied both for decorative effect and to provide a hard surface. Stainless steels, for instance, (e.g., driving shafts, pins, rotating filters, knives ...) can be coated with hard chromium in order to enhance their endurance to mechanical stress. Chromium itself does not suffer pitting corrosion even in the presence of several thousands of ppm of chloride ions. However, corrosion resembling pitting is frequently observed on chromium plating in the field. Figure 17.12 shows an example.

Although hard chromium is resistant to wear, the deposition process generates inevitable inner tensions. Moreover, the expansion coefficient of chromium is usually lower than that of the underlying metal [11]. Hence, cracks take place inside the chromium plating under the influence of thermal changes and mechanical stresses. Cracks allow chemicals to reach the metal beneath and give rise to corrosion. An example of mechanical stress in chromium is shown in Figure 17.13.

The corrosion rate of the underlying metal increases if the metal is sensitive to acids, alkali, or chlorine (chlorides), and this corrosion leads to the detachment



Figure 17.12 Pitting corrosion from chlorinated detergent.

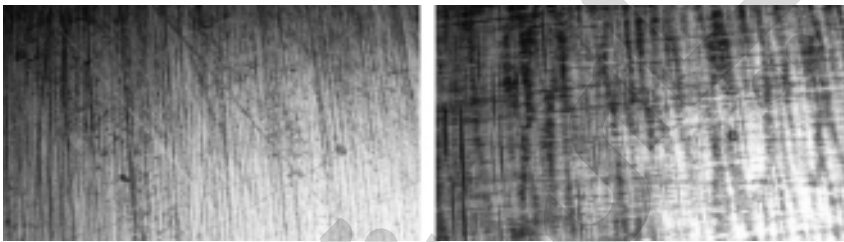


Figure 17.13 Mechanical stress on chromium (photomicrograph).

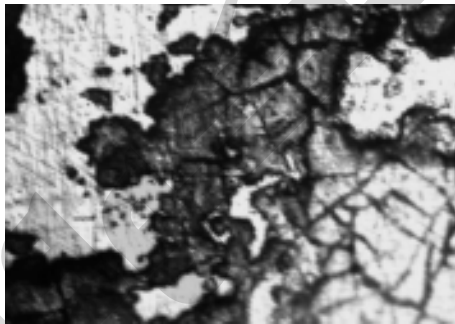


Figure 17.14 Chromium loss by chemical attack (photomicrograph).

of the chromium plating. This process is also aggravated by strong sequestrants such as EDTA in caustic solution (one-step cleaning). Figure 17.14 shows chromium plating corroded from the inside.

Thus, although chromium plating itself is resistant to chemicals, its survival actually depends on the chemistry of the supporting metal.

17.4

Aluminum and Caustics/Acids

Commercially pure aluminium is actually 99.3–99.9% aluminium. Iron, silicon, manganese, and other minor elements are impurities affecting its chemical behavior. Aluminium is an amphoteric element whose stability zone falls within the pH range 6.5–7.0 [12]. Below and above this narrow interval, aluminium dissolves and exposes impurities which accumulate on the surface (mainly iron and manganese oxides). These exogenous elements generate a black coating on the surface of the metal. Acidic (phosphoric acid) and alkaline solutions are responsible for corrosion and darkening. Darkened surfaces transfer black oxides to the food, and this leads to the food being rejected. Black stains on surface of mozzarella cheese are a typical occurrence. Fe-Mn oxides concentrate on the aluminium mold when this is soaked in phosphoric acid solutions. Stain is transferred to the mozzarella during the mechanical shaping. Rejected mozzarella and a contaminated mold can be seen in Figure 17.15.

Similar problems are also well known on the domes and pull-tabs of aluminium cans after tunnel pasteurization. Heated hard water (bicarbonate) loses carbon dioxide and increases in pH. A pH above 7.5 causes aluminium to corrode and produce black stains (see Section 10.1.4).

While increase in pH of heated raw waters can be prevented by adding a weak acid, corrosion by caustics is inhibited by cathodic protection (silicate). Sodium and potassium hydroxide rapidly attack aluminium and its alloys. (Poly)phosphate and gluconate accelerate their dissolution. Silicate usually performs as a corrosion inhibitor despite the fact that the use of silicate in detergents is frequently debated owing to its hazardous nature (see Section 1.2.2). A silicate-free technology has therefore been developed. Combinations of calcium, alkanolamines, and an organic acid (e.g., calcium triethanolamine tartrate/acetate) provide the alkaline solutions with inhibiting properties [13, 14].

Acidic media also corrode aluminium. Phosphoric is the most used acid in food cleaning and descaling. In its usual concentrations (0.5–5%), it corrodes alu-

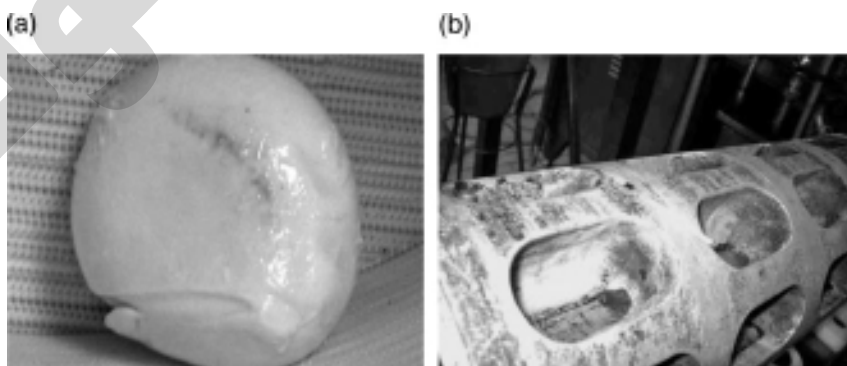


Figure 17.15 (a) Contaminated cheese from (b) stained mold.

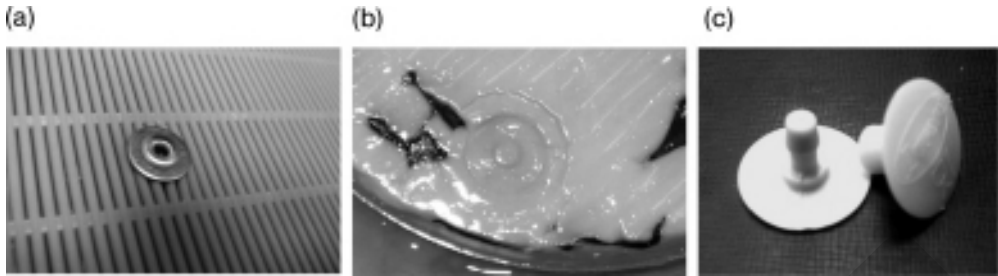


Figure 17.16 (b) Bluish deposit on cheese from (a) stainless steel clamps. (c) Plastic clamps solving the problem.

minium on soaking. Temperature accelerates the dissolution rate. Several sequestrants (polyphosphates and phosphonates) are claimed to be corrosion inhibitors (cathodic protection) in phosphoric acid solutions. Research and experience have led to the selection of two sequestrants: hexametaphosphate (HEMP) and ATMP (see Section 9.2).

The concentration of inhibitor used is in the range 500–3000 ppm. Clear coupons mean slight persistent attack and complexation. Black coupons mean no attack and cathodic protection of the surface. ATMP succeeds in stopping corrosion whereas HEMP keeps surfaces clean because of very slight but continuous dissolution. Citric acid added to phosphoric acid behaves like HEMP. Citric acid is usually added to solution of neutral disinfectants (e.g., based on QAC and EDTA).

Keeping surfaces clean by sequestration (HEMP, citric acid) and preventing corrosion by cathodic protection (ATMP, PBTC) are the two ways in which these chemicals operate. ATMP and PBTC are recommended as co-formulants in phosphoric acid-based detergents for CIP, whereas HEMP and citric acid are suitable additives for soaking applications (e.g., mozzarella cheese molds and dismantled aluminium parts of packaging equipment).

Not only aluminium but also steel alloys can leave black deposits on cheese. Clamps of block molds provide a typical example of this, as shown in Figure 17.16.

The real solution to the problem is to replace steel clamps with plastic ones.

17.5

Copper and its Alloys

Commercially pure metal contains about 99.40–99.95% copper. The remainder of the alloy is made up of negligible quantities of elements such as silver, arsenic, sulfur, antimony, and iron. Although copper is a typical noble element, it is sensitive to dissolved oxygen, with which it forms a protective film [cuprous oxide and basic copper sulfate/carbonate (green-black coating)]. When protective films do not form, copper is easily corroded [4]. Industrial processes of cleaning and descaling remove the protective coat. Acids with inherent oxidizing properties, such

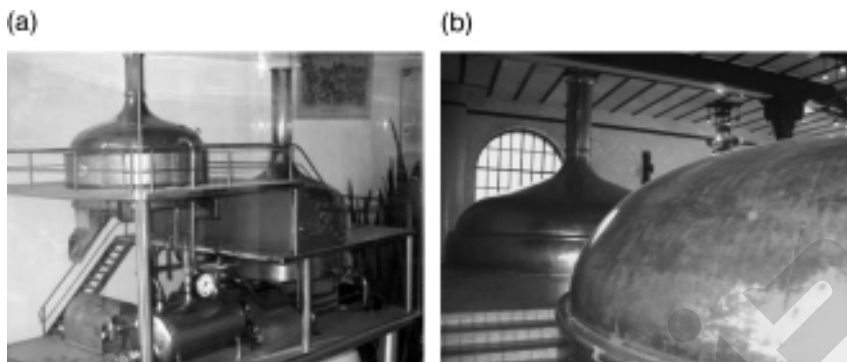


Figure 17.17 (a) Kettles (Doemens-Munich) and (b) lauter tuns (of antiquarian interest).

as nitric and sulfurous and containing metallic salts susceptible to reduction (e.g., Fe^{3+}), rapidly dissolve copper. For this reason, sequestrant-free phosphoric acid gives the best balance and is the most used descaler for copper and copper alloys. Organic acids (e.g., glycolic, formic, citric, tartaric) are good alternatives together with sulfamic.

Copper and its alloys are theoretically resistant to alkaline solutions. However, ammonium hydroxide and nitrogen compounds slowly corrode it to give green-blue complexes. The usual sequestrants formulated in alkaline detergents (e.g., EDTA, phosphonates, and gluconate) help to dissolve and corrode copper. Typical CIPs of copper-containing plant are still performed in breweries (Figure 17.17).

Inhibited alkaline detergents are available. Benzotriazole and mercaptobenzothiazole are specific inhibitors able to prevent corrosion of copper surfaces. They are mainly used as additives to caustic soda.

17.6

Zinc (Galvanized Steel)

A zinc coating on mild steel is extensively used as anodic protection. Zinc provides electrochemical protection where the bare steel acts as the cathode and the zinc as the anode (sacrificial corrosion). A uniform coat never exists. Thus, when an electrochemical cell is set up on a galvanized area, the large cathodic area accelerates the dissolution of the zinc (corrosion) and the protected area decreases exponentially with time [4].

Zinc is very sensitive to chemicals. Atmospheric oxygen, carbon dioxide, and moisture are sufficient to start corrosion. Consequently, acidic and caustic solutions should not be used on zinc because of their strong corrosive action.

Every cleaning, disinfection, and descaling treatment causes loss of the zinc protective coating. The corrosion rate accelerates depending on the temperature, concentration of chemicals, and contact time. Hence, the cleaning of galvanized surfaces makes use of mild alkaline detergents ($\text{pH} < 12$) and neutral disinfectants.

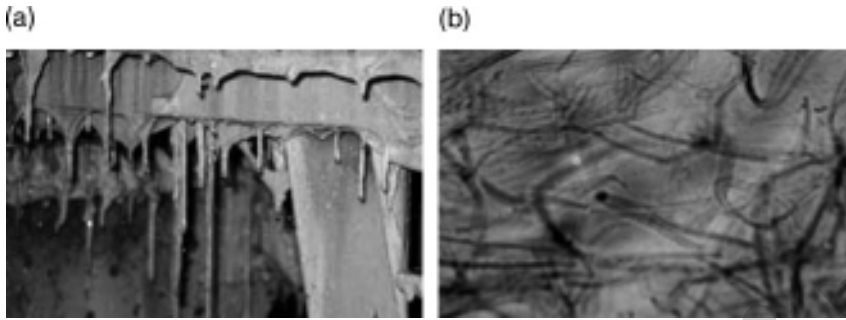


Figure 17.18 (a) Biofilm in a tunnel pasteurizer and (b) iron bacteria co-responsible for corrosion.

tants to sanitize. Descaling is accomplished with phosphoric acid in which corrosion inhibitors specific for zinc are included, such as fatty imidazoline and quaternary arylammonium chloride.

17.7

Biofilm

Biofilm formation, growth and corrosivity on metal surfaces have already been discussed in Chapter 14. It is always opportune to emphasize the importance of preventing microbial growth (Figure 17.18), as this will help in preventing the risk of food contamination, protecting plant from corrosion and the environment from stench. The overall economy of an industry will gain in every respect, from controlling the process to maintaining the integrity of the equipment.

17.8

Reliability of Supply

The austenitic alloys are the most common type of stainless steel used for food. Chromium and iron are the basic metals and nickel is added to form the austenitic alloy. Stainless steel can have the following structures:

- **Ferritic (δ -phase):** body-centered cubic structure where ferritic metals (e.g., molybdenum, silicon) are included in the chromium-iron structure
- **Austenitic (γ -phase):** Face-centered cubic structure where austenitic metals (e.g., nickel, manganese, carbon, nitrogen) are included in the chromium-iron structure

A 1:1 ratio of ferritic to austenitic phase forms biphasic stainless steels (duplex). Austenitic means chromium-iron-nickel steels, although traces of other metals are present either as impurities (e.g., carbon) or as metals improving the

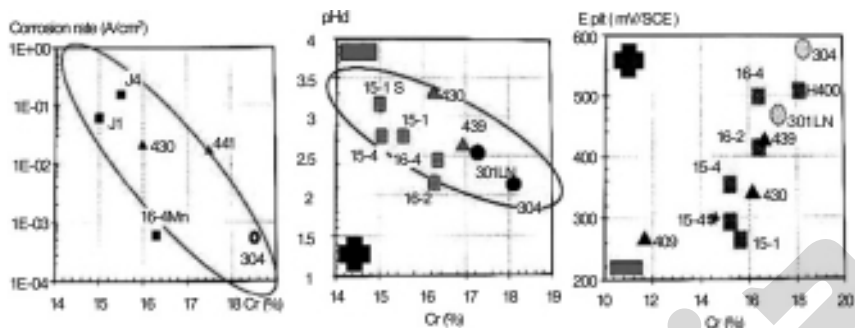


Figure 17.19 Higher sensitivity to corrosion of low-nickel alloys in comparison with AISI 304 (courtesy of J. Charles in *Inossidabile* 162-Dec. 2005).

resistance to corrosion such as molybdenum, niobium, and titanium. Molybdenum forms AISI 316 alloy. Niobium and titanium prevent chromium carbides from forming. The precipitation of chromium carbides decreases the amount of chromium in the alloy grains and, if it falls below 12% (see Section 3.4.5), the remaining chromium is insufficient to prevent corrosion [15].

It is known that the variability of the price of metals such as nickel significantly affects the price of stainless steel. Therefore, low-nickel compositions were investigated in order to manufacture austenitic stainless steels with behavior comparable to AISI 304. Thus, manganese (cheaper) can replace nickel. Alloys where manganese totally or partially replaces nickel are known as the AISI 200 series. When specific applications are well identified and properly evaluated (e.g., aesthetic design, civil buildings, and office architecture) AISI 200 series can replace AISI 304. However, equipment for chemistry need more reliable material. Thus, if the interchange of categories is carried out only for cost reasons, such that sulfur, carbon, and copper concentrations are ignored and ratios of metal contents are incorrect or even misquoted [16], users can experience problems, in particular corrosion during operation. Figure 17.19, taken from Charles's report [17], shows higher sensitivity to corrosion for low-nickel alloys in comparison with AISI 304.

J1 (Ni 1%), J4 (Ni 4%) and other ratios show higher current density (corrosion), higher pHd of depassivation, and lower critical pit potential. They are not suitable to be treated by chemical sanitation methods.

As well as wrong applications, scant accuracy in analyzing the composition of recovered scrap metal leads to polluted alloys which in turn gives castings rich in manganese, copper, carbon, and sulfur. Indiscriminate use of Cr-Mn (200-series), nonobservance of standards, and uncertain composition without adequate and honest information to buyers leads to deceit and damage [18]. Figure 17.20 is an example of how it is clearly questionable to say that a given stainless steel is 'safe' if its surface reacts in the way shown in the pictures.

A metal claimed to be stainless steel but which unexpectedly corrodes in contact with a common foaming alkaline solution is clearly a swindle. Corrosion is frequently inexplicable when a new plant, built close to an old one which is free

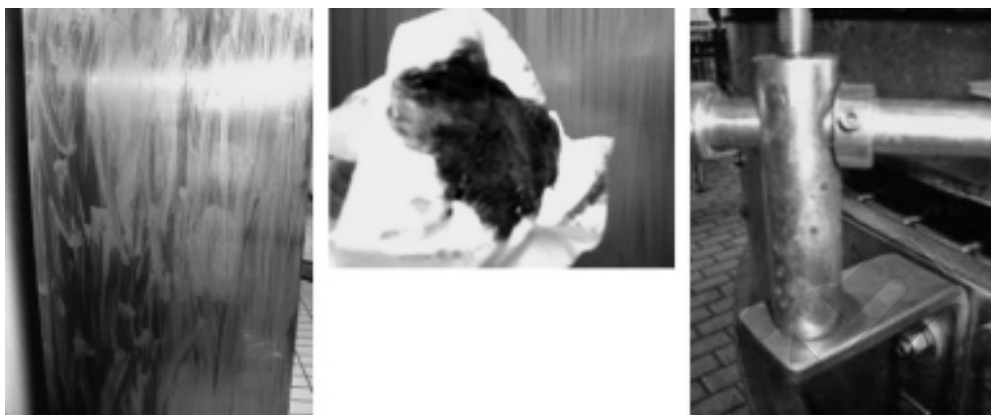


Figure 17.20 Type of stainless steel sensitive to corrosion.

of corrosion, rapidly develops pit and rust under the same environmental conditions and treatment procedures. The tendency of several new AISI 304 stainless steels to undergo pit corrosion more easily than in the past must be ascribed to the use of uncontrolled scrap metal for casting, manganese replacing nickel, and a higher carbon content. Simply, the stainless steel is cheap but out of standard. The user realizes that something different from what claimed has been bought only when running and after several disputes and analyses. The negotiation for saving is limited by the quality of what is bought. The higher the saving, the bigger is the risk of deceit. However, non-conformity to an agreed declaration is considered fraud. Users of stainless steel for manufacturing plants must demand to be guaranteed about:

- 1) exact correspondence to the set of rules for stainless steel
- 2) exact compliance with the chemical-physical characteristics of the material
- 3) traceability of the product in order to be acquainted with the steelworks which has cast and laminated the material (certificate of traceability).

Detergents and disinfectants are not responsible for corroding stainless steel not complying with the specification. The buyer is recommended to demand the technical data sheet in writing and, afterwards, to submit a piece of stainless steel for analysis (chromium-nickel ratio, carbon, manganese, copper concentration and heat sensitivity) in order to verify the truth of what is declared by the supplier.

17.9

Post-Installation Treatment of Stainless Steel

The surface condition of stainless steel is critical in processed food, dairy, brewing, and bottling applications. The surface must not be a source of contamination and

must be corrosion resistant. Stainless steel is protected by a tenacious and durable chromium oxide film which is self-healing in the presence of oxygen. However, this film can become damaged and a site of corrosion if correct post-installation procedures are not followed. It is not uncommon to see new stainless steel tanks with rust streaks after storage in moist air. This is caused by iron embedded in the stainless steel surface during fabrication because of the use of carbon steel tools, wire brushing, mechanical scraping and polishing, and welding squirts. This rusting, apart from being unsightly, could be said to be harmless, but the larger particles of embedded iron can start the process known as crevice corrosion, which could create the right conditions for corrosion all the way through the tank wall and pipelines [19].

Prevention of problems of this nature starts right back at the specification stage. Steps should be taken to ensure that the stainless steel is of the correct specification, that is, that the alloy constituents are correct, with a minimum of inclusions. The surface finish is important and will normally be to 2B finish (ASTM and EN Standards). Certificates to support this should be provided by the supplier.

Stainless steel is often coated with a protective film of oil as part of the production process and sometimes with a plastic film. Responsible fabricators carry out degreasing, pickling, and passivation of the finished equipment before shipment and/or before starting the food process.

When the equipment is received and installed, it should be inspected for embedded iron. One simple method for this is to wash down with clean water, drain completely, and wait for 24 hours. Most embedded iron will then show up as rust streaks. However, this is not professional and will not show small amounts of embedded iron. A more sensitive test is the ferroxyl test using a solution of potassium ferrocyanide such as the following [19]:

• distilled or demineralized water	94%
• nitric acid (63%)	3%
• potassium ferrocyanide	3%.

The solution, when sprayed onto the metal surface, shows iron contamination as a blue coloration after a few minutes contact. If the reaction is positive (blue coloration), the embedded iron must be removed by an acidic pickling (nitric and hydrofluoric acids) after degreasing. If iron is not detected, passivation by a product based only on nitric acid can follow the degreasing step. Nitric acid is sometimes used on its own as a pickling agent but is not very effective. Pickling removes a very thin layer of metal ($<0.25\mu$) as well as any embedded iron. Local pickling, where for example a localized area of contamination needs to be treated, can be dealt with by using pickling pastes (nitric/hydrofluoric acid mixture).

Once pickled (if necessary), the surface of stainless steel is in a reactive or nonpassive state. When left exposed to air, sufficient passivation to give the normal corrosion-resistant surface will occur over the next few weeks. Normally, this time is not available and the equipment needs to be put into production. The danger is that the unpassivated surface will be corroded by the products used to clean it during the normal production. It will even rust when exposed to water.

It is therefore essential that the equipment is quickly re-passivated. A solution of nitric acid-based products will achieve this.

Welded areas can become sites of corrosion and they should be treated with pickling pastes if the entire equipment is not going to be pickled.

17.9.1

Procedures and Recommendations

With new equipment that is expected to give many years of service it would not be wise to take any chances. The recommendation is, therefore, that the full degreasing, pickling, and passivation process is carried out. Only when the reliability of the supplier and the composition, manufacture, and handling of the stainless steel are undoubted, can pickling and passivation by a product based only on nitric acid be accepted.

17.9.2

Example of Complete Program

1) Inspection

When the equipment is received and installed, it should be inspected for damage including embedded iron and weld tint. Badly affected areas can be treated with pickling paste, which is rinsed off after use.

2) Degreasing

The entire assembly is degreased with caustic detergent, which should be recirculated at 3% and a temperature above 60°C for at least 2 hours.

3) Rinse

Rinse with water (hot/fresh) until the pH is ≤ 8 .

4) Pickling

Pickling is achieved by using nitric/hydrofluoric acids at 5–10%, 60–80°C for at least 1 hour. Alternatively, nitric/phosphoric acids can be used at 10–20%, 60–80°C for at least 2 hours

5) Rinse

Rinse with water (hot/fresh) until the pH is ≥ 6 .

6) Passivation

This is achieved by using products based on nitric acid at 5–10%, 60–80°C for at least 1 hour.

7) Rinse

Rinse with water (hot/fresh) to reach neutrality. If necessary, add a little alkalinity (caustic soda or a caustic product) to achieve thorough neutralization.

17.9.3

Example of Simplified Program

1) Inspection

When the equipment is received and installed, it should be inspected for damage including embedded iron and weld tint. Badly affected areas can be treated with pickling paste which is rinsed off after use.

2) Degreasing

The entire assembly is degreased with a caustic detergent which should be recirculated at 3% and a temperature above 60°C for at least 2 hours.

3) Rinse

Rinse with water (hot/fresh) until the pH is ≤ 8 .

4) Passivation

This is achieved by using products based on nitric acid at 5–10%, 60–80°C for at least 3 hours.

5) Rinse

Rinse with water (hot/fresh) until neutrality is reached. If necessary, add a little alkalinity (caustic soda or a caustic product) to achieve thorough neutralization

Tanks and pipeworks should be exposed to a full standard CIP process prior to commencement of product processing.

17.9.4

Gaskets

Gaskets commonly used in the CIP process do not suffer damage with the usual detergents. Common gasket materials are EPDM, PVDF, PTFE, FPM (Viton), PE, and silicone.

NBR, POM, BUNA and gaskets filled with graphite should be avoided because of their low resistant to chemicals in these conditions. Frequently gaskets are also filled with inorganic (e.g., talc, soot) and oily materials. Such gaskets do not resist caustic detergents when strongly sequestered (e.g., EDTA, NTA, MGDA, and HEDTA). The capacity in stripping metals typical of strong sequestrants damages these gaskets even if their basic polymer is resistant in itself (Figure 17.21).

Figure 17.21 shows Viton, one of the most resistant and used gaskets, corroded because the basic polymer was filled with a material reacting with a caustic one-step cleaner.

It is therefore useful to test gaskets with detergents and disinfectants selected for sanitizing in order to verify whether polymers and fillers are compatible with them.

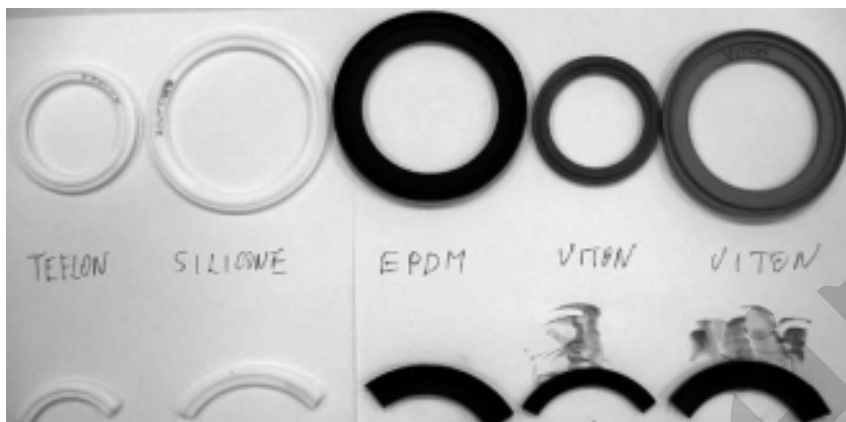


Figure 17.21 New gaskets (top) and after the chemical resistance test (bottom).

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18

Disinfectants and Sanitation Technology

The concept of sanitation is not a personal opinion. Sanitation is measurable, and can be proved, documented, and filed (Figure 18.1).

Microbial contamination differs from chemical contamination since microorganisms are invisible to the naked eye and their presence can only be proved after a relatively long microbiological analysis or as a result of a dramatic deterioration in the quality of processed food. People sense microbial contamination, using terms such as those listed in Table 18.1.

A surface is defined as disinfected when the total viable count (TVC) is not strictly zero but has a value compatible with safe food production. As there are no official TVCs to indicate what level signifies a disinfected surface, good manufacturing practice (GMP) arbitrarily requires a total absence of pathogens and harmful microbes.

The concept of disinfection cannot be divorced from the concept of cleaning. It is impossible to disinfect if a surface is still soiled. Thus, disinfection is an important step but cannot be achieved without previous cleaning steps. It simply concludes the hygiene process. Biofilm is a representative example of fouling often neglected and not considered in terms of chemical contamination (Figure 18.2).

Biofilm is the microorganism's home, consisting of metabolized organic matter inside which microorganisms live and defend themselves (see Chapter 14). A surface cannot be disinfected without removing such biofilm with suitable cleaners. Immediately after cleaning, the surface can be satisfactorily sanitized. It is known that a good cleaning removes up to 97% of microbes and, as a major result, makes disinfection easier and rapid. Thus, in terms of sanitation biofilm does not signify microorganisms but rather the organic metabolites that defend them.

Microbial problems come from

- water
- manufacturing environment
- processed foods and beverages
- a selection of microorganisms

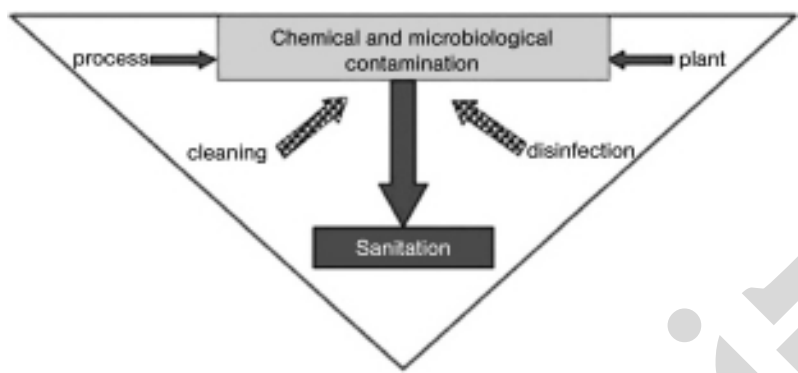


Figure 18.1 Contamination and sanitation processes.

Table 18.1 Popular words indicating microbial activity.

Musty	Rotten	Gassy
Cloudy	Smelly	Putrid
Swollen	Poisonous	Bad
Colored	Sticky	Curdled

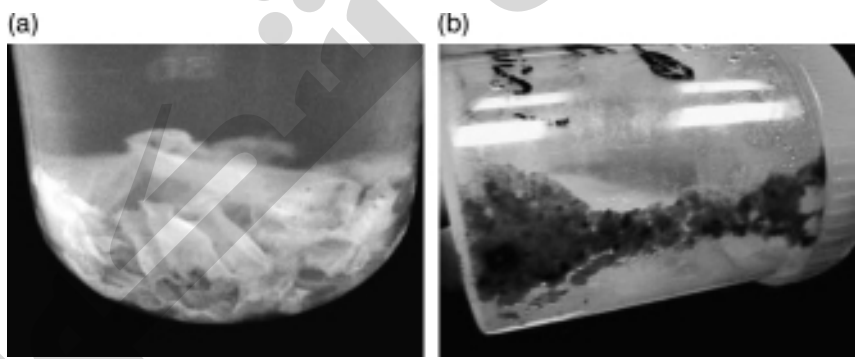


Figure 18.2 Biofilm from (a) tunnel pasteurizer and (b) bottlewasher head.

18.1
Water

Around the world water is suspected to be the vehicle for 80% of infection in people and usually does not reveal its danger. The initiation of biological reactions depends on the quantity of water in the food or environment. The less water there is, the less likely is the event. Where water is absent either there are no microbes or they have no bio-activity (Figure 18.3).

Water can be either removed or made inert in different ways:

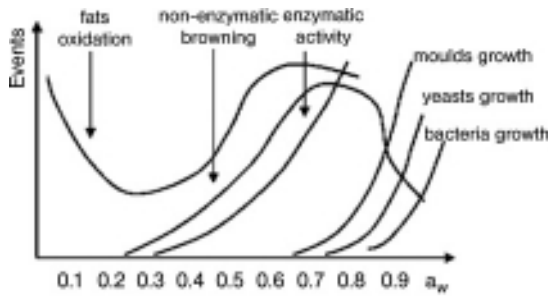


Figure 18.3 Events as a function of water activity (adapted from [1]).

- **Drying/de-humidifying:** (environmental drying)
- **Taking water away:** (desiccation and lyophilizing)
- **Making water inert:** (salting, sugaring, freezing).

Care in keeping floors dry and reducing moisture generally is part of good manufacturing practice and prevents unpredictable niches of infection.

Water also brings chemical hazards. Addition of alkalinity and rise in temperature cause limestone to precipitate. Dissolved chloride and silicate lead to corrosion. Sulfate is involved in bio-reactions (see Section 1.1.1). Water is a source of serious problems of cleaning and microbiology. Therefore, water is really the main factor for success or failure according to the basic rule which asserts that, to achieve cleaning, all must be kept or redissolved in the aqueous solution.

Water destroys part of the detergent by its hardness. Experience tells us that 10dF of hardness consumes 0.3–0.5% of the detergent concentration (on average). Hence, it is not conceivable to clean with the same concentration of detergent in sites having different hardness. Contract cleaners should take into consideration this obvious fact when they have teams working with similar categories of food (e.g. swine or cattle slaughterhouse) sited in different regions. In the presence of different hardnesses, a corresponding careful differentiation in the detergent concentration helps to save money and enhance cleaning.

Cleaning with inorganic chemicals (e.g., caustic soda) causes limestone to deposit. It is calculated that 10dF hardness deposits 0.1 mm of limestone (on average) after every cleaning with caustic soda. Limestone is a porous substance. A porous layer on a surface means that microorganisms are protected and difficult to disinfect. The choice of a detergent formulated with suitable sequestrants saves time and personnel and benefits safety and productivity.

The smoother and shinier a surface, the less the microorganisms cling. However, a smooth surface does not prevent but only slows microbial growth (biofilm) because there are fewer peaks and troughs (fewer trapped micro-



Figure 18.4 The surface finish traps microorganisms or delays their attachment.

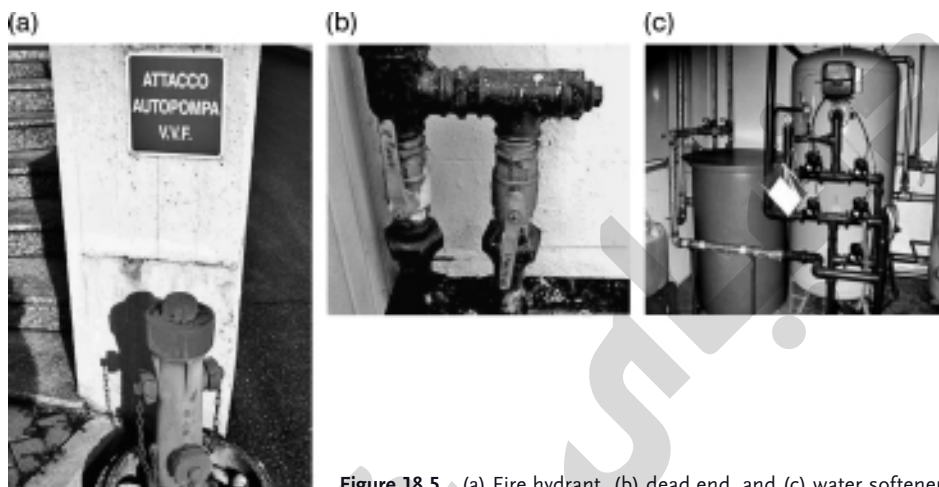


Figure 18.5 (a) Fire hydrant, (b) dead end, and (c) water softener.

organisms). If a microbe stays attached, the growth of biofilm is independent of the surface finish. However, a coarse and dull surface traps microbes more easily (Figure 18.4), so that rusted and scaled surfaces are particularly favorable to the adsorption of microorganisms, initiating the growth of biofilm.

Neglected areas are frequently hosts to biofilm, such as fire hydrants, isolated pipework, softeners, deionizers, and surge tanks, shown in Figure 18.5.

Regular dismantling, cleaning, and disinfection prevent problems of colonization by biofilm in these niches.

18.2

Manufacturing Environment and Types of Microorganisms

Over 10^8 particles of size below 0.5μ may be present in one cubic meter of unfiltered air. Microbes, spores, viruses, and mites can be suspended along with dust (Figure 18.6).

Microorganisms are thought of as carriers of disease, although in fact only a few are harmful. The majority plays a crucial role in the life of our planet. They provide food for fish, nutrient for plants, and digestion for ruminants. Several of them are beneficial to human foods and directly involved in their preparation. For instance:

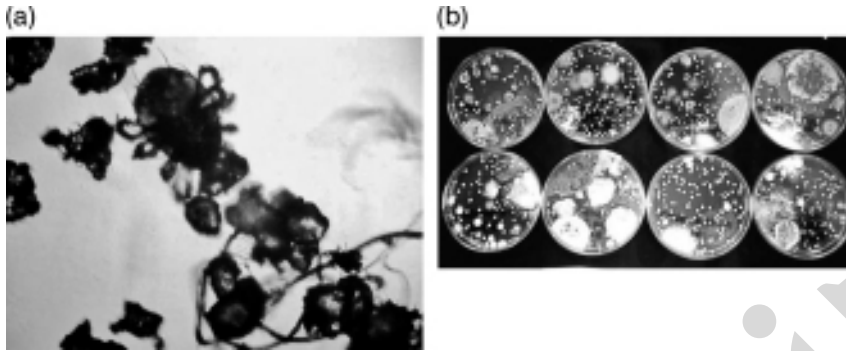


Figure 18.6 (a) Mites in dust (photomicrograph) and (b) cultures of microbes on Petri dishes (1 h of exposure to atmospheric air).

- Beer and wine depend on the fermentation of sugars by yeasts to produce alcohol and flavor.
- Yogurt is derived from metabolized milk in which microbes live.
- The fragrance and variety of cheeses and sausages would be impossible without bio-activity.

A second group of generic microorganisms harms food without causing disease. They are principally responsible for physical and organoleptic modifications and rapid decay of food (shorter shelf life).

The last and most dangerous group consists of the pathogens, microorganisms directly responsible for disease. Examples of microorganisms of this group are

<i>Salmonella typhimurium</i>	<i>Clostridium botulinum</i>	<i>Campylobacter</i>
<i>Legionella pneumophila</i>	<i>Clostridium perfringens</i>	<i>Shigella</i>
<i>Listeria monocytogenes</i>	<i>Bacillus cereus</i>	<i>Cryptosporidia</i>
<i>Staphylococcus aureus</i>	<i>Pseudomonas aeruginosa</i>	<i>Calicivirus</i>
<i>Escherichia coli</i> O157:H7	<i>Aspergillus niger</i>	<i>Giardia lamblia</i>

Although microorganisms are roughly similar, each category of industry pin-points some of them as especially hazardous. Thus, the food industry can be characterized by its microbial selection, which depends on

- **Microbial peculiarity:** for example, *Salmonella* is endemic for poultry, eggs, and their derivatives
- **Environmental peculiarity:** for example, *Listeria* and *Pseudomonas* are ubiquitous
- **Incorrect operations:** for example, coliforms from accidental cutting of intestines (slaughtering)
- **Improper individual behavior:** for example, *Staphylococcus* from poor hygiene, acne, and latent disease.

Thus, in general and schematic terms:

- Slaughterers look out for *Salmonella*, *E. coli*, *Staphylococcus*.
- Meat processors look out for *Listeria* and *Campylobacter*.
- Egg processors look out for *Salmonella* and *E. coli*.
- Breweries and wineries look out for yeasts.
- Water bottling plants look out for algae (nonsparkling water) and *Pseudomonas*.
- Dairies look out for *Listeria*, coliforms, and pigmented bacteria causing color spots (e.g., *Pseudomonas putida*, *Micrococcus luteus* and *Rhodotorula*) [2, 3].
- Fresh-cut food preparers look out for pathogens (*E. coli*), gas-producing bacteria (lactobacters and yeasts) and molds.

The environment of a food is potentially a source of microbial contamination: air, water, ground, surfaces, plants, insects, animals, and man. In order to protect specific food preparations from environmental pollution, clean rooms can establish and maintain an aseptic environment (see Section 6.9 and Chapter 15).

Carelessness and poor hygiene of personnel is the second leading cause of all food-borne illness. The care of personal hygiene should just be a matter of common sense in the food industry. However, common sense depends on the culture of a person's country of origin, and this can vary from one country to another. Therefore, all industries should ensure that individuals have received adequate and appropriate training in the design and proper application of the Hazard Analysis and Critical Control Points (HACCP) system and process control. Specific training is required to work in high-risk areas.

18.3

Disinfectants

Chemicals possessing a killing activity against microorganisms are defined as disinfectants (4log reduction, at least). Mono and multicellular microbes have several points of chemical attack such as nucleic acids and proteins, enzymes and co-enzymes, membrane and its transport pumps. As the cellular points of reaction are different, chemicals perform as killers of vegetative and reproductive forms of microbes, with target differentiation. Table 18.2 shows the targets for the most common disinfecting agents with a schematic simplification.

A good disinfectant for industrial use meets the following criteria:

- broad spectrum, able to kill all pathogens
- fast acting, in order to limit the application time
- harmless to operators
- nonaggressive toward surfaces
- easy to rinse off
- nontainting
- not detrimental to waste water treatment
- active even in the presence of residual contamination.

Table 18.2 Targets for the most common disinfectants.

Chemicals	Target
Halogens Peroxide Alcohols Anhydrides Aldehydes Heat Radiation	CELLULAR CONSTITUENTS (nucleic acids, proteins, enzymes)
Quaternary ammonium compounds (Poly)biguanides Chlorhexidine Polyamines Imidazoline Amphoteric polyamines Phenol, cresol, and their derivatives	CELLULAR MEMBRANE (lipids and proteins, transport pumps)
Metals	THIOLIC GROUPS (S-S) (enzymes and co-enzymes)

However, it is quite impossible to find all these characteristics in one disinfectant. Rotation of disinfectants is good practice. The use of a single disinfectant might create selective pressures that favor the emergence of strains which are less susceptible (resistant) to the disinfectant. Nevertheless, this occurrence happens in a few well-known cases such as hospitals, specialized laboratories and, sometimes, the pharmaceutical industry. As far as the food industry is concerned, either a surface is disinfected or something wrong has occurred (choice of disinfecting agent, operational procedure, or negligence of personnel). So, if the disinfection is working well (microbiologically proved), why change the disinfectant to prevent something that might not happen! In actual fact, mutation, from which resistance depends, is attributed to the plasmid's stability, which is dependent on the size of the plasmid pool in the cell and the time or frequency of cell division. The plasmid is a non-nuclear self-replicating structure carrying genetic information nonessential to the existence of the bacteria. It easily mutates, and is thus believed to be responsible for the genotypic mutations of bacteria. With time (several generations of bacteria, i.e., cell divisions) mutation could establish a new specific-resistant strain. Thus, time is needed to develop resistance. However, the food industry cannot allow time for mutation. Either a surface is disinfected or a disaster affecting the prepared food soon occurs. For this reason, the development of resistance during a manufacturing process is quite impossible if the sanitation operations are well planned and punctually observed. Knowledge of disinfectants and partnership with a reliable supplier are the key factors to ensuring a smooth-running operation and living with peace of mind.

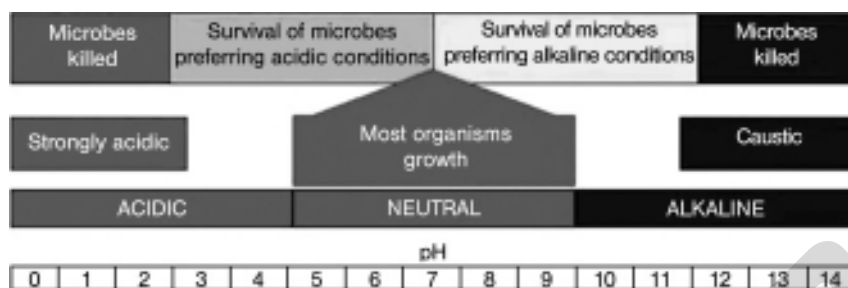


Figure 18.7 Microorganisms and pH.

18.3.1

Main Disinfectants for the Food Industry

Microbes are living organisms, and their survival first of all depends on the pH of life, which is close to neutral. Although a few microorganisms have elaborated techniques for survival far from a strictly neutral pH (Figure 18.7), in practice extreme acidity and causticity are fatal to their life.

However, the hygiene essential to a food industry is not accomplished by control of pH. Chemicals capable of killing microorganisms wherever they are found have been developed. Disinfectants for the food industry are suitable from the point of view of methods of application, personnel, and safety of machinery. Table 18.3 lists the most common disinfectants used in the food industry.

The characteristics of each of them are described in the subsequent tables. Descriptions are concise and represent average behavior as reported in the literature and as experience teaches (Tables 18.4–18.17, Figures 18.8–18.10).

18.3.2

Biocides from the Haber-Willstätter Reaction

The mechanism of the decomposition of peroxides in the presence of an oxidable metal or compound generates several intermediate chemicals able to contribute to the biocidal activity of the system. In 1876, Fenton [4] first described the oxidation of tartaric acid by the addition of iron(II) and hydrogen peroxide or hypochlorous acid. Iron acts catalytically, giving dihydroxymaleic acid [5, 6]. Haber and Willstätter proposed the following reactions



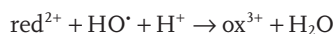
to explain the action of catalase as the starter of the radical reactions instead of iron [7, 8]. Haber and Weiss explained how catalase worked via a mechanism developing the above reactions and how hydrogen peroxide is consumed by a chain reaction initiated by the Fenton's reaction:

Table 18.3 Disinfectants in the food industry.

Chemical category	Disinfectant
Halogens	Chlorine Bromine Iodine
Oxides and peroxides	Peracids (peracetic, percitric, peroctanoic) Hydrogen peroxide Chlorine dioxide Ozone
Alcohols	Ethyl alcohol Isopropyl alcohol Benzyl alcohol
Anhydrides	Sulfur dioxide
Aldehydes	Glutaraldehyde Formaldehyde Glyoxal
Quaternary ammonium compounds (QACs)	Benzalconium compounds Didecyl dimethyl ammonium compounds Polymeric QACs
Guanides	Chlorhexidine (biguanide) Polybiguanide
Polyamines	Fatty di- and tri-amines
Amphoteric polyamines	Fatty diamine-glycines
Isothiazoline derivatives	Chloro-methyl isothiazolin-3-one (isothiazolone)
Halogen-releasing hydantoins and propionamides	1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH) 2,3-dibromo-3-nitrilopropionamide (DBNPA)
Phenols	Phenol and bisphenol Halo-phenols Cresols
Metals	Silver Copper Zinc



where superoxide ($\text{O}^{\bullet -}$) is the chain carrier [Eqs. (18.1) and (18.2)] and the chain end is caused by:



Chlorine donors:

Sodium hypochloride: NaClO

Chloramine T $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{N}(\text{Cl})\text{Na}$

Di and trichloroisocyanurate $\text{CO} \begin{matrix} \diagup \text{NCl} - \text{CO} \diagdown \\ \diagdown \text{NCl} - \text{CO} \diagup \end{matrix} \text{NNa}$ $\text{CO} \begin{matrix} \diagup \text{NCl} - \text{CO} \diagdown \\ \diagdown \text{NCl} - \text{CO} \diagup \end{matrix} \text{NCl}$

Chlorophosphate $\text{Na}_3\text{PO}_4 \cdot 11\text{H}_2\text{O} \cdot x\text{NaClO} \cdot y\text{NaCl}$

Figure 18.8 Chemical structures of chlorine donors.

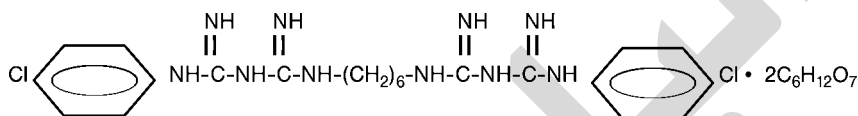


Figure 18.9 Chlorexidine digluconate.

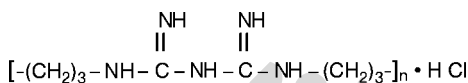


Figure 18.10 Polybiguanide.

As they mentioned neither Fenton nor Willstätter, the chain reaction has become known as Haber-Weiss cycle [6]. One of the reasons for the omission was the German language of the Haber-Willstätter earlier paper. Therefore, the cycle should be more properly named the Haber-Willstätter cycle [6, 8].

The application of the Haber-Willstätter reaction in several sectors of human activities took different paths in powder and liquid form. Powders are easier to manage because the formula includes stable precursors of the disinfecting agents and needs less demanding stabilization. Aqueous liquids keep chemicals in equilibrium through specific stabilizers. Schematizing precursors and biocidal agents, products available on the market are based on the following reactions, elaborated to describe only the main precursors and final biocide compounds:

Powder products (alkaline or slightly acidic pH when diluted in water)

- 1) percarbonate + enzyme (protease group) + $\text{NaCl} \rightarrow \text{NaClO} + \text{Cl}_2 + \text{H}_2\text{O}_2 + \text{O}_2$
- 2) persulfate + carbonate + enzyme + $\text{NaCl} \rightarrow \text{NaClO} + \text{Cl}_2 + \text{H}_2\text{O}_2 + \text{O}_2$
- 3) [9] persulfate + Cl^- + sulfamic acid $\rightarrow \text{ClO}^- + \text{Cl}_2 + \text{chloramine} + \text{H}_2\text{O}_2$

Liquid products (neutral–slightly acidic pH)

- 1) $\text{NaCl} + \text{H}_2\text{O}_2 + \text{stabilizer} \rightarrow \text{HClO} + \text{Cl}_2 + \text{H}_2\text{O}_2 + \text{O}_2$
- 2) persulfate + $\text{NaCl} + \text{sulfamic acid} + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{Cl}_2 + \text{chloramine} + \text{H}_2\text{O}_2$

Table 18.4 Halogens.**Chlorine**

available as chlorine gas, hypochlorite, chlorophosphate, chloroisocyanurate, chlorinated detergents

Complete spectrum of action	Unstable at acidic pH (evolution of Cl_2 gas)	Corrosive, increasing as the temperature and time of contact increase	Formation of medicine off-taste with polyphenols	Molds and cork: formation of aftertaste with anisole
Temperature limit of 50°C to prevent risk of corrosion	Formation of chloramines with amines and peptide group (solution pollution)	AOX, POX, THM formation with hydrocarbons (environmental pollution)	Cleaner alone and in alkaline formulations	Chemical demand of chlorine in raw water

Bromine

Activity similar to that of chlorine, available as liquid hypobromite or solid in tablets

Complete spectrum of action. 5 times less active than chlorine	Unstable at acidic pH	Corrosive, increasing as the temperature and time of contact increase	Formation of medicine off-taste with polyphenols	Chemical demand of bromine in raw water
Temperature limit of 50°C to prevent risk of corrosion	Formation of bromamines with amines and peptide group (solution pollution)	AOX formation with hydrocarbons (environmental pollution)	No cleaning activity	Sometimes used in combination with chlorine

Iodine

available linked to organic molecules such as surfactants and polyvinylpyrrolidone (iodophors), as iodine chloride and dissolved in alcoholic solutions

Complete spectrum of action. 3 times more active than chlorine	Stable at acidic pH; iodine loses its biocide activity in alkaline pH	Corrosive, increasing as the temperature and time of contact increase (sublimation)	Weak bonds allow iodine to be active in depth.	No chemical demand of iodine in raw water
Room temperature use to prevent risk of corrosion	No free iodamines formation with amines and peptide group	Plastic material turns yellow with iodine solutions	No cleaning activity	Tendency of iodophor solutions to foam. Difficulty in rinsing

Table 18.5 Oxides and peroxides.**Peracids**

available as peracetic, percitric, phthalimidoperhexanoic, peroctanoic acids and other short chain (<6C) organic monoacids and di-functional acid/esters

Complete spectrum of action	One of the most rapid killing activities. It can be synergized by wetting surfactants	A pungent irritant smell is typical of peracetic acid. Peroctanoic acid has a billy goat odor.	Noncorrosive on stainless steel if chloride content of water is below 25 ppm	Kinetics of chloride corrosion (pitting) increases when corrosion is in progress
Although usually utilized at room temperature, they show the peak of activity at ~52 °C	Sensitive to dissolved heavy metals (destruction of peroxide)	Partial loss of activity at alkaline pH (salt formation)	No cleaning activity	As they are very sensitive to dirt, they are typical terminal disinfectants

Hydrogen peroxide

Complete spectrum of action	Relatively high concentration required for a good killing action ($\geq 3\%$)	Disinfection activity increases as temperature and alkalinity increase	Noncorrosive on stainless steel if chloride content in water does not exceed 25 ppm	Kinetics of chloride corrosion (pitting) increases when corrosion is in progress
Unstable at alkaline pH. Added to alkaline detergents as separate product	Sensitive to dissolved heavy metals (destruction of peroxide)	Additive to alkaline detergents to boost the cleaning performance	Sensitive to dirt. Dirt changes H_2O_2 from disinfectant to cleaner.	High purity required for disinfecting containers in contact with food

Chlorine dioxide

Complete spectrum of action	Active at very low concentration (even <1 ppm)	One of the most active agents against biofilm	Formed in situ usually from a reaction between sodium chlorite and hydrochloric acid	Active as gas dissolved in water
Temperature promotes loss by evaporation	Corrosive agent mainly around the processed plant (by-products of dispersed ClO_2)	Safety systems required on the equipment to produce it (explosion risk)	The residual chlorite in drinking water is strictly limited (≤ 0.2 ppm)	Although it has low sensitivity to dirt, it is applied as a terminal disinfectant

Ozone

Complete spectrum of action	Active at very low concentration (even <1 ppm)	One of the most oxidizing agents and one of the actives with the shortest life	Developed in situ and added to water as gas by ozonizers	Temperature promotes loss by evaporation
Corrosive toward plastic materials after long or repeated contact (cracking)	For safety reasons a check system is required in the environment	No cleaning activity	Negligible activity as surface disinfectant (too short life)	It is a pure disinfectant mainly for water sterilization

Table 18.6 Alcohols.**Ethyl alcohol**

No activity against spores	Active at high concentration ($\geq 65\%$)	Also fungicide in sealed pack and soak application	Evaporation reduces time of contact and disinfecting activity	Evaporation makes alcohols applicable where water is not wanted
Corrosive toward specific plastic materials such as PC and PET (cracking)	It only performs as a cleaner when manually applied alone on open surfaces	By adding a small quantity of QACS or fatty diamines the alcohol activity is enhanced and completed	Directly absorbable through breathing. It causes a hypnotic action after long exposure	Highly flammable. Alcoholic products must be kept in a suitable warehouse and handled with care

Isopropyl alcohol

No activity against spores	Active at high concentration ($\geq 65\%$)	Also fungicide in sealed pack and soak application	Evaporation reduces time of contact and its disinfecting activity	Evaporation makes alcohols applicable where water is not wanted (disinfecting detergent)
Corrosive toward specific plastic materials such as PC and PET (cracking)	It only performs as a cleaner when manually applied alone on open surfaces	By adding a small quantity of QACS or fatty diamines the alcohol activity is enhanced and completed	Directly absorbable through breathing. It causes higher hypnotic action than ethyl alcohol after long exposure	Highly flammable. Alcoholic products must be kept in a suitable warehouse and handled with care

Benzyl alcohol

No activity against spores	Active at lower concentration than C_2 and C_3 alcohols ($\leq 4\%$)	Negligible evaporation (boiling point at 205°C). It remains on the surface for a long time	Low toxicity. It is used in a different way for human and animal cosmetics	Farm application against bacteria causing mastitis (disinfectant for teats after milking)
Corrosive toward specific plastic materials such as PC and PET (cracking)	Natural constituent of essential oils, it is also used for pharmaceuticals	Solvent in paint stripper and waterborne coatings application	Preservative in personal care, hair dye and conditioner	Not applicable for cleaning

Both powder and liquids can include surfactants to wet (enhanced disinfection) and clean (detergent disinfectant). Biocides develop through a chain reaction where each of them depends on a sequence which can become cyclic. No new disinfecting molecules are given, but they are slowly produced *in situ* and their aggressiveness is reduced and better governed.

Products are safe and, according to their formulation, provide industrial surfaces, equipment, tools, medical devices, and animal and human skin with a rapid disinfection. Owing to different redox activities, they prove effective against bacteria and mycobacteria, fungi, spores, and viruses in industry, farm, and health care facilities.

18.3.3

How to Choose a Disinfectant

In the food industry, users of disinfectants have to keep in mind

- surfaces coming into contact with food
- open surfaces allowing the manufacturing process to be carried out without biological risk of airborne, aerosol and incidental contamination, even if those surfaces will never be in contact with food
- open surfaces connected to the environment
- surfaces kept in their integrity
- enclosed surfaces (e.g., CIP)
- dismantled surfaces (manual application).

Moreover, ubiquity and viability of microbes must not be confused with sensitivity to the killer agents (disinfectants). *Listeria monocytogenes* is a typical example. *Listeria* is ubiquitous, and survives and reproduces in severe conditions (even

Table 18.7 Anhydrides.

Sulfur dioxide				
Complete spectrum of action	Active at low concentration (<200 ppm of free SO ₂)	Active only at acidic pH (anhydride of sulfurous acid).	Generated by burning sulfur (disinfection of wooden vessels in winery)	Generated from bisulfite by reaction with acids (wine preservation)
Generated from sulfite and bisulfite by reaction with acids (crossflow filtration disinfectant and membrane preservative)	It absorbs oxygen up to the final sulfuric form (inactivation)	Corrosive (acidic behavior). Emission into atmosphere causes acid rain	Highly irritant and toxic gas. Its concentration in wine is limited. ('contains sulfites' on wine labels)	It adds disinfection to acidic cleaning and descaling

Table 18.8 Aldehydes.**Formaldehyde (formalin HCHO)**

Complete spectrum of action	Active at low concentration (<1%)	Active at every pH, usually applied in neutral-acidic pH	Highly pungent, toxic and harmful gas causing cancer to respiratory tract	Its use is only admitted in specific procedures (pharma, hospital, laboratory)

Gas at room temperature, it is most commonly sold as a 37% aqueous solution.	Industrial products include lower concentration often in combination with QACs and fatty polyamines	No corrosion and no cleaning activity from its application	Still used: • as hoof care in farm • as litter treatment in breeding with its cyclic trimer (paraformaldehyde slowly releasing formaldehyde)	

Glutaraldehyde (pentanedial $\text{OCH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CHO}$)

Complete spectrum of action	Active at low concentrations on bacteria and fungi. At least 1% needed on spores	Active over a narrow range of pH (6–9)	Pungent sweetish smell. Less toxic than formaldehyde. Still usable in food industry	Easily polymerizable, it is stabilized at slightly acidic pH

Labeled toxic above 25%, it is most commonly sold as 24% aqueous solution.	Industrial products include lower concentrations, often in combination with QACs and fatty polyamines	Unstable in the presence of ammonia and alkanolamines	No corrosion and no cleaning activity from its applications	Typical terminal disinfectant when used alone. Often added to QACs to provide them with sporicidal action

Glyoxal (ethanedial, OCH-CHO)

Complete spectrum of action	Less active than formaldehyde and glutaraldehyde. It is never used alone	Active over a narrow range of pH (6–8) where its polymerization rate is reduced	Orally and dermally less toxic than the other aldehydes, but genotoxicity proved in the laboratory	Easily polymerizable, its aqueous solutions really are a blend of different oligomers

It is most commonly sold as 40% aqueous solution. Terminal disinfectants may include 10% glyoxal	Commonly formulated together with glutaraldehyde, QACs and fatty polyamines	Since its oligomers react slowly, this may preserve and prolong the biocidal activity of products	No corrosion and no cleaning activity from its applications	Practically: no further benefit in food industry from disinfection based on this chemical

below 4 °C). Nevertheless, disinfectants easily kill it. The difficulty usually consists in discovering the niche of pollution rather than in killing the microbes.

A further consideration comes from experience in applying disinfectants: microbial resistance and tolerance do not exist in the food industry or, rather, resistance and tolerance cannot be permitted in the food industry. Either the microbe is destroyed or something is wrong with type of disinfectant selected, procedure, time of contact, or negligence of personnel. The concept of bacteriostaticity is only exploited on open surfaces such as lubrication on tracks moving containers, tunnel pasteurization, cooling towers, rinse zone of bottlewashers, or brine for cheese hardening. Bacteriostaticity is the typical property of the nitrogen compounds. Microorganisms continuously fall on open surfaces, and sterility is unattainable except in a clean room. A disinfectant on open surfaces aims at keeping microbes below the limit defined as critical for good manufacturing practice (GMP). Limiting the increase in the number of microbes is a part of the bacteriostaticity concept.

Death, bacteriostaticity, tolerance, and resistance are linked to two inseparable parameters: the lowest applicable concentration and the contact time. No comparison between disinfectants is possible and no conclusion can be drawn without knowing the lowest applicable concentration and the contact time. The lowest concentration is the concentration below which the disinfectant is no longer active. Of course, the concentration must not be decreased below this value even if a very large amount of time is available. Nevertheless, when a disinfectant is running at a good concentration, time of contact is crucial to have an assessment of its capacity to kill microorganisms.

Being a sporicide does not depend on the contact time. It is a property of the chemical. Conversely, effectiveness in suspension and on a surface can also depend on the contact time. The results of official tests are linked with a concentration and a running time. Then, any test, graph, report, publication, affirmation, and documentation that compares the activity of disinfectants without mentioning concentration and contact time is valueless.

18.3.3.1 Basic Behavior Typifying the Application of Disinfectants

Most disinfectants for the food industry fall into two groups according to their basic behavior:

- redox agents
- nitrogen compounds (cationics).

The groups do not correspond to a theoretical concept. They are the key to understanding the rationale of their application in the field.

- a) **The group of redox agents** includes oxidizing (ox) and reducing (red) agents. Halogens, peracids, hydrogen peroxide, chlorine dioxide, ozone, sulfur dioxide, and aldehydes belong to this group. Four features characterize them:
 - rapid action
 - no residue
 - complete rinsability
 - high sensitivity to dirt.

Table 18.9 Quaternary ammonium compounds (QAC).**Benzalconium chloride (BAC)**

No direct killing action on spores. Spores are made inert (preventing germination)	One of the most applied disinfectants both in industrial and domestic sanitation	Less active than DDAC (higher concentration needed)	Gram negatives prove to have higher resistance, for example, <i>Pseudomonas</i> , (higher concentration needed)	Noncorrosive on stainless steel at the use concentration (pitting by chloride when concentrated)
Noncorrosive toward copper and its alloys when rapidly rinsed	Bluish-greenish complex formation with copper and its alloys after a long contact (avoid soak)	No cleaning activity in practice	Usually used at room temperature as ready-to-use or dilutable product. Highly foaming	Typical terminal disinfectants for open surfaces

Didecyl dimethyl ammonium compound (DDAC)

No direct killing action on spores. Spores are made inert (preventing germination)	Less common than BAC in industrial and domestic sanitation only because more expensive	More active than BAC mainly in surface tests (against fungi)	Gram negatives prove to have higher resistance, for example, <i>Pseudomonas</i> , (higher concentration needed)	Noncorrosive on stainless steel at the use concentration (pitting by chloride when concentrated)
Noncorrosive toward copper and its alloys when rapidly rinsed	Bluish-greenish complex formation with copper and its alloys after long contact (avoid soak)	No cleaning activity in practice.	Usually used at room temperature as ready-to-use or dilutable product. Highly foaming	Typical terminal disinfectants for open surfaces

Polymeric ammonium compounds (PAC)

No direct killing action on spores. Spores are made inert (preventing germination).	Less common than BAC and DDAC in industrial and domestic sanitation (less active and more expensive)	Appreciated for their nonfoaming behavior and nonfading paints	Gram negatives prove to have higher resistance, for example, <i>Pseudomonas</i> , (higher concentration needed).	Noncorrosive on stainless steel at the use concentration (pitting by chloride when concentrate)
Noncorrosive toward copper and its alloys when rapidly rinsed	Bluish-greenish complex formation with copper and its alloys after a long contact (avoid soak)	Used at room temperature as dilutable products	No cleaning activity in practice. Higher concentration in use than BAC and DDAC	Frequently used as sanitizer for tunnel pasteurizers, cooling towers and swimming pools

Table 18.10 Guanides.

Chlorhexidine (biguanide)

No direct killing action on spores.	Also known as chlorhexidine (di)gluconate, it is highly skin compatible and a nonfoaming agent	It is used in a different way for human and animal therapeutics and cosmetics	Used at relative high concentration (0.5–3%), it reveals good activity also against Gram negatives.	Noncorrosive on stainless steel, ceramics and plastics at every concentration
Noncorrosive toward copper and its alloys when rapidly rinsed	Bluish-greenish complex formation with copper and its alloys after long contact (avoid soak)	Used at room temperature as ready-to-use or dilutable product	No cleaning activity in practice. Used in sanitizing hand cleaners.	Farm application against bacteria causing mastitis (disinfectant for teats after milking)

Polybiguanide

No direct killing action on spores. Spores are made inert (preventing germination).	Less skin compatible than chlorhexidine, it is a typical disinfectant for industrial plants.	More active than chlorhexidine, it is used at lower concentration ($\leq 1\%$).	It shows better activity than chlorhexidine against Gram negatives.	Noncorrosive on stainless steel, ceramics and plastics at every concentration.
Noncorrosive toward copper and its alloys when rapidly rinsed	Bluish-greenish complex formation with copper and its alloys after a long contact (avoid soak)	No cleaning activity. Nonfoaming agent.	Used for environment sanitation, CIP terminal disinfection	Farm application against bacteria causing mastitis (disinfectant for teats after milking)

Their complete rinsability is a guarantee of no residue after rinsing. As a result, the surface is no longer protected from the bio-contamination at the end of the sanitation process and undergoes everything that happens in the environment (e.g., fall-out of suspended and airborne microbes). Thus, the group of oxidants is primarily used in closed plants (CIP and SIP). A closed plant cannot be re-contaminated after the final rinse because of being an enclosed space. Moreover, complete rinsability is very suitable for surfaces coming into contact with food. The rapid action of disinfection makes this group highly sensitive to dirt. They, obviously, are not able to distinguish a protein or a lipid belonging to a cellular membrane from those coming from chemical contamination.

These considerations do not preclude carrying out cleaning and disinfection on open surfaces with detergents based on redox disinfectants (one-step sanitation). They only mean that they are unsuitable for application as terminal disinfectants on open surfaces.

Table 18.11 Fatty polyamines.**1,3-propanediamine-N-C₈-C₁₄**

No direct killing action on spores. Spores are made inert (preventing germination).	Low foaming behavior in comparison with the amphoteric fatty polyamines and QACs	Active at concentration $\leq 2\%$ in neutralized form (protonated)	Gram negatives prove to have higher resistance, for example, <i>Pseudomonas</i> , (higher concentration needed).	Noncorrosive on stainless steel and plastics
Noncorrosive toward copper and its alloys when rapidly rinsed	Bluish-greenish complex formation with copper and its alloys after a long contact (avoid soak)	Toxicity higher than that of QACs	No cleaning activity in practice. Disinfecting action less sensitive to dirt than QAC	Used as terminal disinfection on open surfaces and SIP

N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine (simply known as triamine)

No direct killing action on spores. Spores are made inert (preventing germination).	More foaming than a fatty diamine, it cannot be used in CIP without a suitable defoamer.	Active at concentration $\leq 2\%$ even in alkaline condition	Gram negatives prove to have higher resistance, for example, <i>Pseudomonas</i> , (higher concentration needed).	Noncorrosive on stainless steel and plastics
Noncorrosive toward copper and its alloys when rapidly rinsed	Bluish-greenish complex formation with copper and its alloys after a long contact (avoid soak)	Low toxicity but nasty smell emphasized when applied in small rooms	No cleaning activity in practice. Disinfecting action less sensitive to dirt than QAC and amphoteric fatty amines	Used both as terminal disinfection and in sanitizing foam cleaners and defoamed alkaline CIP

b) **The group of nitrogen compounds** includes all disinfectants containing one or more nitrogen groups in a molecular structure suitable to kill microorganisms. Monomeric and polymeric QACs, chlorhexidine, polybiguanide, imidazolines, fatty polyamines, and amphoteric polyamines belong to this group. Three features characterize this group of disinfectants:

- killing action slower than redox. Differences between them exist depending on the molecular structure
- incomplete rinsability (residue)
- sensitivity to dirt lower than that of redox. Differences exist depending on the molecular structure.

Table 18.12 Amphoteric fatty polyamines.

C ₁₀ -C ₁₆ -N-1,3-propandiamine-glycine				
No direct killing action on spores. Spores are made inert (preventing germination)	Fatty diamine amphotericized by glycine	Active in neutralized form at lower ($\leq 1\%$) concentration than its fatty diamine	More foaming than its fatty diamine, it cannot be used in CIP	Noncorrosive on stainless steel and plastics
Noncorrosive toward copper and its alloys when rapidly rinsed	Bluish-greenish complex formation with copper and its alloys after a long contact (avoid soak)	Toxicity lower than its fatty diamine but higher than QAC	Disinfecting action more sensitive to dirt than its fatty diamine. It shows a weak cleaning activity	Used as terminal disinfectant on open surfaces and in one way SIP (not re-cycled)

Table 18.13 Isothiazoline derivatives.

Chloro-methyl-isothiazolin-3-one (and its group C ₄ H ₄ ClNOS, C ₄ H ₅ NOS) (simply known as isothiazolone)				
No killing action on spores in practice	Disinfectant constituted of a blend of similar molecules	Active at relative low concentration (<100 ppm) according to applications	Used both as bacteriostatic in industrial plants and preservative in finished goods	Noncorrosive on stainless steel and plastics
High toxicity. Skin sensitizer. Caustic agent on skin difficult to removed	Nonfoaming agent. Suitable for process with highly turbulent water	It shows no cleaning activity, conversely, high efficient in biofouling detachment	Needs a relatively long time of contact. Used as preservative in many different products (paint, paper, formulas ...)	Used as bacteriostatic in tunnel pasteurizer, cooling tower, and lubrication

Their incomplete rinsability derives from the electro-attractive behavior of the positive charge on the nitrogen toward negatively charged surfaces. According to the zeta-potential theory (see Section 1.1.2.4), the positive charge effectively neutralizes the surface [10], to which it strongly clings. Attraction is so tenacious that rinsing only succeeds in removing cationics to a certain extent. Thus, some layers of cationic molecules still remain on the surface after rinsing. Incomplete rinsability means that a residual layer of still-effective disinfectant covers the surface.

Table 18.14 Halogen-releasing hydantoin.

1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH)				
Complete spectrum of action	Solid biocide in tablet form. To be used with specific brominator	Corrosive. Corrosion derives from release of halogens (see Cl and Br)	Off-taste formation by redox on colloids and complex phenols (tannins)	Toxicity comparable to that of halogens
Temperature limited to 50°C in use to keep corrosion slow	Halo-amines formation with amines and peptide group (solution pollution)	AOX, POX, THM formation with hydrocarbons (environmental pollution)	No cleaning activity. Biofouling controlled by halogens	Mainly used in process water treatment. (0.3–0.5 ppm kept in tunnel pasteurizer and cooling tower)

Table 18.15 Halogen-releasing propionamide.

2,3-dibromo-3-nitrilopropionamide (DBNPA)				
Complete spectrum of action	Unstable in acids and even in water with bromine release	Corrosive. Corrosion derives from halogen release (Br)	Off-taste formation by redox on colloids and complex phenols	Toxicity comparable to that of bromine
Temperature in use limited to 50°C to keep corrosion slow	Halo-amines formation with amines and peptide group (solution pollution)	AOX formation with hydrocarbons (environmental pollution)	No cleaning activity. Biofouling controlled by bromine	Mainly used in process water treatment. (20–50 ppm in tunnel pasteurizer, cooling tower)

Thus, the surface is protected for a longer time from pollution which can occur after the final rinse. The quantity of cationic molecules left behind is so low as not to affect the food in contact with the surface either from the organoleptic nor from the toxicological point of view. On the contrary, it is the essential feature of cationic disinfectants, which are expected to provide long-lasting disinfection of open surfaces. Consequently, the group of cationic disinfectants is principally used on open surfaces that could be recontaminated after the final rinse. Their use gives prolonged sanitation.

Table 18.16 Phenols.

Phenol other phenolic compounds (biphenols, halo-phenols, cresols)

No action on spores.	Relatively high concentration needed ($\geq 2\%$).	Low stability. It is destabilized by organic material and cationic hardness.	Nonfoaming, but they show a typical disagreeable smell.	Noncorrosive on metals and ceramics.
Easily absorbed into plastics. Difficulty to rinse off.	Highly toxic both by ingestion and by absorption through the skin. Can cause leukemia and poisoning.	Slowly biodegradable. Highly dangerous to the environment. Highly restricted and monitored	Disinfectants specific for hospitals and laboratories. Sometimes still used as product preservative.	Not to be used in the food industry. It is considered outdated in every respect

Table 18.17 Metals.

Copper, Silver, Zinc

No action on spores.	Active at low concentration (<50 ppm).	They are destabilized by organic materials and anionic hardness (made inert by sequestration).	Nonfoaming. To be stabilized in their specific field of stability (acidic pH)	Noncorrosive on metals. Copper salts cause cementation (metal exchange).
Silver is sensitive to the chlorides in water (precipitation).	Toxic, they cause poisoning (interference on enzymes).	Dangerous to the environment. Can be disposed of in limited amounts only (specific to each metal).	Disinfectants with specific application: Copper: treatment of grapes, anti-algae in cooling towers and swimming pools. Silver: co-formulated with hydrogen peroxide against <i>Legionella</i> . Zinc and copper: hoof care in farming	

This does not preclude carrying out cleaning and disinfection in enclosed space (CIP and SIP) with detergents based on suitable cationic disinfectants, since the detergent also cleans off the cationic component at the end of the process. It only means that the application of nitrogen compounds as terminal disinfectants on open surfaces is more beneficial than in enclosed spaces.

18.4

Physical Disinfection

Microorganisms are living matter. They suffer from any change in the physical conditions that support their life. Heat, radiation, electric and magnetic fields, high pressure, and ionization can interfere with the mechanism of life and can harm organisms, even causing death. All these influences differ from filtration methods. Filtration does not inactivate microorganisms, but treats biofouling as a contamination to pull out of the system. Traditional and crossflow $<0.2\mu$ micro-filtration can be used to achieve sterilization before or below every system processing liquids. Unlike chemical methods, some physical processes of disinfection can be applied directly to foods without causing deterioration.

18.4.1

Disinfection by Heating

Life appeared in the environment when the carbon chemistry encountered steady conditions of temperature. Bacteria exploited the opportunity first. Bacteria can theoretically grow at all temperatures between the freezing point of water and the temperature at which protein or protoplasm coagulates, apart from archaic bacteria, which can survive high temperature, even $>90^{\circ}\text{C}$. Bacteria grow best at $(16\text{--}40^{\circ}\text{C})$, mesophilic bacteria, but beyond these limits life has problems (psychrophilic and thermophilic bacteria). Temperatures below minimum stop bacterial growth but do not kill the organism, whereas temperatures above the maximum soon kill bacteria. Most cells die after exposure to temperatures in the order of 70°C for 15 seconds (pasteurization). Spore-forming organisms require more severe heat treatment, for example, steam at 121.1°C for 3.33 minutes to obtain D_1 reduction (90% reduction of *Bacillus stearothermophilus* spores, equal to 1 log cycle) [11]. In order to reach 99.999% reduction (5 log cycles), several minutes could be required. It is usual to choose a reference microorganism for a given process. Besides *Geobacillus stearothermophilus* for sterilization processes, *Mycobacterium tuberculosis* may be used for pasteurization processes, *Enterococcus* or *Legionella* species for disinfection of devices [12].

The rate of the thermal destruction rises in logarithmic fashion. Thus, bacteria subjected to heat are killed at a rate proportional to the number of organisms. Thus, for thermal treatments it is necessary to know the concentration of microorganisms (or spores) to be destroyed. If the number of microorganisms rises, the time of heating has to be increased in order to bring the population down to the tolerated level. The thermal process depends on the temperature of exposure and the time required to accomplish the desired rate of destruction at that temperature. Table 18.18, adapted from Kramer and Cantoni [13] and Quaglia [14], gives temperatures and times to inactivate bacteria in preserves.

Some treatments (e.g., aseptic rooms) bring up the concept of risk protection, which asks for 6 log reductions in the number of the viable spores counted in the plant. For instance, if 2 log spores are counted, the risk protection demands a

Table 18.18 Temperature and time to inactivate bacteria in preserves.

Preserves and microorganisms	Temperature (°C)	Inactivation (minutes)
Low-acidic preserves (pH > 4.6)		
<i>B. stearothermophilus</i>	120	4–5
	100	3000
<i>C. thermosaccharolyticum</i>	120	3–4
<i>C. botulinum A and B</i>	120	0.1–1.5
<i>C. botulinum E</i>	80	0.3–3
<i>C. perfringens</i>	100	0.3–20
<i>C. sporogenes</i>	121	0.8–1.5
<i>B. subtilis</i>	100	11
	121	0.5–0.7
<i>B. cereus</i>	100	5
<i>Salmonella spp</i>	65	0.2–2
<i>Staphylococcus aureus</i>	65	0.2–3
Medium-acidic preserves (pH 4.0–4.5)		
<i>B. coagulans</i>	120	0.1
<i>C. pasteurianum</i>	100	0.1–0.5
<i>B. polymyxa</i>	100	0.1–0.5
High-acidic preserves (pH < 4.0)		
<i>Byssochlamys ascospore</i>	90	30
<i>Lacti c bacteria, yeasts, molds</i>	65	0.5–1

Adapted from Kramer and Cantoni in Leali [13] and Quaglia [14].

procedure able to give 8log reductions. Therefore, the D and Z values should be known. The D and Z values are the bases for determining the heat sensitivity of microorganisms:

- **D value** is expressed as a time. It is the time in minutes (or seconds) required to destroy 1 log cycle (90%) of the target microorganism at a given temperature. For example, D₁ at 72 °C means that the bacteria population undergoes 90% reduction for each minute at 72 °C.
- **Z value** is expressed as a temperature. It is the temperature change required to give a change in the D value by a factor of 10. For instance, if D is 30 min (D₃₀) at 60 °C, the Z value is the interval of temperature required to change D₃₀ to D₃. Figure 18.11 explains a Z value of 20.

Heat is lethal to microorganisms, however,

- Each species has its own particular tolerance.
- Spores behave in a way different from the vegetative forms.
- Microbial cells may contain enzymes more resistant to heat than the microbe itself.

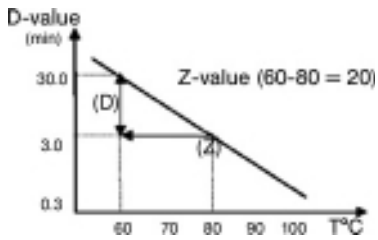


Figure 18.11 D and Z values.

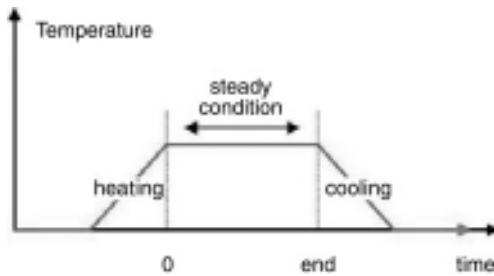


Figure 18.12 Limits of the steady condition.

The disinfection temperature is the actual temperature detected on the surface or at the middle of the food mass. The temperature in a boiler or set in a pasteurizer or an oven is not the temperature of the disinfection. Consequently, the time of the sterilizing process starts when the surface or the food mass is at this temperature. Heating and cooling times are not included, as reported in Figure 18.12.

A wrong procedure of disinfection by heating can have a positive effect on spores and make them sprout. Moreover, even if a microbial cell dies, enzymes more resistant to heat could remain active. After cell lysis, enzymes spoil food as if microbes themselves were present. As a typical example, the life of milk can be shorter because of improper pasteurization. Thus, stimulation and enzyme release affect the process in a way worse than expected.

Tyndallization concerns a particular thermal treatment of temperature-sensitive liquids, including proteins and carbohydrates, which aims at preventing germination of spores after packaging or bulk storage in a warehouse. It consists of repeated cycles of heating and cooling over 3 days. Tyndallization inactivates the vegetative forms, stimulates the spores to germinate, and re-disinfects the sprouted microorganisms [12].

Some bacterial endotoxins have higher resistance to heat than their related bacteria and fungi. An effective destruction of heat-resisting toxins requires a sterilizing temperature (long time and/or $>100^{\circ}\text{C}$). Uniform heat penetration preventing barriers of cold spots, organic and inorganic soil, and dried salts inside the treated foods and plants should be ensured by means of probes recording data in progress.

The conclusion is that heat disinfection is effective, flexible, and reliable only when all factors are known and controlled, and a margin is given to the sheer predetermined limits of the wanted microbiological safety.

18.4.2

Disinfection by UV Radiation

Air, liquids, and surfaces are targets of UV light disinfection. The characterization of the UV radiation and its exploitation in environmental disinfection are described in Section 15.2.2. As well as sterilizing the environment (air), UV rays are suitable for the sanitation of water and surfaces. Feed water and recirculating water in swimming pools and potable and process water in industry are typical examples of the use of UV radiation. However, there are a great number of other activities that benefit from the UV disinfection, affording a system simple to install and very safe. Public waterworks and private wells, trains and ships, cosmetics and microelectronics, fruit and vegetable washing, and terminal treatment of waste water are some examples of the application of UV rays.

The intensity of the light and its killing capacity decrease as a function of distance, reflection, moving solids (blind areas), radiation time, water speed, and turbidity, requiring planned geometrical combinations of several lamps. Figure 18.13 shows some UV lamps, which are available for small installations and devices, but demand careful planning.

As pipelines, autoclaves, and tanks may be sources of microbial pollution, the UV source should be located as close as possible to place where the water is used.

UV radiation is effective for disinfecting the surfaces of containers, plastic films and food before packaging (e.g., seals for yogurt), ready-to-eat food packets, PE film, plastic containers in clean rooms and food laboratories, tracks, and food in a tunnel (e.g., fresh-cut produce) moving to the packaging stage.



Figure 18.13 A selection of UV lamps (courtesy of A.D.P. Idrosteril and Prominent).

Wooden barrels (barriques) in winery can be freed from pollution due to *Brettanomyces* by UV lamp treatment for 1.5–3 min (Section 8.5.3). Corks and caps can be fed to the capper in a UV box where they are freed from yeasts and molds.

18.4.3

Disinfection by Filtration

Disinfection or physical removal of bacteria from a liquid can be performed by the use of a membrane filter. A sterile bacteria-retaining membrane has a nominal porosity of $<0.22\mu\text{m}$. A $0.45\mu\text{m}$ membrane is small enough for applications where specific microorganisms are the target (e.g., yeasts in a brewery or winery). In general, the food industry adopts the pore size to remove those microorganisms that allow the product to meet the agreed standards.

Filtration is extensively used in the production of sterile and potable water, process water, and in the microbiological stabilization of many liquid foods such as juices, essences, milk, wine, and beer. Basically, the filtration process consists of passing a fluid through a porous medium which entraps the microorganisms and retains them on its surface (screen filter) or in a matrix (depth filter) (Figure 18.14). Depth filtration does not ensure an absolute removal of microorganisms, but it absorbs the bulk of the particulates and is usually placed before the screen filter where it helps to prolong the process of absolute filtration (Figure 18.14).

The retention by a screen is well defined, relying on the pore size being smaller than the size of the microorganisms. However, particles that are smaller than the pores can also be retained, but by different mechanisms, which to arrest their movement through the tortuous capillaries of the filter. Electrostatic attraction and adsorption play a decisive role in holding the particles, while Brownian diffusion, inertia, and sedimentation promote contact with the capillary wall. As mentioned, the depth filtration is unsuitable for a satisfactory removal of microorganisms. Thus, the disinfection by filtration is accomplished by a sieving action. Although made of plastic, the filter is rigid and has discrete and fairly uniform capillary passages. Thus, the microorganisms larger than the size of the holes are entirely retained on its surface even at high pressure differential. This becomes a disadvantage. The high retention decreases the time of filtration of the liquid rich in particles. Such particles form a filter cake and prevent the fluid flow. If the fluid is different from pure water, pre-filters are recommended so as

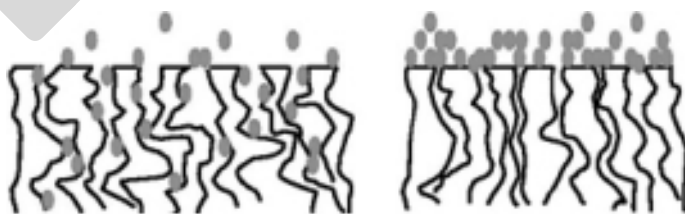


Figure 18.14 Depth and sieve filtration.

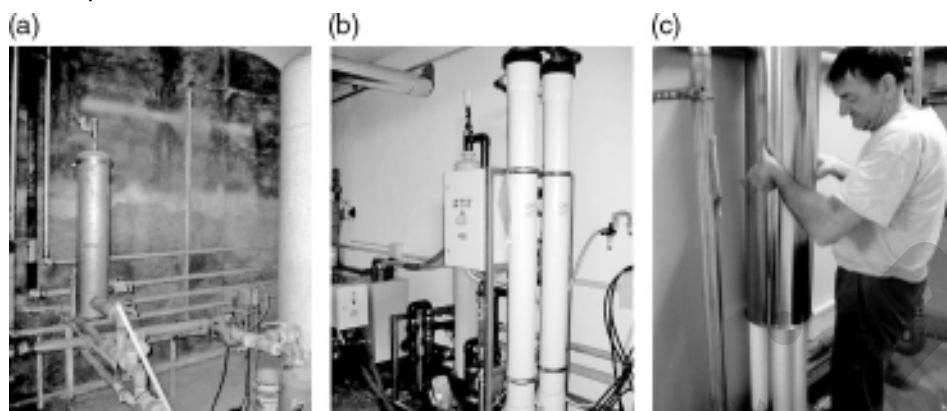


Figure 18.15 Filtration of water in a bottling: (a) depth, (b) large screen and (c) sterile screen microfiltration (courtesy of Q. Decordi).

to extend the life of the main membrane which performs the removal of the microorganisms. In order to remove colloids and sterilize water, there are three consecutive filtrations (Figure 18.15).

- 1) rough filtration before the buffer tank collecting water from the well
- 2) large screen microfiltration to remove destabilized and agglomerated colloids to provide water for the bottling process
- 3) third screen filtration to produce sterile water for rinsing bottles.

This is a serial filtration. Serial filtration involves filters having progressively finer pores so that they progressively remove impurities, ensuring that the final screen filtration will have longer productivity. A general simple equation connects the filtration parameters [15]:

$$Q = C_1 \frac{AP}{V}$$

where:

- Q = flow rate
- A = filtration area
- P = differential pressure
- V = liquid viscosity
- C = filter resistance

The flow rate is directly proportional to the filtration area and differential pressure, and is inversely proportional to the viscosity of the liquid. The decision when to clean the filter is based on its productivity. Either membranes are cleaned at a pre-established differential pressure (using a simple flow reversal) or when the permeate decreases to a pre-established volume. Membranes for sterilizing pure water are usually not soiled, so that only a periodic disinfection is performed.

Treatment with peracetic acid achieves this (on-line or by soak). Soiled membranes are replaced with new ones or, if possible, back-flushed or cleaned by chemicals (see also Chapter 12).

Microorganisms are a problem not only alive but also dead. Heat sterilization, for instance, is a possible source of residues capable of causing pyrogenic reaction (fever). In some processes (e.g., pharmaceutical products), killing bacteria may not be enough and their complete removal may be required. Also, besides being a direct source of pyrogenic activity, dead microorganisms can undergo cell lysis which releases active constituents significantly smaller than the vegetative forms. Besides being potentially allergenic, cell enzymes continue their specific activity in the liquid. They can modify the organoleptic system and reduce food shelf-life (e.g., inadequate pasteurization of milk). Therefore, as a $0.22\mu\text{m}$ membrane filter removes intact cells but not their pyrogenic constituents, ultrafiltration, nanofiltration and reverse osmosis are applied to produce sterile apyrogenic water with the targeted purity.

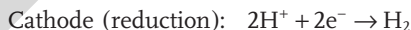
Membranes must be tested for integrity at regular intervals or just prior to filtration according to the procedure recommended by the membrane supplier. If in doubt, the classical microbiological analysis before and after the point of filtration removes the doubt.

18.4.4

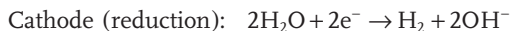
Disinfection by Electrolyzed Water

Sanitation by electrolyzed water is regarded as a physical disinfection although the biocides are actually chemicals generated by the electrolytic process in the presence of selected substances, usually pure sodium chloride. Electrolyzed water is also known as electrolyzed oxidizing water (EOW).

In an electrolytic cell, the negative polarity is applied to the cathode, where reduction occurs. Hydrogen gas is evolved, the arriving electrons having neutralized the metal ions. The anode has positive polarity; oxidation occurs here. At the anode, anions give off electrons (oxidation) that flow into the driving circuit to the cathode. The flow of electrons in an electrolytic cell is always from anode to cathode and the conventional current is from cathode to anode. Applying an electrical power source to two electrodes in water, hydrogen is evolved at the cathode and oxygen at the anode:



and



The unidirectional current produces a volume of hydrogen twice that of the oxygen. The reaction cannot occur without adding energy by an external electrical

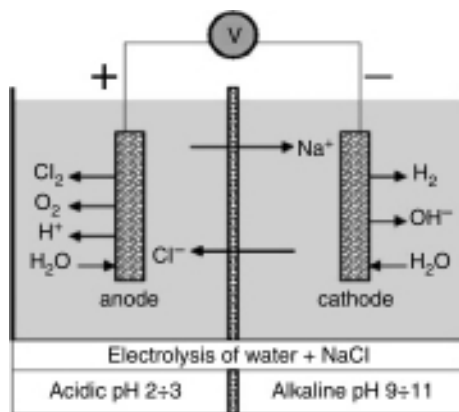
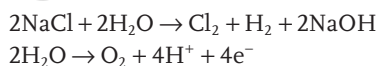


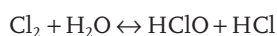
Figure 18.16 Chemicals from electrolyzed water with dissolved NaCl.

power source because of the negative potential of the water electrolysis cell (-1.23 V at 25°C). The quantity of decomposed substance is proportional to the quantity of electricity passing through the solution (part of the energy is lost by heat, cell and operational conditions, and overpotential ...). According to the reaction, hydrogen cation (H^+) concentrates at the anode, where the pH decreases, and hydroxide ion (OH^-) accumulates at the cathode, where the pH increases. The electrolysis of pure water is slow because of its very low conductivity. Accumulation of charge repels the further migration of ions and the reaction proceeds slowly. The addition of a soluble conducting electrolyte makes the conductivity of the water increase considerably. However, if different substances are present in the solution, those having a lower oxidizing potential are first oxidized at the anode and those having a higher oxidizing potential (that is, those requiring less electrical work) are first reduced at the cathode. Thus, a competition starts between anions and hydroxide ion, cations and hydrogen ion. The redox potential of the electrolytes can generate a system where an anion oxidizes instead of hydroxide and a cation reduces instead of the hydrogen ion. The redox potential of sodium (Na^+) and chloride (Cl^-) falls into this preferential redox, making electrolyzed water suitable for disinfection by the elemental chlorine generated, according to the following reactions:



and schematically represented in the electrolytic cell shown in Figure 18.16.

Chlorine reacts with water giving hypochlorous acid, which is a weak acid but an oxidizing agent stronger than chlorine.



When the anodic solution is mixed with the cathodic one, the acid is partially neutralized to sodium hypochlorite. At pH 7.3 the solution contains equal concen-

trations of hypochlorous acid and hypochlorite ions. Starting from pure water (soft or even tap water) and pure sodium chloride, the equilibrium between the acid and its salt at neutral pH forms an ideal condition for a disinfection performed with pure agents. This is a remarkable advantage in several sectors (e.g., drinking water and sanitation of carcasses). The disadvantage of the system is the instability of the disinfecting agents. It is therefore recommended that the electrolysis process should be carried out *in situ*, preparing the disinfecting agents only at the time of use. Efficient electrolysis devices operating at low voltage (even 10–20 V) are commercially available for producing the electrolyzed oxidizing water just before use. The ensuing disinfection by the electrolytic process is basically based on chlorine in its two forms: hypochlorous acid and sodium hypochlorite.

In practice, a saturated solution of sodium chloride (~28% NaCl) is prepared in softened water. The solution is diluted with soft water to 0.5% (or more) of NaCl and pumped to the electrolysis cell. The electrolyzed solution is stored in an intermediate tank from which it is dosed to the final application at the desired concentration, usually up to 0.5% of disinfectants.

The process is considered to be one of the most efficient and safe methodologies to disinfect pipelines of potable and utility water, preventing the formation of biofilm. The circulation of warm water can be particularly dangerous (growth of *Legionella pneumophila*) every time aerosol is breathed (e.g., showering, hydro-massage, steam sauna, fountains in enclosed spaces...). The disinfection rapidly eliminates bacteria and preserves the process from this pollution hazard. EOW is a useful method of disinfecting fresh-cut produce (4th gamme), giving a remarkable reduction in aerobic bacteria, coliforms, molds, and yeasts without affecting the sensory quality of the food [16]. In particular, acidified electrolyzed water can effectively inactivate *Escherichia coli* O157:H7, *Salmonella enteritidis*, and *Listeria monocytogenes* on lettuce [17], giving negligible AOX formation (e.g., chloroform). *E. coli* and *L. monocytogenes*, typical contaminants in the meat and cheese processing industry, are inactivated by soaking the tools and cutting boards in electrolyzed water [18]. Even Staphylococcal enterotoxin-A can be inactivated in contact with EOW [19]. It is also effective on *Campylobacter jejuni* (washing fresh poultry carcasses) [20] and on *S. typhimurium*, *S. aureus*, and *L. monocytogenes* (cleaning fresh eggs) [21].

Thus, the food industry benefits from the use of this hybrid disinfection. Disinfecting chemicals prepared *in situ* provide advanced sanitation not only because disinfectants free of interfering co-formulants and stabilizers are used on food surfaces and even directly on foods (e.g., carcasses), but also because of the improved handling safety. Storage and handling of chemicals are unnecessary when performing sanitation with EOW.

18.4.5

Disinfection by Cold Plasma

Plasma is the so-called 4th state of matter. Melting, vaporization, and ionization cause matter to change its state. Matter can change from solid to liquid, liquid to

Table 18.19 Cold argon plasma characteristics.

Species	Physical characteristic	Value
Neutrals	Density (0.1 mbar)	$2.4 \cdot 10^{15} \text{ cm}^{-3}$
	Temperature	293 K = 0.03 eV
	Mean velocity	$4 \cdot 10^2 \text{ m/s}$
Ions	Density	$5 \cdot 10^9 - 5 \cdot 10^{10} \text{ cm}^{-3}$
	Temperature	500 K = 0.04 eV
	Mean velocity	$5 \cdot 10^2 \text{ m/s}$
Electrons	Density	$5 \cdot 10^9 - 5 \cdot 10^{10} \text{ cm}^{-3}$
	Temperature	23 000 K = 2 eV
	Mean velocity	$9.5 \cdot 10^5 \text{ m/s}$
UV	Wavelengths of strongest Argon (I) lines	104.82 nm (11.6 eV)
		106.67 nm (1.8 eV)

Courtesy of Chapman-1980 [24].

gas, and gas to plasma according to the energy supplied to the system. Plasmas represent the most high-energy state, characterized by their electron energy and density and subdivided into cold and hot plasmas according to the type of electrical discharge. Hot plasma can immediately kill any living cells because of its high temperature of thousands of degrees centigrade. However, being quite difficult to control, it is unusable in the food industry. On the other hand, the development of a partially ionized gas at low pressure and temperature (cold plasmas) has led to successful use in several industrial processes of surface activation and cleaning, disinfection of surfaces and liquids, deposition, and surface etching. The visible glow discharge of a cold plasma is a blue-white to dark purple emission depending on the type of gas [22].

Ionization yields highly reactive particles consisting of electrons, ions, and free radicals. Reactions generate excited states. The relaxation to the ground state of atoms, molecules, and metastable species (long lifetimes in excited gases, e.g., noble elements) usually leads to the emission of very energetic UV radiation [23]. Chapman [24] gives some typical characteristics of a radio-frequency cold argon plasma in Table 18.19.

The reactive particles react in direct way with any surface. When a bacterial cell is encountered, they destabilize the membrane and the inner cellular organization. It follows that any bacteria, fungi, parasites, and other organisms they find are inactivated. The main applications of cold plasma are in surface activation, cross-linking, and deposition. In terms of disinfection, surface activation and cross-linking by the reactive particles lead to biofilm inactivation. An oxygen plasma discharge can be used for a period of time sufficient to kill the living bacteria cells and cross-link them to the surface as an inactivated substrate [25]. When, besides the direct action on biofilm, the surface is also functionalized by deposition of macromolecules and a micro-layer of bactericidal agents, the

decrease in biofilm attachment and growth is obvious on comparing the result with an untreated surface. Polyethylene glycol, activated quaternary ammonium groups, and silver nanoparticles are used to destroy biofilm and prevent it from adhering [26, 27].

Even liquids can be sanitized by reacting with plasma species including electrons, ions, and free radicals generated when water or solution are vigorously stirred between two electrodes. If electrodes release nanoparticles (e.g., silver), the combination of both systems enhances the result and the rate of disinfection [28].

A further industrial application of cold plasma is in farming. The transfer of bacteria from contaminated milking equipment to individual cows is one of the commonest ways to transmit diseases such as mastitis (Chapter 13). The stainless steel teat cup shell, which receives the rubber teat cup liner, is provided with an electrode. After the milking of each cow, a second wand-like electrode is lowered into the teat cup liner within the shell. A cold plasma is then generated between the electrodes to disinfect the inside of the liner [29]. Bacteria are destroyed in as little as one minute.

As far as cleaning is concerned, RF and DC cold plasmas are difficult to use in the food industry. They do not remove bulk contamination whether organic and inorganic. Only nonvisible oil films and sub-particles can be removed by plasma. Thus, chemical decontamination by plasma is called superfine cleaning [22]. The interesting application of the plasma process is in surface modification for subsequent fine and critical processes. Thus, it is exploited in microelectronics and surface preparation before gluing, printing, coating, and bonding critical surfaces.

18.4.6

Disinfection by High Pressure

High-pressure processing (HPP) is a method of subjecting foods to elevated pressures up to 8000 bar. Also known as high hydrostatic pressure processing (HHP) and ultra high-pressure processing (UHP), it can be carried out with or without adding heat to achieve microbial inactivation or alter some attributes of foods while keeping their sensory quality. For instance, proteins can denature, and, by applying enough pressure over a specific time, denaturing will become irreversible. Proteins gel and increase in viscosity at room temperature, leading to a possible restructuring of the food. Denaturing of the cellular proteins, enzymes, and cell membrane will inactivate living microorganisms. Pressures of 4000–8000 bar are enough to kill most vegetative forms of microorganisms in a few minutes. Pressures required to kill various organisms are given by Rovere [30] in Table 18.20.

Pressure is uniformly applied to the food product packaged in a flexible container and transmitted to the interior in every direction (isostatic pressure), the packaged food being immersed in a hydraulic liquid (usually water) and pressurized in the processing chamber for 3–5 min. Many traditional types of packages can be used with HPP (e.g., plastic bottles, cups, tray, and pouches). They must, however, be flexible enough to allow for a 10–20% decrease in volume under pressure [31]. Glass and metal containers are not suitable. Simultaneously

Table 18.20 Pressure to kill microorganisms.

Microorganisms	Pressure (bar)	T°C / minutes	Substrate
Gram+ vegetative cells			
<i>Lactobacillus casei</i>	5000	20 / 1	Apricot nectar
<i>Leuconostoc mesenteroides</i>	3000	20 / 9	Apricot nectar
<i>Bacillus cereus</i>	5000	20 / 1	Culture broth
<i>Staphylococcus aureus</i>	7000	20 / 1	Culture broth
<i>Listeria monocytogenes</i>	7000	20 / 3	Culture broth
<i>Enterococcus faecalis</i>	8000	20 / 5	Egg
<i>Microbacterium sp</i>	8000	60 / 0.5	Phosphate buffer
Gram– vegetative cells			
<i>Serratia marcescens</i>	3000	20 / 1	Culture broth
<i>Enterobacter aerogenes</i>	4000	20 / 1	Culture broth
<i>Escherichia coli</i>	4000	20 / 1	Culture broth
<i>Klebsiella oxytoca</i>	4000	20 / 1	Culture broth
<i>Salmonella seftenberg</i>	5000	20 / 05	Culture broth

Adapted from Rovere–ABB Pressure System Co. [30].

pressured in every direction, food retains its shape. Unlike heat, HPP does not disrupt chemical bonds, so the nutrient and flavor components of the food are left intact. As pressure must be transmitted to all parts of the food, HPP cannot be applied to all types of food. The food must contain water and must not contain entrapped air to avoid being crushed. Thus, the technology is not applicable to dry solids because these do not allow an effective microbial destruction.

HPP inactivates microbes by damaging their outer cell membrane, essential proteins, and enzymes in the cell. It can also inactivate some enzymes such as pectinases, which affects the stability of orange and other fruit juices. As an acidic pH is a primary factor in reducing bacteria, the microbial inactivation of acidic foods has an advantage over low-acid products (e.g., milk, soups, and low-acidity vegetables). However, the inactivation of spores still requires the addition of mild heat to ensure a good result. The Table 18.21 shows the HPP and heat synergism in inactivating spores [30].

The high-pressure press, being a discontinuous process, is put into the system of food preparation, filling, and packaging machines. HPP should be used when traditional processes are insufficient to provide a certain quality of product; the production volumes are reasonable and the logistics are efficient.

18.4.7

Disinfection by Pulsed Electric Field

Pulsed high-voltage electric fields (PEF) are one of the most important treatments for the nonthermal preservation of foods, and are suitable to replace (or be combined with) the thermal process of pasteurization. Pulses of high voltage flood

Table 18.21 Pressure and temperature synergism in killing spores.

Gram+ spores			
Microorganisms	Pressure (bar)	T°C / minutes	Substrate
<i>Bacillus cereus</i>	9000	20 / 1	Phosphate buffer
	8000	60 / 5	Phosphate buffer
<i>Bacillus licheniformis</i>	9000	50 / 5	Phosphate buffer
	8000	60 / 5	Phosphate buffer
<i>Bacillus stearothermophilus</i>	7000	70 / 5	Phosphate buffer
<i>Bacillus coagulans</i>	9000	70 / 5	Phosphate buffer
<i>Clostridium pasteurianum</i>	8000	60 / 12	Tomato serum
	9000	60 / 5	(pH 4.5)
<i>Clostridium sporogenes</i>	14 000	60 / 5	Meat broth
	8000	90 / 5	Meat broth
	8000	65 / 11	Distilled water

Adapted from ABB Pressure System Co. [30].

the food placed between two electrodes releasing repeated impulses in the 20–80 kV cm⁻¹ range, usually for a few microseconds (μs). The food quality, in its sensory and physical properties, is retained as well as its nutritional aspects [32]. The pulse generation (exponential decay, square wave, bipolar, or oscillatory) is produced by an array of capacitors, inductors, and switching devices that expose liquid or semi-liquid foods to consecutive bursts of a high-intensity electric field. During the PEF process, microorganisms undergo cell lysis by irreversible structural changes of the membrane, leading to pore formation and breakdown.

The electric field intensity is one of the main factors in the microbial inactivation. Increase in electric field intensity, enhances microbial inactivation. To attain inactivation, the intensity must exceed the critical transmembrane potential [33], which is associated with a critical electric field below which inactivation does not occur. Hence, spore inactivation is considerably more difficult, requiring additional thermal energy to affect the external protective cortex.

A further important factor is the time of treatment, equal to the product of the number of pulses and their duration. Increasing duration (μs) decreases the critical electric field and improves the efficacy of the treatment. However, increase in duration also results in temperature increase, often undesirable.

Conductivity, ionic strength, and pH are three factors pertaining to products and able to influence the result of microbial inactivation. Foods with large electrical conductivities generate smaller peak electric fields across the treatment chamber and are therefore not suitable for PEF treatment [34]. Because the conductivity of a liquid results from its ionic strength, increase in the ionic strength of a food results in decrease in the inactivation rate. Salty liquids are thus not suitable for PEF treatment. The addition of salt and other electrolytes, if necessary, is done after the treatment.

Table 18.22 PEF and heat synergism in killing bacteria.

Microorganisms	Treatment (pulse/kV/cm)	Reduction (log)
<i>Lactobacillus delbruekii</i> ^a	40 / 16	4–5
<i>Bacillus subtilis</i> (vegetative cells) ^a	50 / 16	4–5
<i>Bacillus subtilis</i> (spores) ^b	60 / 16 (200–300 μs)	3–4
<i>Bacillus subtilis</i> (spores) ^c	30 / 50	3.4
<i>Bacillus cereus</i> (spores) ^c	50 / 50	5
<i>Escherichia coli</i> ^a	20 / 25	3
<i>Escherichia coli</i> ^d	50 / 36	6
<i>Saccharomyces cerevisiae</i> ^a	18 / 25	4
<i>Candida albicans</i> ^e	30 / 20	4.5
<i>Listeria monocytogenes</i> ^e	30 / 20	2
<i>Pseudomonas aeruginosa</i> ^e	30 / 20	3.0–3.5
<i>Staphylococcus aureus</i> ^e	30 / 20	3.0–3.5

a) Adapted from [36].

b) Pothakamury-1995.

c) Marquez *et al.*-1997 adapted from [35].d) Qin *et al.*-1998.e) Hülshager *et al.*-1983.

As the main effect of an electric field on a microorganism cell is to increase the membrane permeability by membrane compression and pore generation, an acidic pH of the medium improves the lethality of PEF. Among bacteria, gram-positive cells are more resistant to PEF than gram-negative ones. In general, yeasts are more sensitive to electric fields than bacteria [34]. The number of microorganisms in food has usually little or no effect on their inactivation with electric fields. Some small effects of microbial concentration on inactivation may be related to the formation of clusters of yeast cells or possibly microorganisms concentrating in low-electric-field regions [34]. Spores are highly resistant. Usually, PEF does not succeed in inactivating them. This treatment, however, induces the germination of spores (e.g., *B. subtilis*), making them sensitive to subsequent pasteurization heat treatments. Thus, combinations of PEF and heat treatment constitute an alternative to the protection of food from spores [35] (Table 18.22).

Processing of fruit juices, milk, liquid eggs, and vegetable soups benefits from PEF technology. The fluid handling unit allows continuous treatment and delivers a microbiologically stable food to the packaging process. Modular equipment can suit every productivity need.

18.5

Regularity and Perseverance in Sanitation

Concentration (chemical energy), temperature (thermal energy), mechanical force (mechanical energy) and time are the important parameters when prepar-

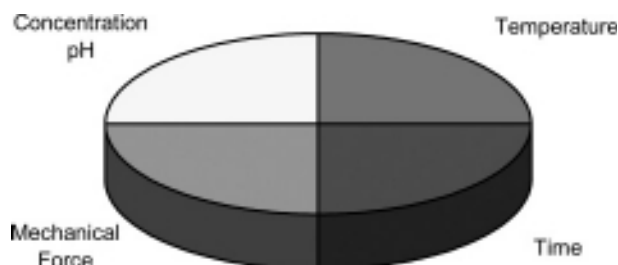


Figure 18.17 Cross-linked parameters in CIP.

ing a sanitation plan. Figure 18.17 shows these four contributions linked in a cross, the segments of which can be adjusted to make the sanitation fit the requirements.

If one section decreases, another (or more than one) has to increase in order not to have a void. A void in one of the contributions to the cleaning process means a mistake made in the sanitation plan. It is possible that mistakes associated with its application can explain the name of the diagram, which is known as the *Sinner's* diagram. The origin of the word 'Sinner' is not clear (as far as our research is concerned). However, it is reasonable to suppose that someone, playfully commenting on this subject, has pointed to it as the diagram of a person 'who could make mistakes' if not carefully observed. Anyone who makes mistakes is a sinner.

It is easy to understand the concepts of the diagram, but experience shows that mistakes in its application are still frequently recorded in industry.

Deciding on a product and a procedure takes into consideration efficacy together with the cost of the entire application. It follows that production quality and sanitation are interconnected within the bounds of desired results at the cheapest cost. If sanitation is inadequate or skipped and any parameter is not set correctly, microorganisms grow beyond the acceptable limit. If concentration, temperature, time, and mechanical force are not re-adjusted, the usual procedure will not be able to restore the steady condition, as schematized in Figure 18.18.

Only when the system comes back to the usual standard is it possible to restore the usual procedure. As a result:

- If any condition of cleaning changes, the basic procedure must also change.
- If the sanitation step has been skipped or wrongly carried out, the basic procedure cannot be used to restore the original state. An emergency procedure reinforced in one or more parameters (concentration, time, temperature, or mechanical force) must be decided upon for a number of cleanings suitable to achieve the required standard of the manufacturing process.

Regularity, perseverance, and carefulness are not a matter of personal opinion. Hygiene is measurable, to be maintained within pre-established limits, proved to be as established, documented to be assessed by a third party (auditors), and filed as a reference for consumers.

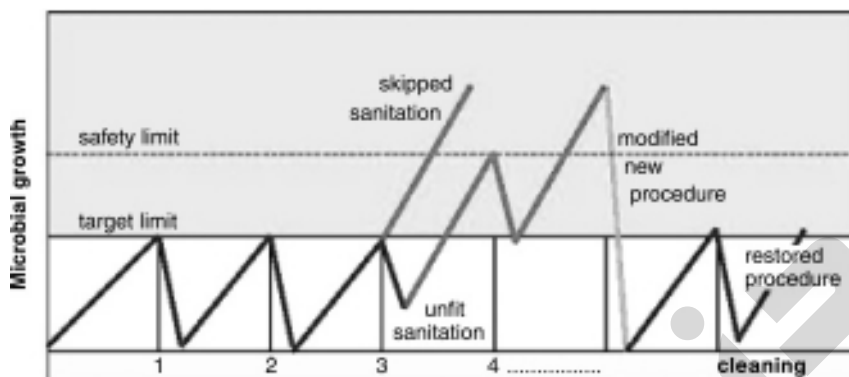


Figure 18.18 Regularity and perseverance in sanitation.

18.6

Sanitation Plan

The sanitation plan is a document reporting all the information needed to pursue and maintain a proper attitude toward hygiene in the food industry. The document is an integral part of the Quality System, defines objectives, and standardizes procedures able to achieve and keep them. Five steps are involved in drawing up a plan:

- early stage → initial inspection
- planning → preliminary draft
- validation → assessment of the attainment of targets
- application → final editing
- revision → periodic updating.

18.6.1

Early Stage

The initial inspection aims at assembling all the information necessary to obtain the knowledge of the whole manufacturing process in order to have an assessment of its hygienic quality. Therefore, the early stage involves:

- identification of the manufacturing flowchart
- assessment of the manufacturing steps
- assessment of the post-manufacturing steps
- assessment of the environmental condition.

This allows:

- defining targets
- defining areas of intervention
- identifying the key personnel.

18.6.2

Planning

The draft of the sanitation plan includes the systematic identification of interventions in selected areas and the definition of procedures, materials, products, and strategies designed to immediately correct out-of-control risk factors and prevent their recurrence. The drawing up of the document inclusive of generic references to procedures, products, and equipments concludes with the definition of the assessment of timing of the drafted plan.

18.6.3

Validation

Verifying the actual attainment of the projected targets is part of the validation step of the drafted plan. Validation states that the planning stage is appropriate to the process and achievable with the tools available to whoever has to work on the process.

18.6.4

Application

After checking the actual attainment of the established targets (validation), the sanitation plan is finally drawn up. Summing up the content:

- targets to pursue
- identification of each area of intervention
- limits considered valid to make the plan effective
- definition of procedures and products of intervention
- directives on the implementation of the established procedures
- directives on the personnel delegated to execute them
- directives on keeping the involved systems effective. More specifically, it must be clear
 - *where, when* and *how* to check the manufacturing, to clean, disinfect and check the result
 - *who* must check the manufacturing, cleaning, disinfection and the result of sanitation
- periodical revision.

Deciding the cost of safety measures supporting a balanced risk (P-point) is a critical moment in every industry which establishes and accepts its degree of safety, as schematically presented in Figure 18.19.

The graph is exponential. It is clear that a high degree of safety is not achieved by cheap decisions. However, just as it is foolish to disregard risk and safety, it is also thoughtless to demand a degree of safety greater than required.

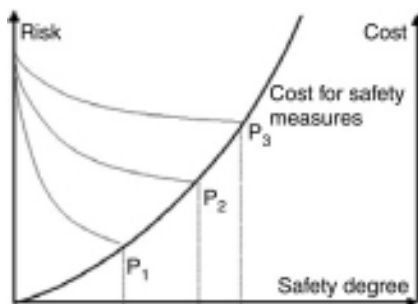


Figure 18.19 Risk and cost of sanitation measures as a function of the desired degree of safety.

18.6.4.1 Assessment of the Sanitation Result

The efficacy of the sanitation must be proved and recorded. This can be carried out after the sanitation process and before the manufacturing cycle. Methods should provide responses as rapid as possible. The assessment is subjective and objective.

Subjective assessments relate to the sense organs and experience. It is rapid but does not provide absolute certainty:

- **Sight** can reveal macroscopically contaminated parts, zones with different light reflection, hydrophobic surfaces with formation of water drops
- **Touch** can recognize fat films, coarse micro-deposits, initial gelatinous biofilms
- **Sense of smell** reveals the presence of hidden residues of production and typical odors of detergents and disinfectants (inadequate rinse).

Objective assessments yield a result analytically measurable and officially reproducible. The desired accuracy depends on time.

- **Chemical analysis** is aimed at determining specific substances (HPLC), components of reference (e.g., phosphorus-containing, cationic, anionic, and nonionic materials), completeness of rinse (neutral pH), and organic matter (Kübel test)
- **Microbiological analysis** measures microbial charge, presence or absence of specific microorganisms (pathogens, yeasts ...), sterility (clean rooms)
- **Bioluminescence** is a simplified unspecific microbiological analysis (ATP enzymatic analysis)
- **Proteins-check kit** immediately establishes the presence of proteins down to 50 µg concentration
- **CIP parameters** are determined by measuring instruments able to monitor concentration of detergent (conductivity), mechanical force (flux), thermal energy (temperature). All of this is recorded and filed.

An example of a sanitation plan sheet is given in Table 18.23.

Table 18.23 Sanitation document.

Sanitation plan		District:.....		Factory:.....		Site:.....	
Processing line:	Area:	Sheet n°	Date	Revision			
Surface	Operating modality	Equipment	Product	Frequency	Inside Outside	Man	Cost

The United States Food and Drug Administration (FDA) is recognized as a basic reference for food safety and applied nutrition. Its HACCP procedures give a comprehensive insight into concepts and applications in every sector of the food industry.

It is clear that the approach to a safe and secure manufacturing operation implies knowledge of the reason for each individual operation. Just as the sanitation plan cannot avoid monitoring the process, the reliability of a process relies on training the personnel involved in it. Each worker must take responsibility for his or her work. General training is no use. Only targeted training can make the individual worker fully acquainted with the consequences of his or her own actions in a specific job.

Standards and Guidelines are available as a general reference for the application, testing, and validation of disinfectants and processes. A summary is given below:

- US FDA 21 CFR 880.6885 and EC Council Directive 98/8/CE (BPD) assist in the notification and registration of disinfectants, sterilizing agents, preservatives, and products
- US EPA DIS TSS01 assists in the registration of disinfectants on hard surfaces
- US APIC gives guidelines regarding antiseptics for health care
- ISO 14937 governs the requirements for sterilizing processes and products
- ISO 13408 provides regulations applying to products, aseptic rooms, and isolators for healthcare aseptic processes
- ISO 11137 assists in developing and validating radiation sterilization processes.

18.7

Rapid Controls of Sanitation

Industrial processes are subject to secondary contamination from working surfaces and airborne microorganisms. A rapid index of the overall condition of the sanitized surfaces is fundamental to prevent disposal of manufactured goods. Standard culture media need a long wait (24 to 48 hours) to count microbes in

Petri plate. In order to short the time of answer after sanitizing, bioluminometric and proteins tests prove to be reliable for a rapid assessment.

18.7.1

Bioluminometer

Adenosine triphosphate (ATP) is a common molecule in every cell (bacteria and animals), transferring energy within cells. Hence, the measurement of ATP can give an index of microbial concentration on a surface. This measurement is based on the luciferin-luciferase system, which changes ATP into ADP and AMP (the di- and monophosphates), releasing energy in the form of light photons at 560 nm. The process is known as bioluminescence, and is revealed by a spectrophotometer (bioluminometer). The reaction is carried out with a test kit (prepared reagents) and is immediate (within a few minutes). The methodology does not distinguish viable from dead cells, microbial cells, or animal cells (meat processing) [37], so that the values found are equal to or higher than those expected. However, a signal, which could be exaggerated, should still be regarded as a positive alert of a possible risk of microbial pollution. Thus, the bioluminescence method does not replace the standard laboratory culture method, but is a tool of approximate rapid assessment. After a due consideration, it can help in revealing the efficacy of sanitation operations by discriminating between clean and dirty areas. A further advantage is its simplicity, which allows even personnel unskilled in microbiological laboratory analysis to perform microbiological assessments. Therefore, every food industry can exploit the bioluminescence methodology as an aid to maintaining quality. An example of the testing equipment used is shown in Figure 18.20.

18.7.2

Proteins Test

Only macroscopic contamination by an organic residue can be assessed by a visual estimation. The sense of touch can hint at the presence of fatty/polymeric contamination. The measurement of a few milligrams of proteic residue per meter squared requires the use of analytical apparatus, and this amount contamination must be detectable when deciding whether or not a surface is clean. However, biological mechanisms of biofouling-producing microorganisms may generate an organic contamination which could be confused with food residue.

The assessment of the presence of protein is only of any practical use if it is simple to do and gives an immediate reading. Strips reactive to proteins are available and give an immediate qualitative demonstration of the presence or absence of microdeposits on limited portions of surface. The presence of proteic residue means that cleaning and disinfection procedures must be repeated in order to restore the surface from its nonideal condition. Examples of the test methods used are illustrated in Figure 18.21.

High microbial charges usually indicate a sizeable organic residue, and the opposite is also true. A combination of bioluminescence and protein testing meets the need for a rapid and reliable assessment of a sanitized surface.

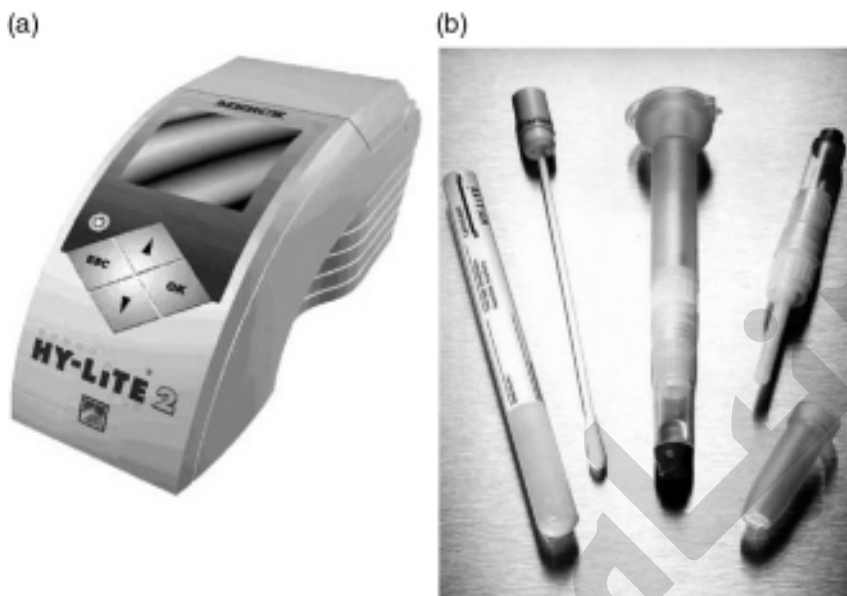


Figure 18.20 Examples of (a) a bioluminometer and (b) bioluminescence reagents etc.

18.8 European (EN) Microbiological Tests

Within the European Community the legislation concerning disinfecting products has become a harmonized system. The Biocide Products Directive 98/8/EC (BPD) governs the definition, classification, testing, and authorization of the use of disinfectants related to application areas (PT 1-4, at least). Historically, there exists a variety of test methodologies to prove the microbicidal efficacy of raw materials and formulations. Methods widely known and mostly applied locally include

- AFNOR-/BSI-standards
- procedures to support the DGHM/DVG/DLG approval system
- SST-/EST tests.

Experts from all over Europe have developed a common set of harmonized standards in the CEN TC 216 microbiological test standards [38–40]. The basic principles are laid down in EN 14885, where scope, normative references, terms and definitions, categories of tests, and procedures for claims concerning target microorganisms and applications are clearly outlined. To make a ‘-cidal’ claim with respect to the target microorganisms (bactericidal, yeasticidal, fungicidal, sporicidal, virucidal ...) in the areas of application PT 1-4 (human medicine, veterinary, food and domestic areas), raw materials and products must pass the obligatory test conditions under clean (terminal disinfectants) and dirty (mainly for detergent-disinfectants) conditions. For products applied under PT 1-4, there is a comprehensive range of microbiological tests listed in the EN 14885.



Figure 18.21 Examples of (a) protein test kit and (b) testing method.

The reference standard EN 14885 is modular-based, and includes

- **Phase 1 tests:** basic quantitative suspension test to establish that a product has ...-cidal properties without regard to specific conditions or intended use.
- **Phase 2 tests** comprising
 - Phase 2, step 1 tests, a quantitative suspension test simulating practical conditions appropriate to its intended use
 - Phase 2, step 2 tests, quantitative laboratory tests simulating practical conditions, that is, surfaces, instruments, hands.

The following sections give concise information on microorganisms in EN tests and the main methodology for assessing the activity of disinfectants useful to the food industry.

18.8.1

Bactericidal Activity

18.8.1.1 EN 1040

Chemical disinfectants and antiseptics: a quantitative suspension test for the evaluation of basic bactericidal activity of chemical disinfectants and antiseptics.

Phase 1

*Pseudomonas aeruginosa**Staphylococcus aureus*

18.8.1.2 EN 1276

Chemical disinfectants and antiseptics: quantitative suspension test for the evaluation of bactericidal activity of chemicals and antiseptics used in food, industrial, domestic, and institutional areas.

Phase 2, step 1

*Escherichia coli**Enterococcus hirae**Pseudomonas aeruginosa**Staphylococcus aureus*

18.8.1.3 EN 1656

Chemical disinfectants and antiseptics: quantitative suspension test for the evaluation of bactericidal activity of chemicals and antiseptics used in the veterinary field.

Phase 2, step 1

*Enterococcus hirae**Proteus vulgaris**Pseudomonas aeruginosa**Staphylococcus aureus*

18.8.1.4 EN 13727

Chemical disinfectants: quantitative suspension test for the evaluation of bactericidal activity for instruments used in the medical area.

Phase 2, step 1

*Enterococcus hirae**Pseudomonas aeruginosa**Staphylococcus aureus*

18.8.2

Fungicidal Activity

18.8.2.1 EN 1275

Chemical disinfectants and antiseptics: quantitative suspension test for the evaluation of basic fungicidal or basic yeasticidal activity of chemical disinfectants and antiseptics.

Phase 1

*Candida albicans**Aspergillus niger*

18.8.2.2 EN 1650

Chemical disinfectants and antiseptics: quantitative suspension test for the evaluation of fungicidal or yeasticidal activity of chemical disinfectants and antiseptics used in food, industrial, domestic, and institutional areas.

Phase 2, step 1

*Candida albicans**Aspergillus niger*

18.8.2.3 EN 1657

Chemical disinfectants and antiseptics: quantitative suspension test for the evaluation of fungicidal or yeasticidal activity of chemical disinfectants and antiseptics used in the veterinary field.

Phase 2, step 1

Candida albicans

Aspergillus niger

18.8.2.4 EN 13624

Chemical disinfectants: quantitative suspension test for the evaluation of fungicidal activity for instruments used in medical area.

Phase 2, step 1

Candida albicans

Aspergillus niger

18.8.3**Sporicidal Activity****18.8.3.1 EN 14347**

Chemical disinfectants: quantitative suspension test for the evaluation of basic sporicidal activity of chemical disinfectants and antiseptics.

Phase 1

Bacillus subtilis

Bacillus cereus

18.8.3.2 EN 13704

Chemical disinfectants: quantitative suspension test for the evaluation of sporicidal activity of chemical disinfectants and antiseptics used in food, industrial, domestic and institutional areas.

Phase 2, step 1

Bacillus subtilis

18.8.4**Main Tests Methodology****18.8.4.1 NF EN 1276 Procedure**

Chemical disinfectants and antiseptics: quantitative suspension test for the evaluation of bactericidal activity of chemical disinfectants and antiseptics used in food, industrial, domestic and institutional areas.

Phase 2, step 1

Principle A test suspension of bacteria in a solution of interfering substances is added to a sample of the product diluted in hard water. The mixture is maintained at 20°C for 5 min. After this contact time, an aliquot is taken and the bactericidal action in this portion is immediately neutralized. The number of surviving microorganisms in each sample is determined and the reduction in viable counts is calculated.

Obligatory Conditions

Test organisms	<i>Escherichia coli</i>	ATCC 10536
	<i>Enterococcus hirae</i>	ATCC 10541
	<i>Pseudomonas aeruginosa</i>	ATCC 15442
	<i>Staphylococcus aureus</i>	ATCC 6438
Conditions	Clean (bovine albumin 0.3 g L ⁻¹)	
	Dirty (bovine albumin 3.0 g L ⁻¹)	
Contact time	5 min	
Temperature	20°C	
Product diluent	hard water 30 dF	

Validation Test

- validation of selected experimental conditions or verification of the absence of any lethal effect in the test conditions
- neutralizer toxicity validation
- method validation (membrane filtration or dilution-neutralization).

Results The product, when diluted in hard water and tested in accordance with obligatory conditions shall demonstrate at least a 5 log reduction in viable counts.

18.8.4.2 NF EN 1650 Procedure

Chemical disinfectants and antiseptics: quantitative suspension test for the evaluation of fungicidal or yeasticidal activity of chemical disinfectants and antiseptics used in food, industrial, domestic and institutional areas.

Phase 2, step 1.

Principle A test suspension of fungi or yeast in a solution of interfering substances is added to a sample of the product diluted in hard water. The mixture is maintained at 20°C for 15 min. After this contact time, an aliquot is taken and the fungicidal or yeasticidal action in this portion is immediately neutralized. The number of surviving microorganisms in each sample is determined and the reduction in viable counts is calculated.

Obligatory Conditions

Test organisms	<i>Candida albicans</i>	ATCC 10231
	<i>Aspergillus niger</i>	ATCC 16404
Conditions	Clean (bovine albumin 0.3 g L ⁻¹)	
	Dirty (bovine albumin 3.0 g L ⁻¹)	
Contact time	15 min	
Temperature	20°C	
Product diluent	hard water 30 dF	

Validation Test

- validation of selected experimental conditions or verification of the absence of any lethal effect in the test conditions
- neutralizer toxicity validation
- method validation (membrane filtration or dilution-neutralization).

Results The product, when diluted in hard water and tested in accordance with obligatory conditions shall demonstrate at least a 5 log reduction in viable counts.

18.8.4.3 NF EN 13697 Procedure

Chemical disinfectants and antiseptics: quantitative nonporous surface test for the evaluation of bactericidal and/or fungicidal activity of chemical disinfectants used in food, industrial, domestic, and institutional areas.

Phase 2, step 2.

Principle A test suspension of bacteria or fungi in a solution of interfering substances is inoculated onto a test stainless steel surface and dried. A prepared sample of the product under test is applied in a manner which covers the dried film. The surface is maintained at a specific temperature for a defined period of time. The surface is transferred to a previously validated neutralization medium so that the action of the disinfectant is immediately neutralized. The number of surviving organisms which can be recovered from the surface is determined quantitatively. The number of bacteria or fungi on a surface treated with hard water in place of the disinfectant is also determined and the reduction in viable counts calculated by difference.

Obligatory Conditions

Test organisms	<i>Escherichia coli</i>	ATCC 10536
	<i>Enterococcus hirae</i>	ATCC 10541
	<i>Pseudomonas aeruginosa</i>	ATCC 15442
	<i>Staphylococcus aureus</i>	ATCC 6438
	<i>Candida albicans</i>	ATCC 10231
	<i>Aspergillus niger</i>	ATCC 16404
Conditions	Clean (bovine albumin 0.3 g L ⁻¹)	
	Dirty (bovine albumin 3.0 g L ⁻¹)	
Contact time	5 min / 15 min	
Temperature	18–25 °C	
Product diluent	hard water 30 dF	
Test surface	stainless steel disc, 2 cm diameter, grade 2B according to the requirements of EN 100088-2 finish on both sides. The surface should be flat.	

Validation test

- neutralization control
- neutralization test
- water control

Results The product, when diluted in hard water and tested in accordance with obligatory conditions shall demonstrate at least a 4 log reduction in viable bacterial counts and at least a 3 log reduction in viable fungal counts.

18.8.4.4 NF EN 13704 Procedure

Chemical disinfectants: quantitative suspension test for the evaluation of sporicidal activity of chemical disinfectants used in food, industrial, domestic and institutional areas.

Phase 2, step 1.

Principle A test suspension of bacterial spores in a solution of interfering substances is added to a sample of the product diluted in hard water. The mixture is maintained at 20°C for 60 min. After this contact time, an aliquot is taken and the sporicidal action in this portion is immediately neutralized. The number of surviving microorganisms in each sample is determined and the reduction in viable counts is calculated.

Obligatory Conditions

Test organisms	<i>Bacillus subtilis</i>	ATCC 6633
Conditions	Clean (bovine albumin 0.3 g L ⁻¹)	
Contact time	60 min	
Temperature	20°C	
Product diluent	hard water 30 dF	

Validation Test

- validation of selected experimental conditions or verification of the absence of any lethal effect in the test conditions
- neutralizer toxicity validation
- method validation (membrane filtration or dilution-neutralization).

Results The product, when diluted in hard water and tested in accordance with obligatory conditions shall demonstrate at least a 3 log reduction in viable counts.

18.9

Hand Washing and Disinfection

Personal hygiene has an impact on one's own health and the health of those living around. Even though personal hygiene is a pre-requisite and mandatory for people working in the food industry, it remains a personal choice determined by one's personal culture. Most infectious disease can be prevented by maintaining good personal hygiene on the job, which includes:

- maintaining personal cleanliness and hygiene (hair, teeth, skin)
- washing and sanitizing hands
- well trimmed fingernails, no polish
- no eating, drinking, chewing gum/tobacco
- keeping uniforms, clothing, and footwear clean and free of debris
- wearing appropriate hair and beard restraints

- removal of all jewelry
- wearing gloves that are intact and clean

A majority of pathogen organisms are tracked throughout a facility by the employee's footwear. Separate footwear should be used in the production area and only during working hours.

There are several possible ways in which bacteria can be transmitted: orally, by direct contact, via intermediates (e.g., utensils), and by a respiratory-airborne mechanism (inhalation). Two types of microorganisms are typically found on human skin: resident and transient.

Resident flora bacteria live and grow on skin. Usually, these flora are not only harmless but also aid in keeping the skin and mucous membranes healthy. *Staphylococcus aureus* is an exception to this rule, and 30–50% of the population carry this organism.

Transient flora come from any contaminated object, and virtually any type of organism can be picked up, with a much greater chance of it being pathogenic. These bacteria are transient, that is to say they are loosely attached and easier to transmit than the resident ones. Hands represent the main source of endogenous and exogenous bacteria transmission. Endogenous bacteria come directly from the body and are mostly represented by *Staphylococcus*, *Enterobacters* and *Coliform* species (e.g., from toilet, dirty underwear, and poor cleansing). Exogenous bacteria come from persons who occasionally wash their hands when working in direct contact with food, food-contact surfaces, and food packing materials. Exogenous microorganisms are mostly represented by *Coliforms*, *Listeria*, *Salmonella*, *Staphylococcus*, and *Shigella* species, viruses, usually *Calicivirus*, and parasites such as *Giardia lamblia* and *Cryptosporidia*.

It follows that the foundation of any personal hygiene program is frequent hand washing, which breaks the cycle of contamination. Resident bacteria are firmly attached to the skin and more difficult to remove than transient organisms, but washing will remove transient bacteria and most of the resident ones. Disinfection should be actually regarded as a 'hand pasteurization'. The result of an effective handwashing can reduce a population of bacteria by 99.97%. So, when to wash hands?

- when entering the work place
- after using the toilet
- after handling raw meat, garbage, money, dirty dishes and utensils
- after cigarette, coffee or food breaks
- after touching nose, mouth, beard or hair
- after handling animals or their waste
- after sneezing or coughing
- any time your hands are dirty.

The recommended care, aside from being a legal obligation, is simply common sense.

How to wash hands:

Procedure No. 1

- wet hands with warm potable water
- apply soap
- vigorously rub all the surface of the hands and under fingernails for at least 10–15 s
- rinse with potable water
- dry hands with a paper towel
- apply disinfectant (alcohol or alcohol formulated with specific nitrogen compounds)
- rub hands dry.

Procedure No. 2

- wet hands with warm potable water
- apply soap with disinfectant properties
- vigorously rub all the surface of the hands and under fingernails for at least 10–15 s
- rinse with potable water
- dry hands preferably with hot air or paper towel.

18.9.1**Handwashing Products Structure**

Water alone is insufficient for cleaning because it is incompatible with fat and oil. Thus, a blend of surfactants is required to emulsify and solubilize fatty substances in which solids and microbes are absorbed. Skin is naturally protected with a fat/oil layer. However, detergents do not differentiate between unwanted contamination and protective substances, so that deep cleaning leaves unprotected dry skin and may cause irritation and dermatitis. A balance between sufficient cleaning and preservation of the skin is the target of a good detergent. This desirable equilibrium actually depends to some extent on the final user. Contamination received in the assembly, machine, and repair shops obviously differs from that found in food preparation, a restaurant, or a hotel. Even the skin sensitivity changes according to type of work and the number of washes performed per day. Moreover, cleaning plus sanitation is not always required. Thus, various types of hand cleaners are available:

• mild cleaner	• powerful cleaner
• barrier cleaner	• cleaner and disinfectant
• abrasive cleaner	• terminal disinfectant.

Cakes of soap are no longer used in the food industry because of their sensitivity to water hardness (deposition of calcium soap) and unsuitability for hygienic re-use even in the presence of preservatives. Current products are liquids, usually free of actual soap (neutralized fatty acids) and formulated with synthetic surfactants. However, they are still referred to as soap or liquid soap.

It is known that nonionic surfactants are particularly aggressive toward the skin because of their intense degreasing action. Therefore, mild cleaners either do not contain condensed nonionic surfactants or have an HLB adjusted with low-ethoxylated components (<4EO, e.g., alcohol C₁₃ 2EO). The basic surfactants for handwashing in the food industry belong to the anionic and amphoteric groups (e.g., C₁₂-3EO sulfate, C₁₂ sulfate, C₁₂ betaine, alkyl C₈₋₁₈ amidopropyl betaine).

Powerful cleaners are obtained by increasing the number of moles of EO in the ethoxylated compounds and by increasing the concentration (e.g., alcohol C₁₃-8EO). The abrasive cleaners are pastes in which insoluble abrasive agents mechanically aid cleaning. These can be polyurethane resins, calcium carbonate, fine sand, or sawdust.

Emollients (e.g., glycerine, propylene glycol, and sorbitol) are fundamental components of a good detergent. Their three basic functions are to soften and soothe the skin:

- Occlusion and lubrication restore the layer of oil-like substances, relieve irritation, and give a soft feel.
- humectant properties remove the sense of desiccation. Emollients are hygroscopic substances able to form hydrogen bonds with water and keep skin moist.

Fibrous proteins (e.g., collagen) are excellent emollients for handwashing technology and were widely used until the emergence of the disease bovine spongiform encephalopathy (BSE). Safety, but mainly commercial considerations, have prompted their removal from formulations.

Thickeners (e.g., C₁₂ diethanolamide, hydroxyethyl cellulose, and comb polymers) provide products with a typically viscous appearance. Sodium chloride was historically used as a thickener. However, as it is a promoter of skin irritation and desiccation, it does not form a part of advanced technology.

A buffer system (e.g., citric and lactic acids) decreases and stabilizes the eudermic pH at ca. 5. The food industry demands products free from fragrance and dye. Thus, some hand cleaners do not have the attractive properties typical of household and cosmetic products but unnecessary to the food industry.

18.9.2

Handwashing Disinfectants

A few classes of disinfectants suit handwashing because of the need for rapid action associated with skin compatibility and product stability. A disinfecting residue is often required as well, which further limits the choice of products. Moreover, the demands of health and eco-friendliness incline formulations toward increasingly safe and biodegradable components. It follows that the main disinfecting agents currently belong to the class of the nitrogen compounds.

Using these procedures, the sanitation of hands is attainable either by a one-step process (product performing cleaning and disinfection) or after washing

(terminal disinfectants usually based on alcohols). The former concludes the process with a rinse, the latter with evaporation.

Paper handkerchiefs drenched with alcoholic sanitizing solution are available. Hand washing using hand sanitizing wipes is recommended as a convenient alternative in the absence of soap and water. Their use is uncommon in the food industry.

18.9.2.1 Products Performing Cleaning and Disinfection

The structure of the cleaning agent is adapted to the type of disinfectant. Anionic charges are incompatible with cationic compounds (e.g., chlorhexidine, polybiguanide, QACs, and cetrимide). Thus, amphoteric and nonionic surfactants are selected if these are present. Several disinfectants have been exploited over the years in handwashing technology. The names and chemical structures of the most used ones are given in Figure 18.22.

Trichlosan was and still is one of the most utilized disinfecting agents. It acts on the enzymatic system and stops the bacterial growth. However, its use is currently questionable. Some investigations reveal an increase in the resistance of bacteria. Trichlosan has little or no effect on *Pseudomonas*, can give dioxin if exposed to sunlight and temperature, produces chloroform with chlorinated water, and accumulates in animal tissue and mother's milk. Hence, although the European Scientific Steering Committee states that Trichlosan is a useful and effective disinfectant, it is recommended not to overuse it either alone or in formulations.

The best current handwashing products make use of chlorhexidine and a blend of chlorhexidine, polybiguanide, and the QACs shown in Figure 18.23.

Products are poured neat on hands. Thus, the concentration of the disinfecting agent is proportional to the active ppm required for carrying out cleaning and hand 'pasteurization' roughly within one minute. The effective amount of active matter in a formulation is usually considered to be 2%.

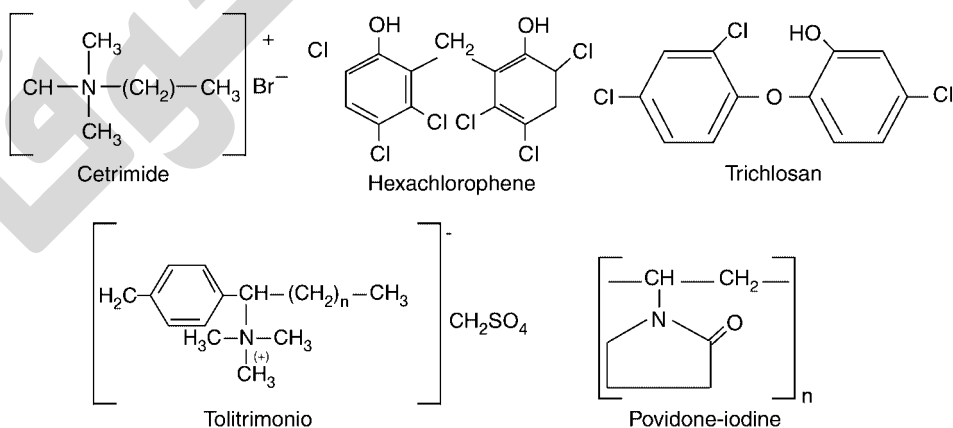


Figure 18.22 Some disinfectants formerly used in handwashing technology.

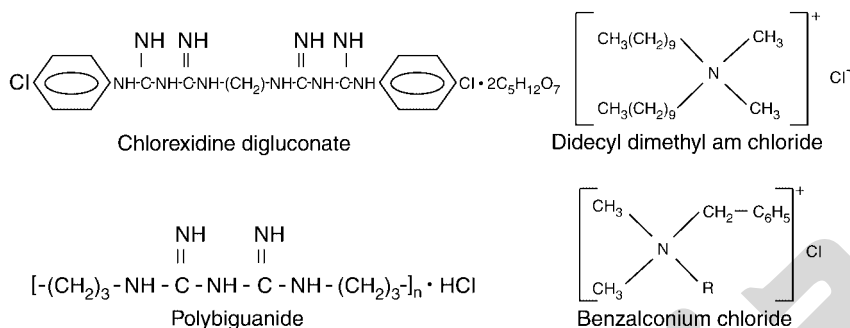


Figure 18.23 Some disinfectants currently used in handwashing technology.

18.9.2.2 Products for Terminal Disinfection after Washing

Hand sanitizers after washing belong to the so-called 'dry' technology, also known as alcoholic products. At concentrations above 65%, ethyl and isopropyl alcohols are effective germ killers. However, there is confusion about their mode of action. As concentration and contact time are basic factors to attain disinfection, alcohols have not enough time to perform disinfection by a rubbing procedure in an open space because evaporation is too rapid. Alcohol is an effective biocide in an enclosed space or by soaking. However, in open spaces alcohols perform as powerful cleaners through their solvent properties. Thus, they remove bacteria rather than killing them. Alcohol is therefore used as a carrier that leaves traces of disinfectant on hands after evaporation. The technique is therefore to use an alcohol blended with an amount of disinfectant, leaving behind a residual layer able to perform an effective disinfection. The product is ready to use and is usually based on ca. 3% of active disinfectant. The alcohol is only considered to be a carrier, its concentration in formula varying in the range 20–70% according to the desired rate of evaporation. Chlorexidine, benzalconium chloride, and iodine on polyvinylpyrrolidone (povidone-iodine) are the current active compounds performing terminal disinfection.

Proper spray equipment delivers the alcoholic solution to the hands, and the user then rubs his or her hands dry.

Frequent use of alcohol-based formulations can cause dry skin, irritation, and dermatitis. Emollients can be added to reduce or eliminate the desiccating effect (e.g., glycerin and propylene glycol).

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19

Waste Water Treatment

Water is the life blood of the environment, essential to the survival of all living things. It has been said that water promises to be to 21st century what oil was to the 20th [1]. It is even foreseen that possible future wars will not be about ownership of territory but availability of water [4].

Pure water is colorless, tasteless, and odorless, and possesses the ability to dissolve every substance. Owing to its solvent property, water carries natural impurities, the type and concentration of which are roughly taken as the reference limit for the purification process. The impurities found in raw water are broadly classified as dissolved and suspended solids and dissolved gases. All the organisms living in water are considered to be organic matter, which sometimes interferes with inorganic salts (e.g., iron, sulfate) in the water and modifies its original salinity. The amounts of organisms in water and sludge disposed of are themselves regulated.

The general rule for water management in industry is environmental protection and preservation. This means that the incoming water must be returned to the environment compatible with it or must be recycled after purification. However, the costs of 'water in' and 'water out' are constantly increasing. Thus, although water saving and preservation should be done to protect the environment, it will certainly be done to save money.

19.1

Understanding Terms

A clear understanding of sewage treatment presupposes knowledge of the operational terms. Some essential terms are defined below.

- **COD (Chemical Oxygen Demand):** the quantity of oxygen needed to chemically oxidize all oxidizable substances, organic and even inorganic such as sulfide, sulfite, nitrite, and ferrous ions.
- **BOD (Biochemical Oxygen Demand):** the quantity of oxygen needed by aerobic microorganisms to degrade the organic constituents. BOD is roughly 1/3 of COD in the food industry. Five days incubation is often the

procedure used to determine the biodegradability index of the organic material (BOD_5). BOD strictly depends on the activity of microorganisms. The life of a microorganism is affected by temperature. Thus, biological processes are slower in winter than in the hot season. The terms domestic and industrial waste are defined through the volume of water (e.g., below or above $10\text{ m}^3/\text{day}$) or through the pollution load expressed as BOD per equivalent inhabitant (e.g., below or above 100 equivalent inhabitants, where 1 equivalent is equal to $54\text{ g/m}^3/\text{day BOD}$).

- **TOC (Total Organic Carbon):** the carbon dioxide produced from the catalytic oxidation at 900°C of the total organic material. It is an assessment alternative to COD and BOD.
- **DO (Dissolved Oxygen):** determination of the aerobic condition of the treatment.
- **Biodegradability:** degradation of the organic material in a preestablished period of time by the microbial metabolism. When the degradation arrives at the simplest molecules (water and CO_2), the process is also known as mineralization. Biodegradability is expressed in percentage. Nonbiodegradable usually means slowly biodegradable.
- **Sludge:** the whole of the organic and inorganic substances, inclusive of auxiliary chemicals, removed during the treatment.
- **Activated sludge:** suspended substance inhabited by living colonies of microorganisms performing the biological step and purifying the sewage.
- **Flocculation:** chemical coagulation producing agglomerates (flocs).
- **Sedimentation:** flocs settling in the clarifying tank (sediment).
- **Flotation:** flocs rising usually because of air blowing (top skimming).
- **Retention time:** time spent by the sewage in a given phase of the process.
- **Equalization, compensation, or balancing:** tank for homogenization of sewage coming from different zones of the factory. It is also used for smoothing peaks of polluting loads.
- **Aerobic process:** digestion bio-process carried out in the presence of air (oxygen) able to degrade the organic content (COD reduction).
- **Anaerobic process:** digestion bio-process carried out in the absence of oxygen. Typically, the process produces noxious odors such as those of ammonia, methane, mercaptans, and hydrogen sulfide. This is the usual process for recovering energy from a biomass (producing fuel gas).
- **Aeration:** agitation by air blowing, usually in aerobic digestion processes. Aeration is also applied to accelerate flotation.
- **Grid and pre-filter:** physical barrier to grit, debris, and bulky solids.

- **Sand filter:** filter constituted of different sizes (graded) of quartzite generally found before the activated carbon.
- **Activated carbon:** filter consisting of carbon with a highly adsorbing surface. It removes residues of organic material still present at the end of the treatment process (e.g., nonionic surfactants).
- **Nutrients:** concentration of carbon, nitrogen, and phosphorus in the biological step to support growth and activity of microorganisms (activated sludge).

19.2

Purification Process

Purification is accomplished by different processes according to the type of sewage. Although industries are unlike, they can be put into categories. Each category has a similar process concept (e.g., bottling, slaughter, poultry, dairy ...). Furthermore, diverse opportunities for sewage disposal are available depending on how the territory is served. Bianucci gives a schematic example in the Figure 19.1 [2]:

Effluent going directly to the environment is not permitted. Either sewage is purified inside the industrial site or it is piped to an external treatment plant. The purification process proceeds through steps, and each factory utilizes those suitable to its own needs. The usual processes involved in a complete treatment are listed in Table 19.1.

Food industries mostly need equalization, neutralization, and biological steps. Each individual process can be carried out in many different ways by exploiting many different devices and layouts. The following sections endeavor to explain concisely the concepts associated with the various steps.

19.2.1

Preliminary Treatments

If sewage contains grit, debris, and coarse material that could cause severe abrasion and obstruction to pumps, valves, and raking mechanisms, such material is

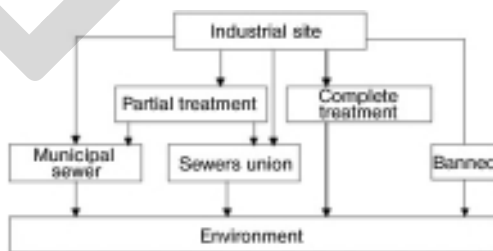


Figure 19.1 Methods of sewage disposal (adapted from Bianucci 1996 [2]).

Table 19.1 Steps of the purification process.

Section	Process
Raw sewage	• Bringing together
Preliminary treatment	• Settling/filtering of grit, debris, coarse matter • Flotation of oil, grease, coarse matter (top skimming) • Equalization (sewage compensation) • Neutralization
Chemical treatment	• Inorganics insolubilization (sludge formation) • Coagulation and thickening of flocs
Physical treatment	• Sedimentation and concentration • Sludge dewatering by filtering/centrifuging • Neutralization of liquid
Biological treatment	• Aerobic, semi-aerobic, or anaerobic digestion
Final physical treatment	• Filtration on quartzite • Adsorption on activated carbon
Purified effluent	• Recycling to the factory • Releasing to the environment

removed through preliminary settling and filtration through rough grilles. Conversely, the froth containing the floating substances (e.g., grease, fats, and oil) is skimmed from the top.

After this step, the material obtained is joined by other sewage from the factory in a large basin or tank where they undergo equalization so as to obtain a homogeneous liquid. This tank provides a flow with a consistent content (no peak of loading) which can be smoothly neutralized. Neutralization adjusts the pH to suit either the chemical treatment or the biological step if the chemical one is unnecessary.

Compensation is usually carried out daily. Thus, equalization is sized to collect the daily sewage of a factory. Buffering tanks can be added to cope with exceptional events.

19.2.2

Chemical Treatment

Chemical treatments are included as a rough purification step if the waste water holds substances that can harm the activated sludge and if the loading to be degraded is too large for the retention time of the biological step. This happens in the food industry in the case of an excess of soluble and colloidal substances from

- ionic disinfectants
- anionic surfactants

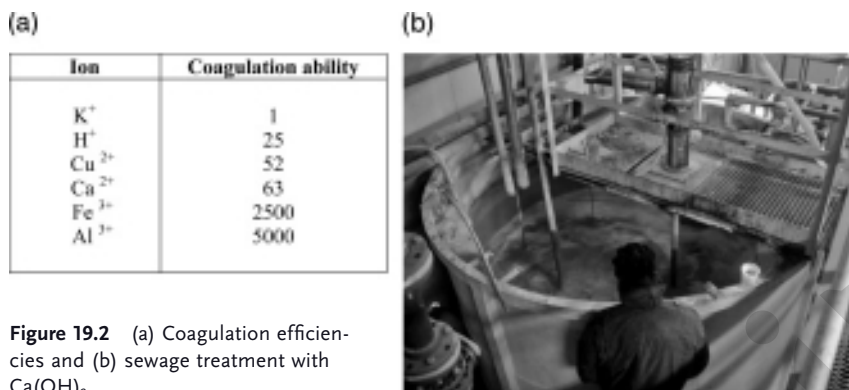


Figure 19.2 (a) Coagulation efficiencies and (b) sewage treatment with $Ca(OH)_2$.

- soaps and polyamines from lubrication
- phosphate and polyphosphate
- proteins, starches, and fats.

Water molecules and ionic barriers stabilize solute and colloid by preventing contact between ions and collapse of the system (coagulation). However, strong electrolytes destroy the electrostatic repulsion, inducing coagulation and precipitation. Miller in Masotti [3] have listed coagulating efficiencies of cations in an electronegative sewage in Figure 19.2, taking K^+ as 1.

The reason for the common use of calcium (hydroxide), iron (chloride) and aluminium (polychloride/polyoxychloride) is evident from the table. Aluminium poly(oxy)chloride is very effective, but Ca^{2+} and Fe^{3+} ions are also used because they are cheap.

After flocculation, aggregates are compacted and densified with high-molecular weight polyelectrolytes in order to obtain faster sedimentation or flotation. Polyelectrolytes are available in different strengths of cationic, nonionic, and anionic reactivity. The choice depends on the chemical behavior of the sewage. Figure 19.3 shows agglomeration and sedimentation by a medium cationic polyelectrolyte after the $Ca(OH)_2$ pre-treatment.

These are two typical chemical treatments: the primary chemical step (addition of inorganic precipitants) and the secondary chemical treatment (addition of a polyelectrolyte coagulant). The rapid sedimentation obtained (heavy flocs) is extremely beneficial to the process of clarification by gravity.

19.2.3

Settling, Concentration, and Dewatering

All treatments so far discussed involve dynamic steps where sewage is kept moved by stirring. Settlers and thickeners (by gravity) need static conditions and time to achieve a satisfactory separation of liquid from sludge (Figure 19.4). This is the bottleneck (rate-determining step) of the plant. The scaling of the plant is

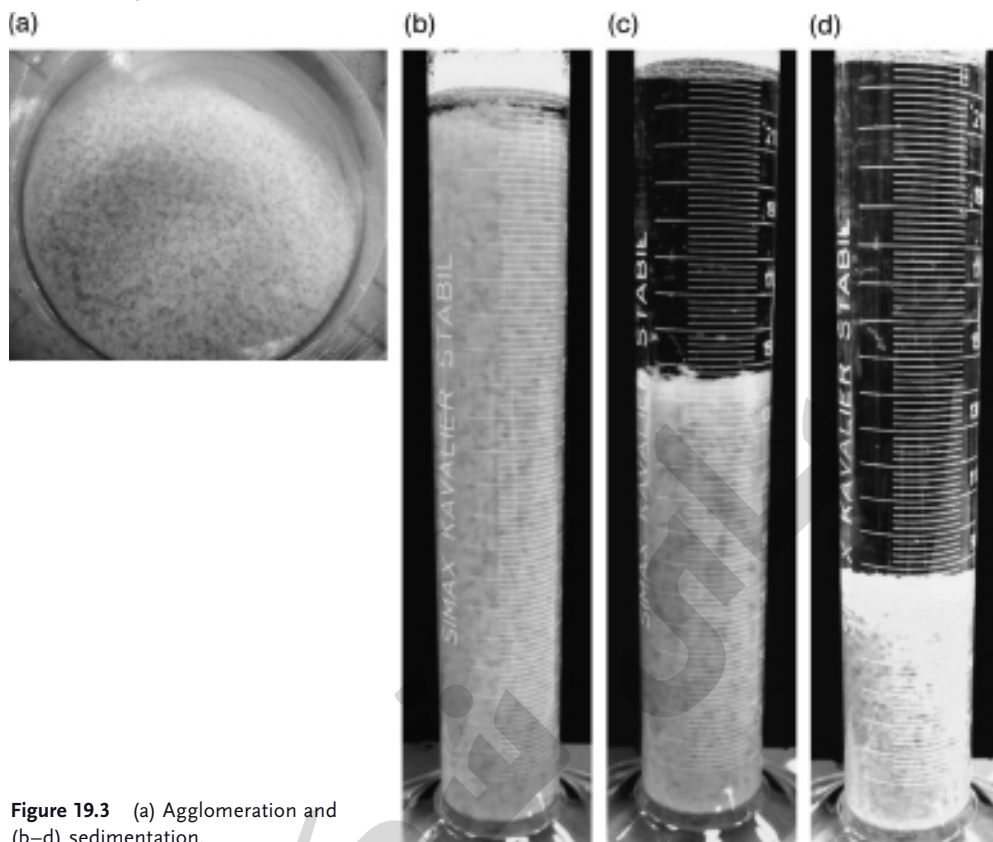


Figure 19.3 (a) Agglomeration and (b–d) sedimentation.



Figure 19.4 Settler and concentrator by gravity.

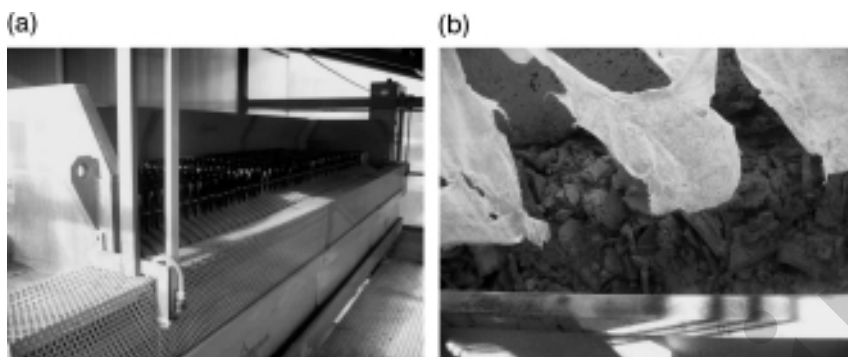


Figure 19.5 (a) Pressure filter and (b) sludge cake removed from the filter.

dependent on the settling and clarifying steps. Sewage treatment plants frequently have problems when a proportionate adjustment of the settling section is not carried out at the same time as an expansion of the rest of the factory (e.g., increase in premises, machinery, or productivity).

Sludge from settler and concentrator still include an excess of water, which is removed by dedicated devices such as a pressure filter (Figure 19.5).

Liquid from the concentrator is rejoined to the main flow. The cakes of sludge are delivered to a special treatment process for disposal (in-house or third party process).

After flocculation and separation, the main flow is neutralized to comply with the (biological) pH requirements. Neutralization is carried out with the cheapest acids (hydrochloric and sulfuric). The use of carbon dioxide instead of mineral acids avoids the reduction of sulfuric acid to hydrogen sulfide.

19.2.4

Biological Treatment

Sewage, both coming from the chemical treatment processes and directly channelled to the biological treatment, is essentially a diluted neutralized aqueous system containing a very complex assortment of organic and, to a smaller extent, inorganic materials in many physical forms. The bio-section in food industries mostly uses aerobic treatment (Figure 19.6). This degrades (removes) the dissolved and suspended organic material in an aerated basin (bubbling air into the aqueous suspension) by the action of bacteria and other microorganisms in the form of microbially active sludge. The COD and the surfactant content are reduced to the permitted limits.

The neutralized liquid is stored in buffer tanks in order to reach the biological section in an established, homogeneous, steady and continuous flow. In simple plants, the buffer tank can be the same one as that used for equalization. The biological basin must provide optimal conditions for degradation by the microbial

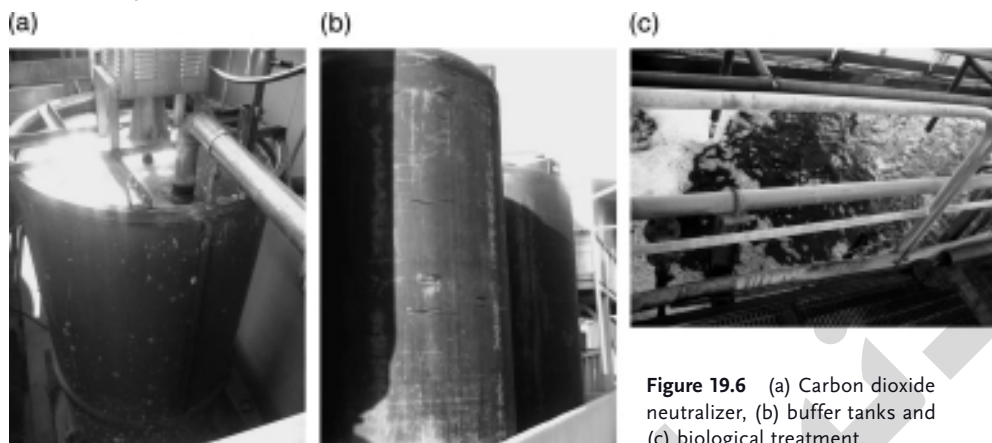


Figure 19.6 (a) Carbon dioxide neutralizer, (b) buffer tanks and (c) biological treatment.

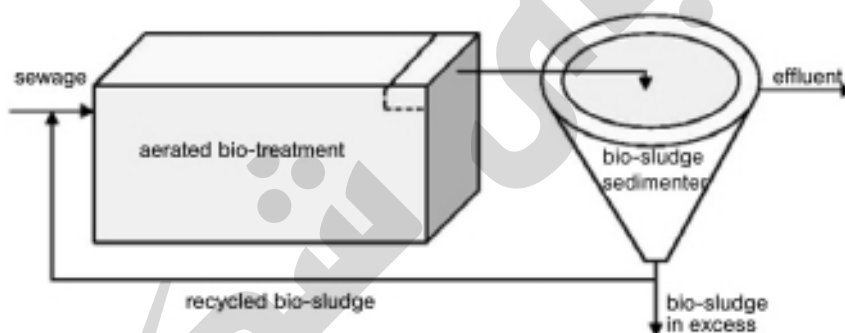


Figure 19.7 Bio-sludge removal and recycling (schematic diagram).

life. Thus, both shortage of carbon, nitrogen, and phosphorus and excess of loading can decrease the activity of the activated sludge. Microorganisms utilize the organic material as food and convert it into simpler compounds, which are metabolized by other organisms to produce still simpler ones. The process continues until the degradation is complete, that is, when the material cannot be any longer used as food. In normal conditions of feeding (sewage with a suitable balance of carbon-phosphorus-nitrogen), bio-sludge grows. Some of the activated sludge is removed and some is recycled as shown schematically in Figure 19.7.

The efficiency of the biological section is directly proportional to the retention time. With a constant effluent feed rate, the retention time depends on the volume of the basin. Therefore, the ratio between feed rate and basin size is crucial to obtaining a good degradation result. Winter and summer conditions affect the bio-activity rate. In winter, more care must be taken to keep the process efficient (slow bio-activity).

19.2.5

Final Treatments

The effluent from the biological section could need a final adjustment such as

- further decrease in COD
- further decrease in nonionic surfactants
- disinfection.

Then, the effluent can be filtered on quartzite and the soluble organic residue removed on activated carbon. Figure 19.8 show examples of quartzite and activated carbon columns.

Three different sizes of quartz form the structure of the filter which aims at separating mechanically the remaining suspended solid from the effluent before passing through the activated carbon.

The adsorption on activated carbon is necessary, for instance, if the biological section is insufficient to degrade the nonionic surfactants below the specified limit. Dilution is not permitted. As the cost of the management of activated carbon is considerable, it is recommended that the choice and use of detergents should be optimized before deciding to implement or modify this section.

If pathogenic organisms are present in the effluent, disinfection of the liquid (before the activated carbon) and sludge (before the filter) is mandatory. Chlorine is usually rejected because of its negative environmental impact. Chlorine dioxide, peracetic acid, and crossflow filtration are available alternatives.

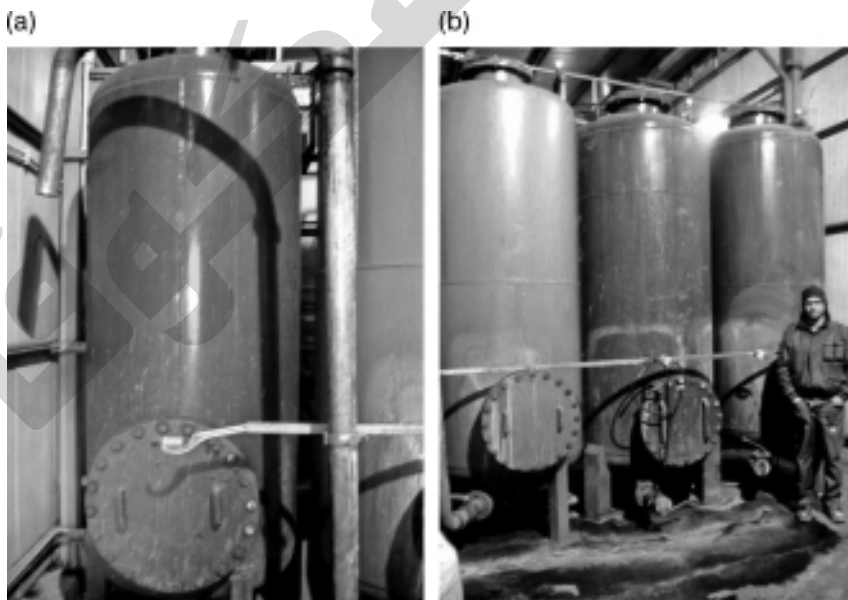


Figure 19.8 (a) Quartzite filter and (b) activated carbon columns.

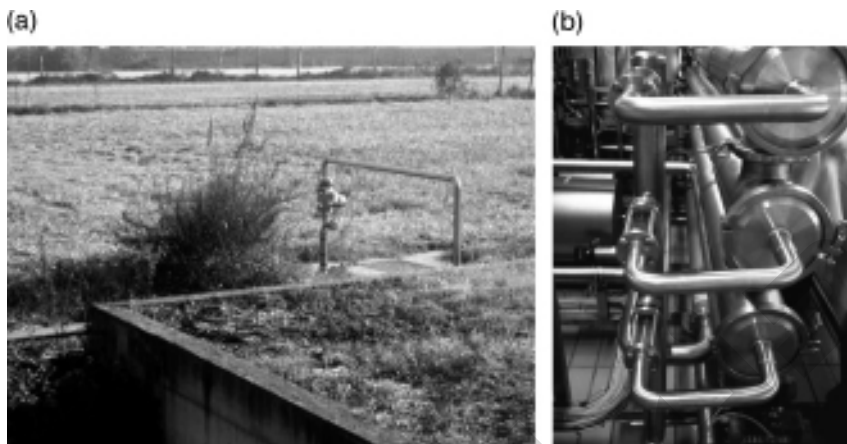


Figure 19.9 (a) Point where the effluent enters the environment and (b) example of RO plant which recycles the effluent to the factory.

The sewage is now purified and can be disposed of or recycled (Figure 19.9).

Reverse osmosis can replace the bio-section and disinfection (Figure 19.9). The permeate is recycled as process water. According to the need, the less demanding NF process could replace RO.

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20

Boiler Treatment

The food industry (i.e. the manufacture, preservation, packaging, and storage of food) is one of the largest users of thermal energy, and most of this thermal energy is derived from steam. Yet the production of steam for direct or indirect application in the food industry is a process often managed by or delegated to third parties or relatively untrained members of staff, depending on circumstances.

Changes made to improve and maintain quality and safety often result in savings in the cost of energy and treatment processes that enable companies to be more competitive. Energy efficiency can be achieved by developing energy-efficient process technologies to improve the efficiency of existing plants and preserve their productivity as long as possible.

Control of the formation of deposits, prevention of corrosion, and maintenance of steam quality are the guiding principles of boiler treatment. A decrease in the ratio of heating surface to evaporation rate is a valuable benefit which can be obtained by removing deposits and corrosion. Although boilers used in the food industry are not as sophisticated and their efficiency is not as important compared with boilers used in other industries (e.g., where they are used in the production of mechanical and electrical energy), reliable continuous operation requires considerable care. The quality of the feedwater turns out to be the key to protecting the boiler from deposition and corrosion. Pre-treatment systems (softening at least) and chemical treatments should ensure a degree of purification able to prevent

- **corrosion** (by deaerated medium)
- **scale** (transformed into sludge)
- **salts decomposition to OH^- and CO_2** (prevented by buffered pH and sludge blowdown)

20.1

Deaeration and the Generation of Noncorrosive Steam

Protecting the boiler from corrosion is one of the main concerns. Oxygen is a highly corrosive gas and can enter the boiler via feedwater and air leakage



Figure 20.1 An example of a boiler used in the food industry.

Table 20.1 Solubility of oxygen in water at various temperatures.

Temperature (°C)	O ₂ solubility in water (ppm)
4	13
16	10
25	8

(pumps). Amounts of dissolved carbon dioxide and oxygen vary as a function of the source and temperature of the feedwater.

The partial pressure of oxygen in air being 0.2 bar, Table 20.1 shows the solubility of oxygen in water at three temperatures, and Figure 20.1 shows a typical boiler used in the food industry.

Pitting is the result of corrosion of the boiler by oxygen, and is a highly dangerous form of corrosion because it concentrates in small areas and causes localized damage without any obvious general corrosion. Mechanical deaeration (either vacuum or thermal deaeration) decreases the oxygen content of the water to a certain extent, but complete removal of oxygen is accomplished either by combining mechanical and chemical treatments or by the use of chemicals alone (medium-to-small boilers).

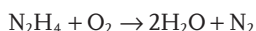
The most common chemical used for this purpose in boilers operating below 70 bar pressure is sodium sulfite (Na_2SO_3). This chemical is rapidly effective, nonscaling, fairly stable, and cheap. The reaction is



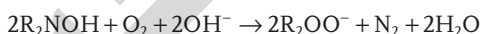
This means that 7 ppm of sulfite will remove 1.0 ppm of dissolved oxygen. Temperature and pH accelerate the reaction. The reaction occurs within a few minutes under the conditions existing in a boiler ($>100^\circ\text{C}$ and 9–10 pH). It is even more rapid in the presence of catalysts such as heavy metal oxides (e.g., copper, iron,

nickel) and organics such as hydroquinones, lignin sulfonates, catechol, and pyrogallol. The concentration should be such as to leave some ppm of residual sulfite, at least, detectable in the boiler by a daily check. The addition to the feedwater must be continuous. As sodium sulfite is usually co-formulated together with other chemicals (sequestrants, dispersants, and pH buffer), the choice of the additive depends on the characteristics of the boiler and feedwater.

Boilers operating above 70 bar need a different oxygen scavenger. Sulfate, the final substance produced from the reaction of sulfite with oxygen, contributes to a dangerous level of dissolved salinity. Also, pressure and temperature cause sulfite to decompose forming sulfur dioxide and hydrogen sulfide which, passing through the system with the steam, corrodes the condensate lines. Hydrazine (N_2H_4) was one of the chemicals preferred in the past as a chemical replacing sulfite, reacting with oxygen to form water and nitrogen:



The removal of 1 ppm of oxygen requires 1 ppm of hydrazine, but in practice it is better to have 2 ppm hydrazine per ppm oxygen to be sure of achieving complete removal. Hydrazine, too, can be catalyzed with hydroquinone, benzoquinone, and metal oxides in order to accelerate the reaction. Although no solid is formed and hydrazine affords enhanced protection of the steel from corrosion (aid to magnetite formation), its use has declined for toxicity reasons (suspected carcinogen) in favor of other less harmful amines. Hydroxylamine (NH_2OH) and its derivatives, such as diethylhydroxylamine, hydroxyethylhydroxylamine, and diethylethanolamine, are now used as corrosion inhibitors in boilers. These compounds (including azo and cyclic compounds) are effective oxygen scavengers. Depending on whether or not it is in excess, hydroxylamine and its R' , R'' derivatives give different by-products:



Excess of hydroxylamine and alkaline buffered pH prevent (or reduce) the formation of nitric and organic acids.

References to conventional boiler corrosion inhibitors are quoted in several patents, for example, Refs[1–4].

20.1.1

Generation of Noncorrosive Steam

A good quality of steam (noncorrosive and free from deposits) derives not only from a satisfactory removal of oxygen but also from preventing carryover of carbon dioxide (CO_2) and silica (SiO_2). Carbon dioxide reaches the boiler either as dissolved gas in feedwater or derived from the bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). When these chemicals are exposed to boiler temperatures, they break down and release carbon dioxide (Figure 20.2).

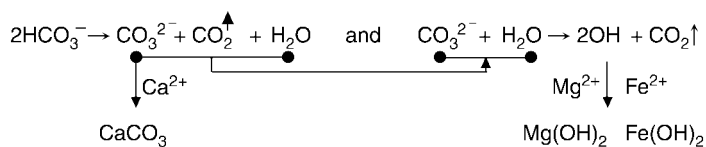


Figure 20.2 Sequence of reactions leading to scale and corrosion.

While calcium precipitates as the relatively stable carbonate, magnesium and iron precipitate as a hydroxy salt sludge. Carbon dioxide, on the other hand, is carried over with steam in which it condenses and yields carbonic acid:



The corrosive carbonic acid can be directly controlled (neutralized) in steam by a chemical treatment of the boiler by amines having a specific vapor pressure. These produces a condensate having a pH in the range 8–9 (e.g., morpholine, cyclohexylamine, and diethylethanolamine).



Steam that is to come into contact with food cannot be chemically treated. In this case, the carbon dioxide is controlled by reducing the salinity of the feedwater (complete or partial demineralization) and by an alkaline buffer continuously present in the boiler, maintaining a pH of 9–10 in low-pressure boilers and 9.0–9.5 in high-pressure boilers.

Silica deposits in steam must be rigorously prevented if the system includes condensing turbines. Silica can vaporize into the steam when the temperature increases. As steam is cooled by expansion, the solubility of the silica decreases and a deposit is formed. Moreover, steam and temperature convert silica to gaseous silicic acid which adds corrosion to deposition. To minimize these problems, the amount of silica in the steam must be controlled. As deposition is not a problem when the silica content in steam is below 0.02 ppm, it is customary to take this value as the ultimate limit. Absence or limited concentration of silica in feedwater is essential to prevent vaporization. Careful demineralization and, secondly, wise management of alkalinity, magnesium precipitation, blowdown, and treatment with dispersants provide sludge conditioning, so as to minimize SiO_2 carryover.

20.2

Scale Prevention

Every substance has a definite solubility in water. When water in the boiler is removed in the form of steam, dissolved salts left behind in the boiler can precipitate out as their concentration exceeds their solubility. This can form either hard scale or dispersed sludge. Sequestrants are used to prevent scale and convert the salinity into a dispersed sludge. The hard deposition reduces the heat transfer

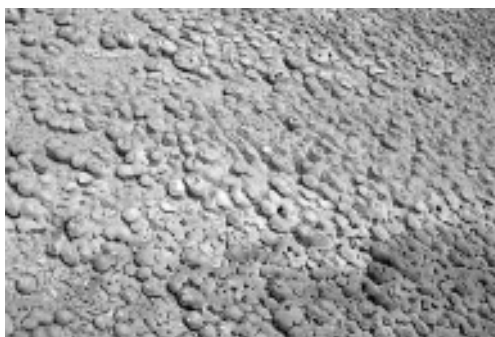


Figure 20.3 Scale in a boiler.

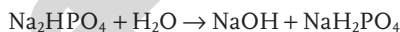
and causes overheating of the metal and tube failure. Figure 20.3 shows an example of a hard deposit.

Explosive bursting of tubes because of overheating associated with accumulation of deposits was frequent in the past. When the technology moved from stoichiometric chelants (EDTA and NTA) and trisodium phosphate (TSP) to threshold conditioners (e.g., ATMP, HEDP, PBTC, and homo- and co-polymers of acrylic and maleic acids), sludge was formed rather than adherent deposits. This also led to exposure of the metal to the water. Thus, the enhanced antiscaling technology prevents overheating but, at the same time, removes the cathodic protection by the deposit. It follows that the antiscaling technology has led to a more pressing need to control corrosion.

Trisodium phosphate (TSP) was the main compound used in boiler treatment for very many years. Its hydrolysis buffers water to an alkaline pH and its complexation of multivalent metals at first leads to sludge.



Disodium phosphate provides the system with a reserve of alkalinity due to a second dissociation:



Thus, TSP was, and sometime still is, regarded as the most suitable chemical to treat boiler water alone. However, too much sludge formation and the reliability and versatility of threshold technology have persuaded users to replace it.

Particular types of deposit can start caustic or acidic attack and embrittlement. Attack and embrittlement are different phenomena. In short, attack dissolves metal whereas embrittlement penetrates metal and breaks it up.

- **Caustic attack:** hard, sticky and nonporous scale may trap and concentrate sodium hydroxide on metal forming iron oxides. Magnetite (Fe_3O_4) is an incoherent oxide which forms continuously, causing a constant loss of metal [5].

- **Acidic attack** occurs if either the pH is kept too low or accidental leakage occurs or unsuitable acidic cleaning is carried out. It is a general attack which causes the metal to dissolve rapidly.
- **Embrittlement** is less evident but is a more dangerous event. It originates from an excess of hydroxyl (OH^-) or from the formation of atomic hydrogen which is trapped on the metal. These chemicals can penetrate the metal structure. Atomic hydrogen reacts with the alloy carbon to form methane. The excessive pressure inside the metal causes the metal to be ruptured along the crystalline boundaries, i.e. the metal cracks [5]. The excess of hydroxyl (OH^-) in zones of high metal stress (e.g., expansion and contraction) and leakage generates intercrystalline cracking. This event is not frequent because all the three factors are required (excess, stress and leakage) [5]. Deposit prevention and pH control together with efficient and careful cleaning are mandatory to prevent attack and embrittlement.

Sludge is preferred to scale. Accumulation of feedwater impurities, salinity, and additives increases conductivity and risk of deposit formation. Conductivity depends on the dissolved solids while deposit formation relates to the undissolved ones. Thus, while the control of oxygen, carbon dioxide, and pH is necessary to prevent harm to the boiler structure, the control of conductivity and total solids is necessary to have surfaces free of scale as well as to minimize corrosion and carryover. This is achieved by regularly discharging some of the boiler water (blowdown) and replacing it with fresh water (makeup). The planned removal of a quantity of boiler water keeps the condition of the interior of the boiler within the prescribed limits. How to plan blowdown? A simple method is to determine the soluble salt present in the feedwater. This concentrates in the boiler without precipitating. The ratio between its concentration in the feedwater and that in the boiler water indicates the percentage of blowdown. If chloride is the ion of reference, the percentage of blowdown is found from the following equation:

$$\% \text{ blowdown} = \frac{[\text{Cl}^-] \text{ in feedwater}}{[\text{Cl}^-] \text{ in boiler water}} \times 100$$

Conductivity determination is the alternative to chemical analysis. Conductivity measures the dissolved solids. Its determination is more rapid and can be automated. The conductivity of the boiler water is set to activate the blowdown if its value exceeds the fixed limit. The limit varies according to the pressure of boilers. Generally, conductivity should not exceed $7000 \mu\text{S}$ for low-pressure boilers (<30 bar). It must be kept below $1000 \mu\text{S}$ for medium pressure (<70 bar) and below $200 \mu\text{S}$ for high pressure (>70 bar).

The decision to use manual, automatic, or continuous blowdown depends on the type of boiler and the purity of the feedwater. The feedwater purity is the key to good operation of the boiler. A softener, at least, must be included in the system. Water of a purity close to that produced by demineralization is required to achieve satisfactory operating reliability of a high-pressure boiler.

20.3

Chemical Treatments

The objects of the chemical treatment include

- **Removal of oxygen:** by sulfite, hydroxylamine and its derivatives
- **Dispersion of impurities:** by phosphonates and polymers, for example, blend of ATMP, 4000 and 80 000 MW acrylic homopolymers
- **Buffered pH:** by amines and/or caustics
- **Neutralization of steam (when permitted):** by a partial vapor pressure of amines, for example, a blend of morpholine, cyclohexylamine, and *N,N*-diethyl ethanolamine.

All of this can be formulated together in a single additive. This approach is usually used for noncritical low-pressure boilers. The disadvantage is its unspecificity. If a higher concentration of one of the components is required, all the others have to increase as well, even if this is not strictly necessary. However, the four treatments can be grouped together in different ways to solve specific boiler problems, as detailed below:

- a) Oxygen scavengers, dispersants, and pH buffers together form the first group of additives. As steam conditioners are not permitted in the food industry, where steam meets food, this group comprises additives for treating boilers that produce steam which does come into contact with food.
- b) Amines at partial pressure form the second group of additives to be used when steam does not come into contact with food.
- c) All these can be blended together for the treatment of small boilers the steam of which does not come into contact with food.

The additives are formulated to be added to the boiler at a concentration of a few hundred ppm in the makeup water.

20.4

Chemical Cleaning

In spite of physical and chemical treatments, corrosion and deposition cannot be completely prevented but only minimized. Boilers accumulate scale and sludge due to hardness, oxides due to corrosion, and contamination. This can lead to significant localized increases in temperature, energy, cost, and risk of harming the boiler where the deposit forms. Figure 20.4 shows the average increase in energy required to give the same heat transfer as a function of the thickness of scale.

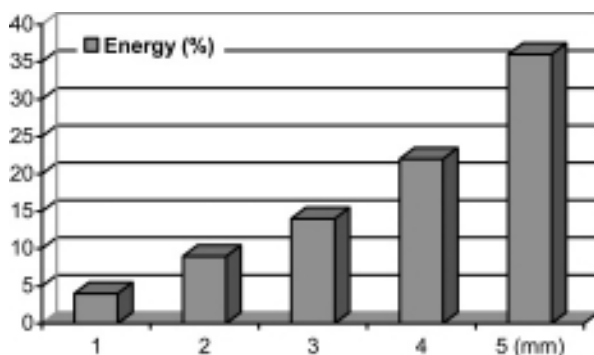


Figure 20.4 Increase in energy as a function of the scale thickness.

Descalers (acidic treatment) are the standard cleaning agents. Of these, inhibited hydrochloric acid is the one most used for the periodic treatment of boilers. The aggressiveness of hydrochloric acid is reduced with the aid of suitable corrosion inhibitors (e.g., branched fatty polyamines) that enable the deposit to be attacked while protecting the metal.

The amount of acid required to dissolve the scale should first be calculated, knowing that 2.5 kg of hydrochloric acid (33% HCl) will dissolve 1 kg of an average scale, which is assumed to be calcium carbonate (silicate, sulfate, phosphate, and metal oxides being minor components). The total amount of scale to be removed is calculated based on estimates of the heating surface area and the thickness of the scale, and assuming the specific gravity of the scale is 2.

The weight of hydrochloric acid needed to remove the scale will thus be

$$\text{Area of scale} \times \text{thickness of scale} \times 2.5 \times 2$$

A recommended procedure to descale is given below.

- clean the boiler with water in order to remove loose scale and save acid
- add water to the boiler until it is ca. 25% full
- add descaler until its concentration is 10%
- allow the descaler to react for 1–2 h, checking the acid concentration
- fill the boiler completely with water and further descaler
- light the burners and heat the acidic solution
- allow the descaler to react for 2–3 h, checking the activity of the solution
- when the reaction stops, discharge the solution
- immediately refill the boiler with water plus a small amount of neutralizer (caustic soda)
- discharge this solution
- fill the boiler with process water

During the descaling process, leave the boiler open (CO₂ gas release) and add a little silicone defoamer in case the evolution of carbon dioxide generates foam.

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دینی جای
مکتبہ

21

Due Diligence (HACCP)

This chapter is intended as a summary of the philosophy of this book, although it might well have formed the introduction, describing the attitude of mind informing the operating practices on which food safety is based independently of the detergency and disinfection plan.

Safe food inspires trust in consumers. Safety requires the application of a rational approach to the process, evolving from terminal analysis (not related to control) to pro-active interventions before and during the process (safety just in time). HACCP (hazard analysis and critical control points) is a philosophy and methodology of work where the analysis is an ancillary tool rather than being merely the assessment of quality. HACCP is the most logical approach to mastering specific risks in a specific process. In this sense, controlling a risk does not mean going and seeing something (analysis) but rather mastering something (control of critical points). Hence, HACCP cannot be achieved through a single action (laboratory control) but derives from a pragmatic approach to the whole process in which reasonable certainties must be formed at those points where we need them.

The basic question is: how dangerous is the microbial, hygienic, and epidemiological risk in my process? There are, in fact, processing steps that cancel every risk (e.g., cooking either during manufacture or just before consumption). Then, if there is a point at which the recognized risks to the food are blocked, the supposed critical points in manufacturing turn out to be much less critical. Actions leading to the stabilization of food are well known:

- **heating:** (e.g., cooking, pasteurization, sterilization)
- **freezing:** (e.g., food preservation by freezing)
- **salting:** (e.g., food preservation by sodium chloride)
- **pH lowering:** (e.g., acetic acid preserves)
- **bacteria:** (e.g., competition from lactic bacteria)
- **controlled acidification:** (e.g., citric acid addition)
- **chemical preservation:** (e.g., smoking process, preservatives)

Mastering a process means accepting only zero tolerance toward the actual risks. Actual risks are normally located in ready-to-eat and fresh foods and in all the operations that follow the point at which the primary risks are arrested. Only

when the risk is identified and the limits of safety are established can the process be measured just to keep the parameters inside those limits of safety (analytical data). Assigning the safety control to a sanitation plan without mastering the overall flow of the process does not answer a simple question coming from auditors: explain to me why I should trust that you are selling safe products?

There cannot be many critical points. If there are, either the manufacturing process is inappropriate or the approach to HACCP has been misunderstood. The critical points have not to be confused with negligence, stupidity, and filthy work. The cleanliness and general attitude of a worker (common sense of working) is part of normal decent behavior, just like the general state of the manufacturing site (closed doors and windows, control of insects, clean walls and floors, decent toilets ...). All of this comes first and is mandatory (prerequisites of the law). The care of personal hygiene should just be regarded as common sense in a food industry. However, common sense depends on the culture of the country of origin, and this can vary from one country to another. Therefore, all industries should ensure that individuals have received adequate and appropriate training concerning the basic rules of decency.

Cleaning and disinfection are themselves pre-qualifications. Hence, they do not represent or characterize the HACCP process. Cleaning and disinfection provide the means to maintain efficiency in manufacturing. They control its critical points but are independent of them. They can be described as auxiliary tools like equipment, physical parameters, manpower, and chemical and microbiological analysis.

Demonstration of the critical points and control of the operation of the manufacturing technology (checking, reactive and corrective actions) do not aim at producing paper and impressing the auditors. They are the passport to successfully keeping one's own industry at the forefront of the market for a long time.

It is also evident that the approach to a safe and efficient manufacturing operation implies knowledge of the reason for each single action. General training is no use. Each worker must take responsibility for his or her specific job. Only targeted training can make workers acquainted with the consequences of their own actions in their specific jobs.

Resources devoted to improving knowledge and responsibility are repaid many times over in safety, efficiency, productivity, and reputation.

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