Part One
Chemistry and Problems of Industrial Water

Sanitation: Cleaning and Disinfection in the Food Industry. Mario Stanga

ISBN: 978-3-527-32685-3

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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 desalinization 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,

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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°C (32°F), boiling point 100°C (212°F), specific gravity (4°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 °C) or solid (below 0 °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

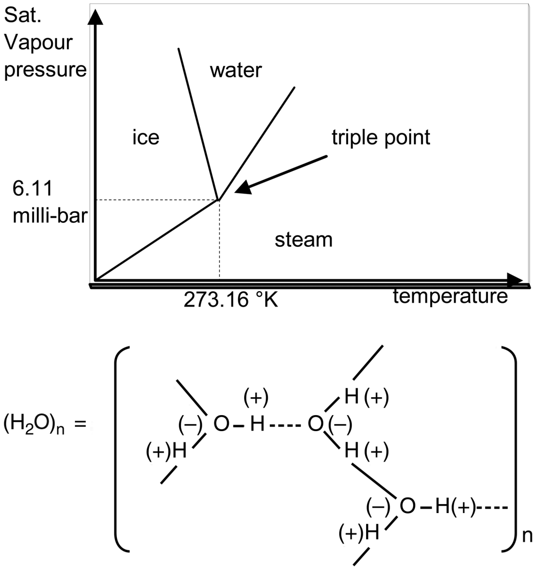


Figure 1.1 Triple point and planar structure of water.

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]:

$$\underset{\textit{K feldspar}}{3\mathrm{KAlSi_3O_8}} + 2\mathrm{H^+} + 12\mathrm{H_2O} \rightarrow \underset{\textit{K mica}}{\mathrm{KAl_3Si_3O_{10}(OH)_2}} + \underset{\textit{dissolved silicate}}{6\mathrm{H_4SiO_4}} + 2\mathrm{K^+}$$

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):

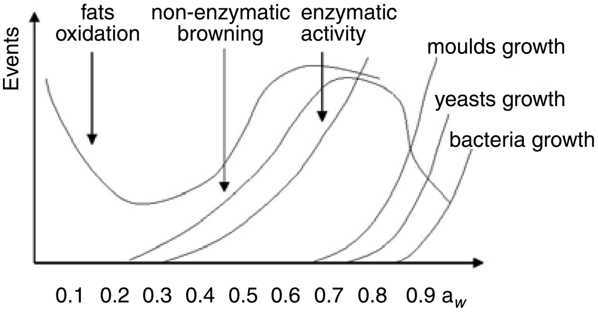


Figure 1.2 Main events in a food as a function of the water activity.

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 multivalent 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/100 g)
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 or 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.

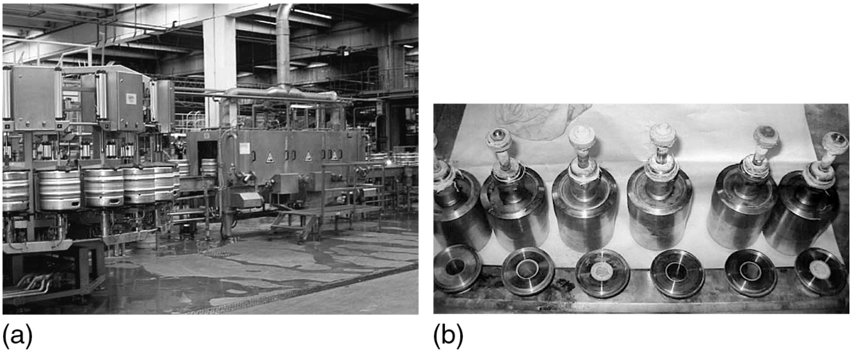
Bicarbonate-carbonate-carbonic acid form a buffer which, acting both as acid and base, may strongly affect categories of products such as lubricants and disinfectants. Generally speaking, the reversible reaction between carbonic acid and carbon dioxide, and the influence of temperature, pressure, and 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



(a) (b)

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

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \rightarrow 18\text{ g} + 44\text{ g} \leftrightarrow 62\text{ g}$$

$$2NaOH + H_2CO_3 \leftrightarrow Na_2CO_3 + 2H_2O \rightarrow 2(40)\text{ g} + 62\text{ g} \leftrightarrow 106\text{ g} + 2(18)\text{ g},$$

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 ($-\log[H^+]$). It depends on the type of dissolved salts. Bicarbonates buffer raw

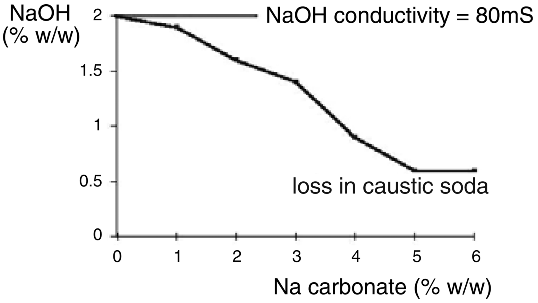


Figure 1.4 Conductivity remains constant even if the caustic soda decrease is replaced by carbonate.

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.

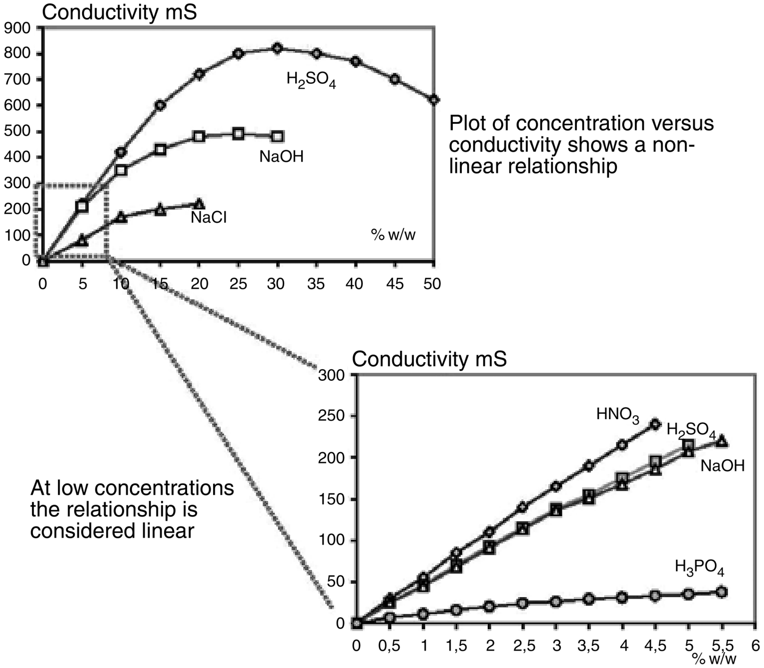


Figure 1.5 Linearity of conductivity at low concentration.

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):

$$\mathrm{LSI} = 2\mathrm{pH}_a - \mathrm{pH}_s$$

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

$$\mathrm{RSI} = 2\mathrm{pH}_s - \mathrm{pH}_a$$

where:

pH_a = pH of water under operating conditions
pH_s = pH of saturated solution derived from the following equation:
$\mathrm{pH}_s = (9.3 + \mathrm{A} + \mathrm{B}) - (\mathrm{C} + \mathrm{D})$

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:

$$\mathrm{ppm} = \mu\mathrm{S} \times 0.55.$$

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
$[Cu^{2+}]$	$[2H_3N^+CH_2COO^-]$	7.9×10^{-16} [12] copper aminoacetate
$[Ca^{2+}]$	$[C_2O_4^{2-}]$	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:

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

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:

$$a = \frac{2[Ca^{2+}] + [Mg^{2+}] + [Na^{+}] + [K^{+}] + \ldots + [SO_4^{-}] + [Cl^{-}] + [SiO_3^{-}] + \ldots}{[HCO_3^{-}]}$$

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.

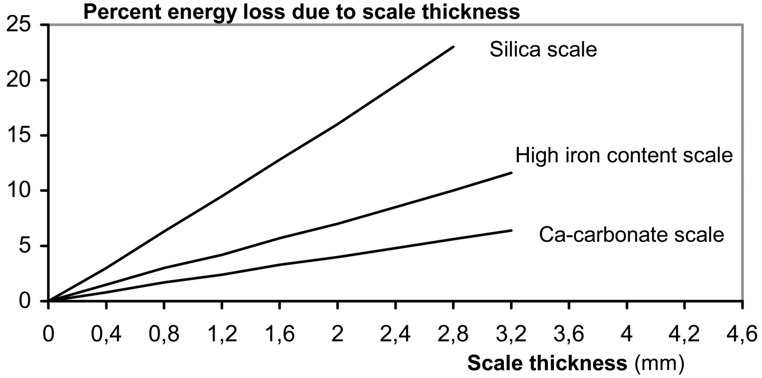


Figure 1.6 Increase in energy as a function of the type of scale.

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.

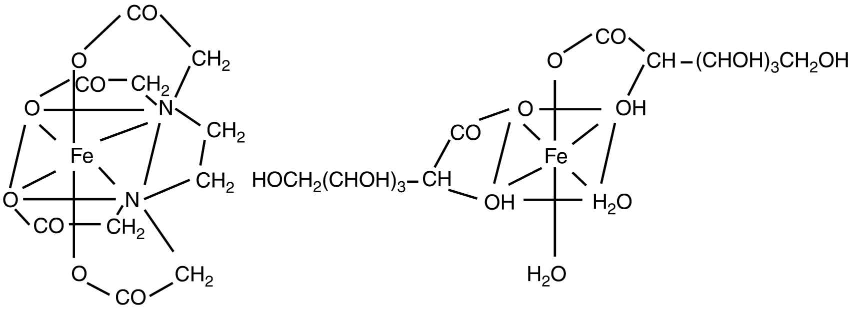
A coordination reaction is likewise described as shown in Figure 1.9 [24].

The reaction is based on the following general reaction:

$$[Me^{2+}]\cdot 6H_2O + 2H_2A \rightarrow MeA_2^{2-} + 4H^+ + 6H_2O$$

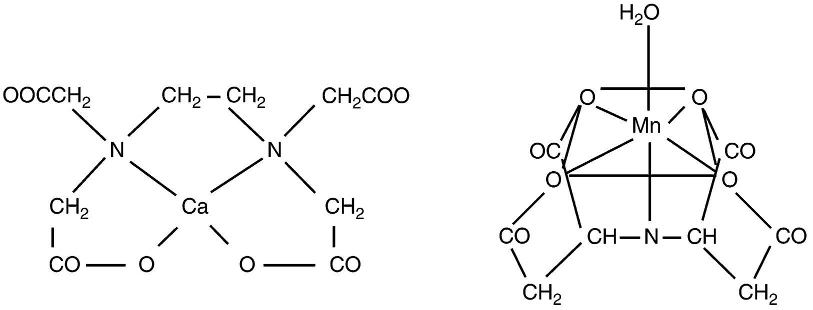
Octahedral, tetrahedral, trigonal and the other spatial structures as well as the theory and principles of coordination bonding are comprehensively reviewed by Cartmell and Fowles [22] and Schläfer and Gliemann [27].

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



Fe(III)EDTA [24] *Fe(III)Gluconate* [24]

Figure 1.7 Iron complexes with EDTA and gluconate.



Ca(II)-EDTA planar representation [25] *Mn(II)-IDS distorted octahedral geometry* [26]

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

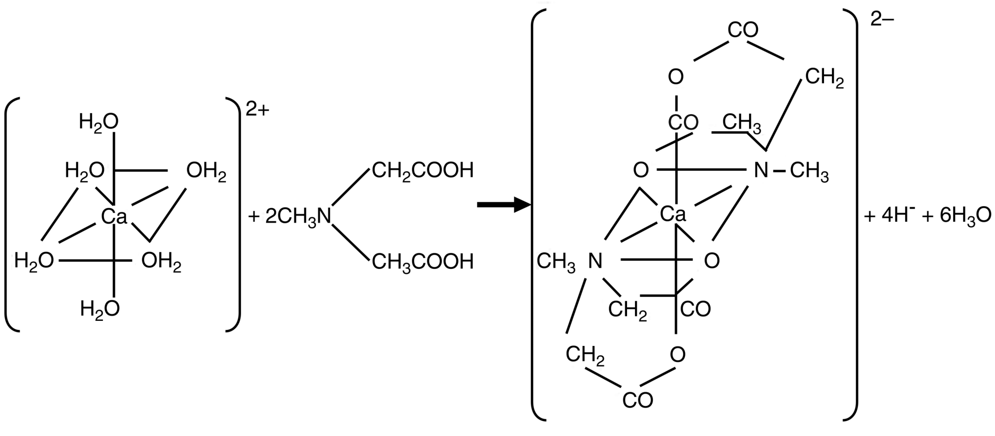


Figure 1.9 Coordination reaction.

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

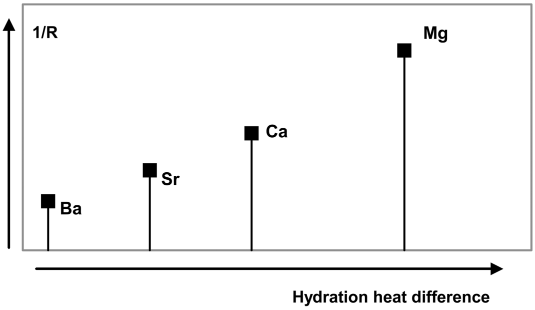


Figure 1.10 Heat of hydration as a function of the reciprocal of the atomic radius.

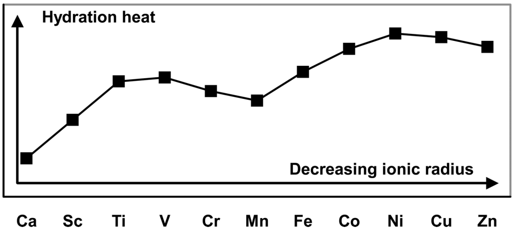


Figure 1.11 Heats of hydration of the transition elements.

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].

$$CN^- > NO_2^- > NH_3 > H_2O > C_2O_4^- > OH^-$$

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

$$-O^- > -NH_2 > -N{=}N- > {=}N- > -COO- > -O- > {=}C{=}O$$

Besides this series, sulfonic ($-SO_2OH$) and phosphonic [$-PO(OH)_2$] together with hydroxyl ($-OH$) and sulfhydryl ($-SH$) 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, Ethylenediaminotetracetic acid; EDTMP, Ethylenediaminotetramethylenephosphonic 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]:

$$\mathrm{Y} + \mathrm{MX_6} \rightarrow [\mathrm{YMX_6}] \rightarrow \mathrm{YMX_5} + \mathrm{X} \quad (\mathrm{S_N2}\ \text{under strong nucleophilic agent})$$

$$\left.\begin{array}{l} \mathrm{MX_6} \rightarrow [\mathrm{MX_5}] + \mathrm{X} \\ [\mathrm{MX_5}] + \mathrm{Y} \rightarrow \mathrm{YMX_5} \end{array}\right\} \quad (\mathrm{S_N1}\ \text{under weak nucleophilic agent})$$

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 stoichiometric[1] 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].

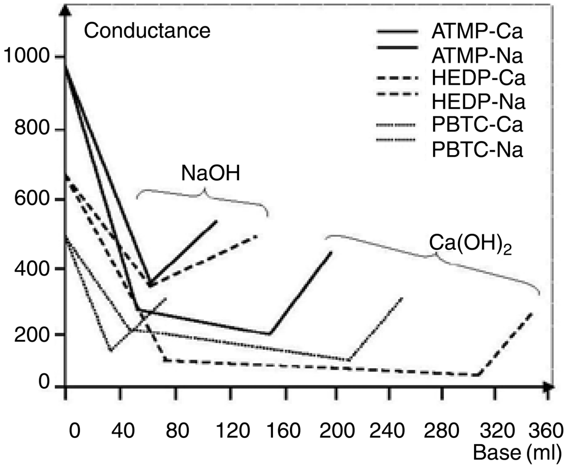


Figure 1.12 Addition of bases (1 M) to sequestrant (5 g L^{-1}); conductance in μS.

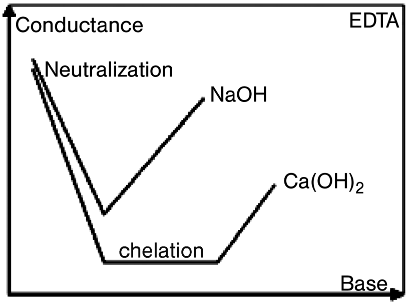


Figure 1.13 Conductance of EDTA.

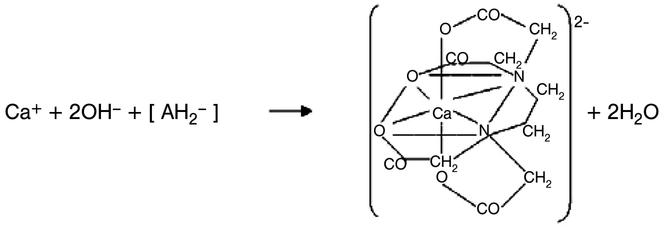


Figure 1.14 Coordination reaction.

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

$$Ca^{2+} + 2OH^- + [AH_4] \rightarrow Ca^{2+} + AH_2^{2-} + 2H_2O$$

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 alkalinity. 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 hydroxyled agglomerates to their precipitation as adherent crystals. In systems such as bottlewashing 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

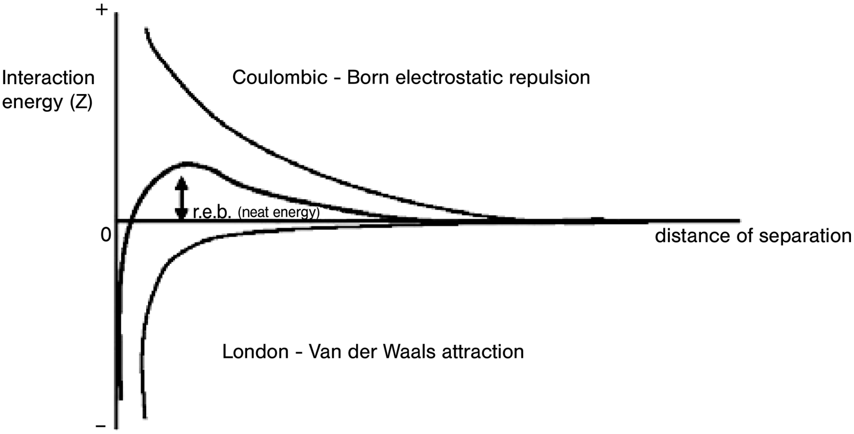


Figure 1.15 Competition between Van der Waals attraction and Born electrostatic repulsion.

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	−65	−41
polyacrylate 25 ppm	−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 benefits. It embodies the ability to keep insoluble particles free to move inside a solution without adhereing 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

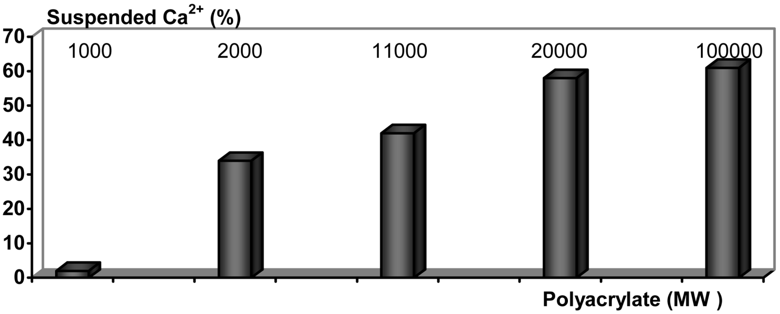


Figure 1.16 Suspending ability of polyacrylates: pH 11, Ca^{2+} 830 ppm, 25 °C, 70 h of rest.

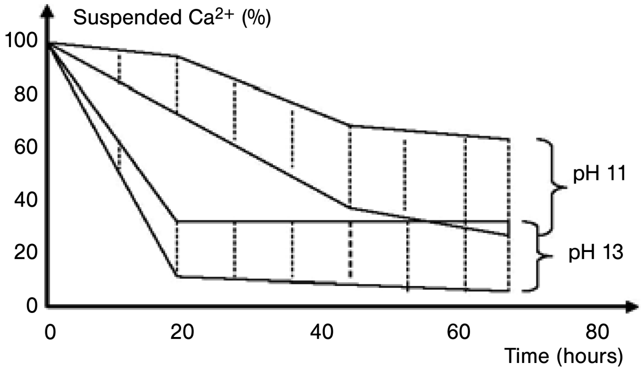


Figure 1.17 Suspending ability of polyacrylates as a function of pH.

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 µm 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 $[2\pi\varepsilon a\zeta^2 \exp^{(-\kappa D)}]$
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:

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

It is the equilibrium constant of the reaction

$$\mathrm{MAn}^{n-m} \leftrightarrow \mathrm{M}^{n+} + \mathrm{An}^{m-}.$$

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

$$K_{sp} = \frac{[Ca^{2+}][CO_3^-]}{[CaCO_3]} = 1.7 \cdot 10^{-8}$$

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]

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

It shows the equilibrium constant of the reaction

$$\text{Sequestrant} + \text{Metal Ion} \leftrightarrow \text{Complex.}$$

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, Hydroxyethylidenediphosphonic acid; EDTA, Ethylenediaminotetracetic acid; ATMP, Aminotrimethylenephosphonic acid; NTA, Nitrilotriacetic acid; EDTMP, Ethylendiaminotetramethylenephosphonic acid; DTPA, Diethylenetriaminopentacetic acid; DTPMP, Diethylentriaminopentamethylenephosphonic acid; HEDTA, Hydroxyethylenediaminotriacetic acid; STP, Sodium tripolyphosphate; PBTC, Phosphonobutanetricarboxylic acid.

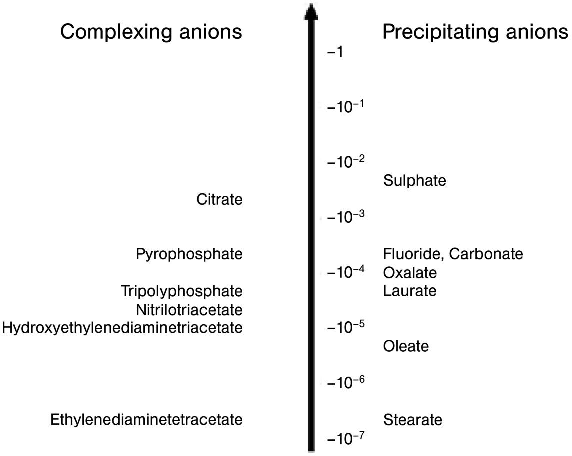


Figure 1.18 Competition between complexing agents and precipitants.

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]

$$\begin{array}{llll} Ca^{2+} + EDTA^{4-} \leftrightarrow CaEDTA^{2-} & K_{st} = 10^{9} & pH = 10 \\ Ca^{2+} + (H)EDTA^{3-} \leftrightarrow Ca(H)EDTA^{-} & K_{st} = 10^{3} & pH = 7 \end{array}$$

NTA [18]

$$\begin{array}{llll} Cu^{2+} + NTA^{3-} \leftrightarrow CuNTA^{-} & K_{st} = 10^{13} & pH > 10.3 \\ Cu^{2+} + (H)NTA^{2-} \leftrightarrow Cu(H)NTA & K_{st} = 10^{2.7} & 3 < pH > 10.3 \end{array}$$

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

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

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 $K_{\mathrm{conditional}}$ 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.

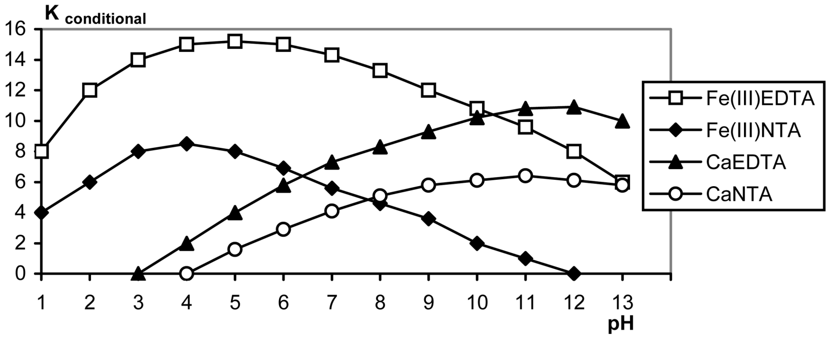


Figure 1.19 Peak of performance for different sequestrants.

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 bottlewashing. The bottlewasher 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, 20 h 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.

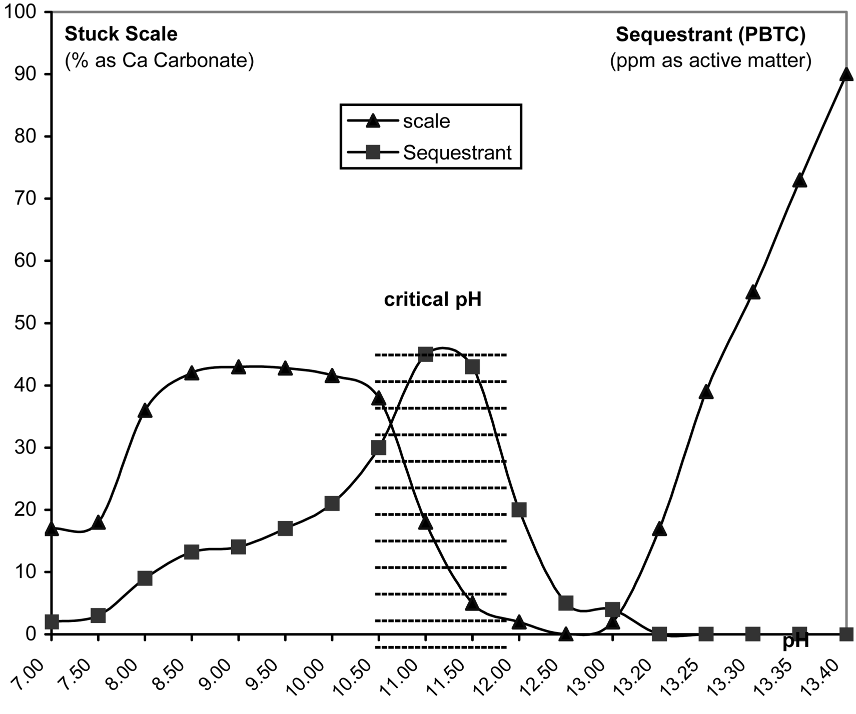


Figure 1.20 Effect of dispersant on deposits. Conditions: 40 dF, 70 °C and 20 h of rest. Ca determined with EDTA.

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 ($K_{\mathrm{conditional}}$, 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.

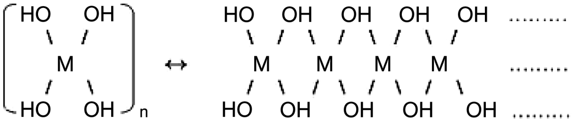


Figure 1.21 Hydroxylated complex with geometry extended to three dimensions.

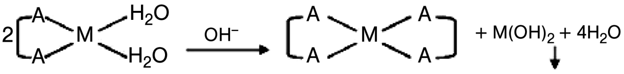


Figure 1.22 Disproportionation reaction.

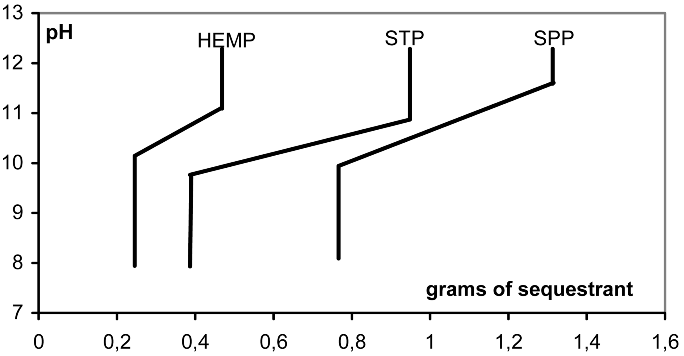


Figure 1.23 Grams of sequestering agents necessary to soften 1 L of water containing 64.8 mg L^{-1} hardness.

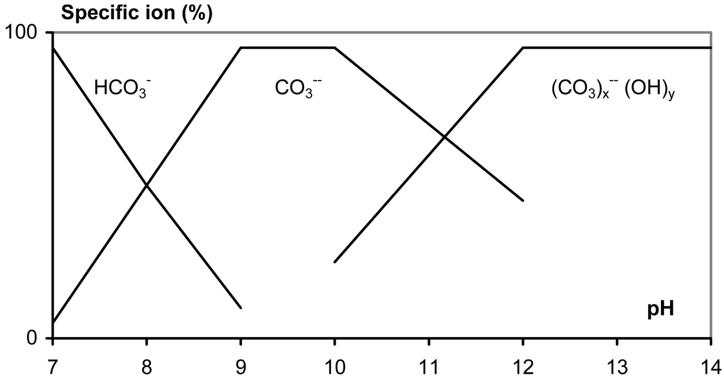


Figure 1.24 Ionic species as a function of pH.

When the alkalinity P is zero (phenolphthalein end point pH ≈ 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 (pH ~ 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 [$Ca_2(OH)_2CO_3$] in a caustic medium (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

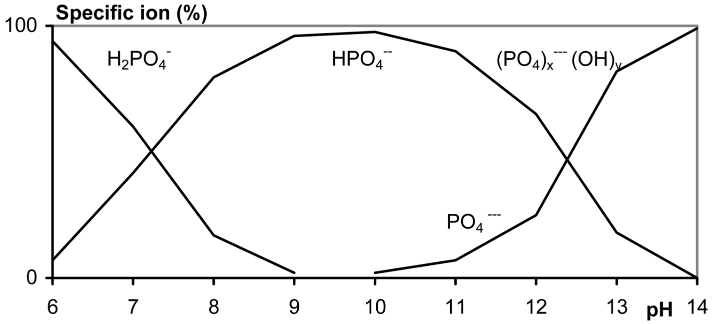


Figure 1.25 Phosphate species as a function of pH.

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].

$$Na_5P_3O_{10} + 4OH^- \rightarrow 3PO_4^{3-} + 2H_2O + 5Na^+ \qquad \text{(tripolyphosphate)}$$

$$(NaPO_3)_6 + 12OH^- \rightarrow 6PO_4^{3-} + 6H_2O + 6Na^+ \qquad \text{(hexametaphosphate)}$$

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 $nCa_5OH(PO_4)_3 \cdot (OH)_m$] forms in caustic solution and precipitates as an inert soft sludge. Below pH 12, a hard deposit of calcium phosphate crystals [$Ca_3(PO_4)_2$] 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

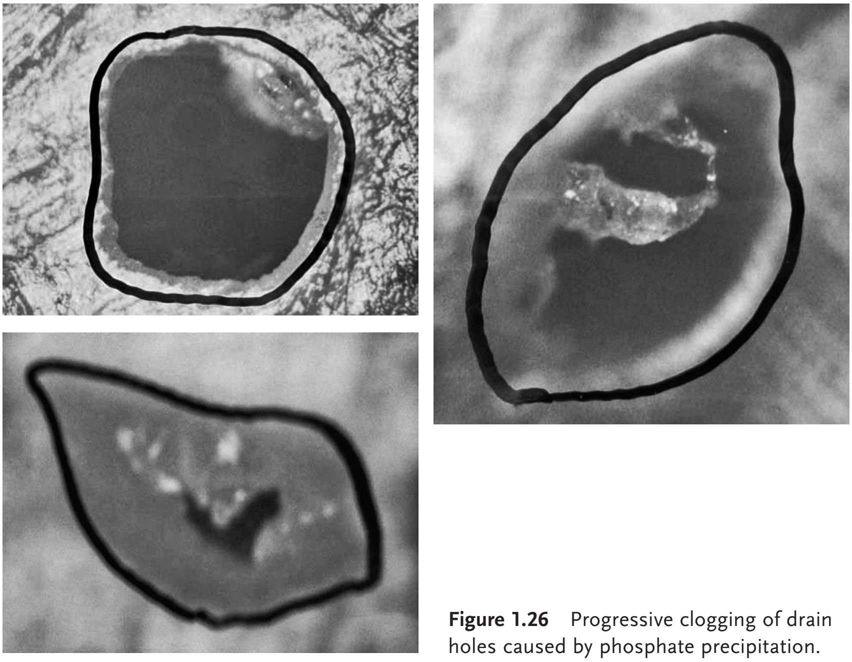


Figure 1.26 Progressive clogging of drain holes caused by phosphate precipitation.

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:

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

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

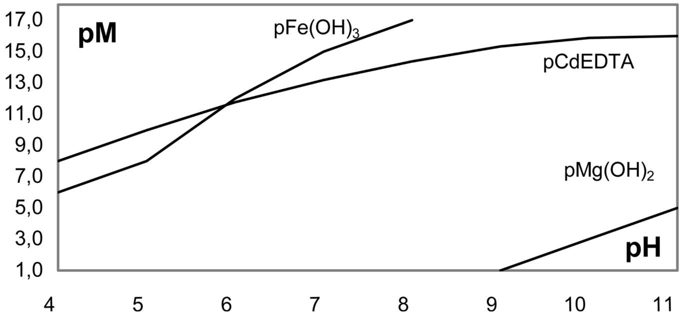


Figure 1.27 Equivalent quantities of some metal complexes as a function of pH.

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:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \qquad \text{(acidic behavior)}$$

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \leftrightarrow CO_2 + H_2O \quad \text{(basic behavior)}$$

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:

$$2HCO_3^- \xrightarrow{T\,°C} CO_2 + CO_3^{2-} + H_2O$$

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 $(SiO_4)^{4-}$ 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 ($<0.02\,\mathrm{mg\,L^{-1}}$) 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:

- $CaSO_4 \cdot 2H_2O$	dihydrate (gypsum, alabaster, selenite);
- $CaSO_4 \cdot ½H_2O$	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]:

$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 + Na_2SO_4$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

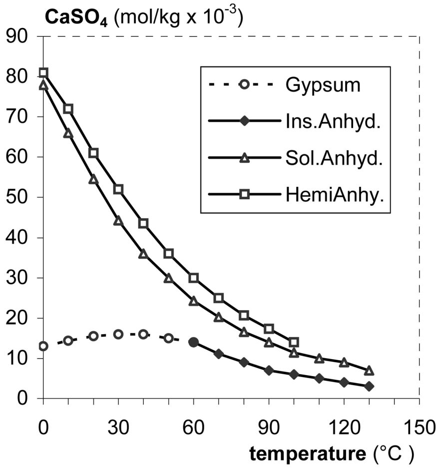


Figure 1.28 Solubility of calcium sulfate species (courtesy of Bianucci [64]).

Figure 1.29 Types of deposition.

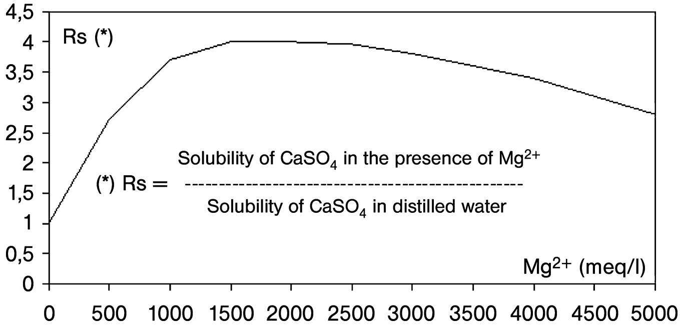


Figure 1.30 Effect of magnesium ions on the solubility of calcium sulfate, (courtesy of Cowan and Weintritt [16]).

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,*

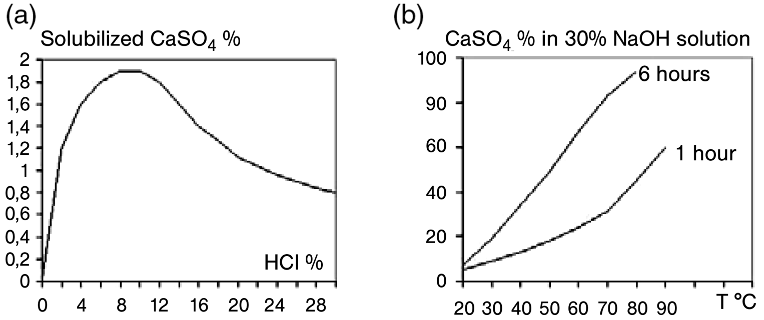


Figure 1.31 (a) Calcium sulfate solubility in hydrochloric acid (courtesy of Ryss and Nilus [66]). (b) Calcium sulfate solubility in caustic soda, (courtesy of Posnjak [67]).

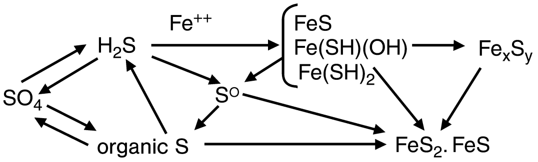


Figure 1.32 Biochemical reactions of sulfur compounds.

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:

$$Fe^\circ \rightarrow Fe^{2+} + 2e^-$$

$$8e^- + 9H^+ + SO_4^{2-} \rightarrow HS^- + 4H_2O$$

$$Fe^{2+} + HS^- \rightarrow FeS + H^+$$

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].

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2 \qquad \text{(A)}$$

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH \qquad \text{(B)}$$

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \qquad \text{(C)}$$

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:

$$Al(OH)_3 + NaOH \leftrightarrow Na^+ + Al(OH)_4^- \qquad \text{(D)}$$

Reaction (D) proves caustic soda to be crucial in keeping aluminates soluble. Aluminium hydroxide [$Al(OH)_3$] 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 bottlewasher 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 bottlewashing.

According to the stoichiometry of the reaction ($2Al + 2NaOH + H_2O \rightarrow 2NaAlO_2 + 3H_2$), 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, bottlewashers are provided with ventilating ducts.

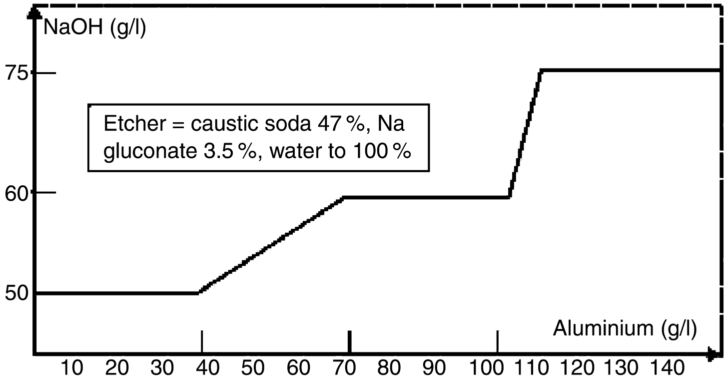


Figure 1.33 Increase in caustic soda concentration required to keep aluminum soluble.

Table 1.18 Metal concentrations in scale (ignited, then digested in HCl/HNO_3).

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%

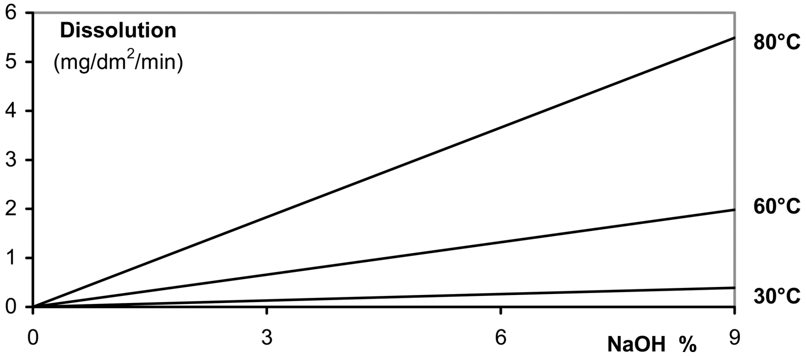


Figure 1.34 Aluminum solubility rate in caustic soda at different temperatures.

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 [$Ca_3(PO_4)_2$] 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 phosphonitric 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.

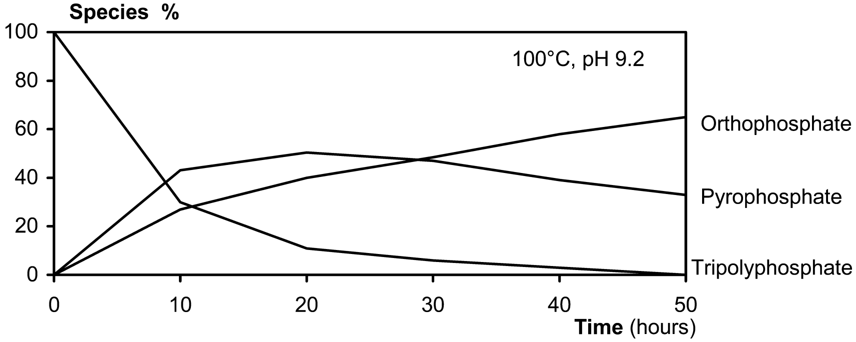


Figure 1.35 Chemical species during hydrolysis of STP (sodium tripolyphosphate).

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 (–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

•–OH	serine, threonine
•–SH	cysteine
•$–CONH_2$	asparagine, glutamine.

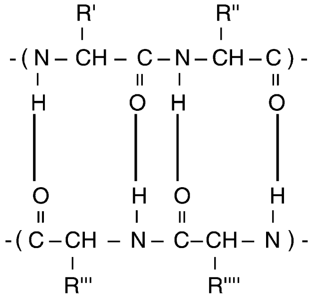


Figure 1.36 In order to visualize the sequestering capacity, proteins can be simply represented as a chain of aminoacids linked by hydrogen bonds.

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
- k	- 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 phosphocaseinate, 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 illusrated 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.

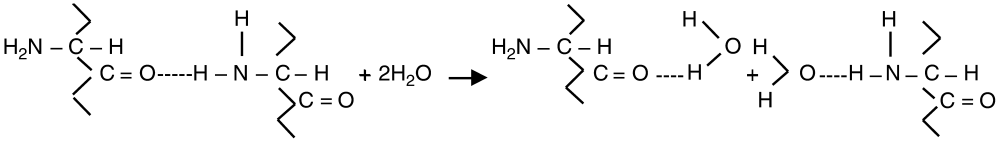


Figure 1.38 Example of reaction with water in denaturation.

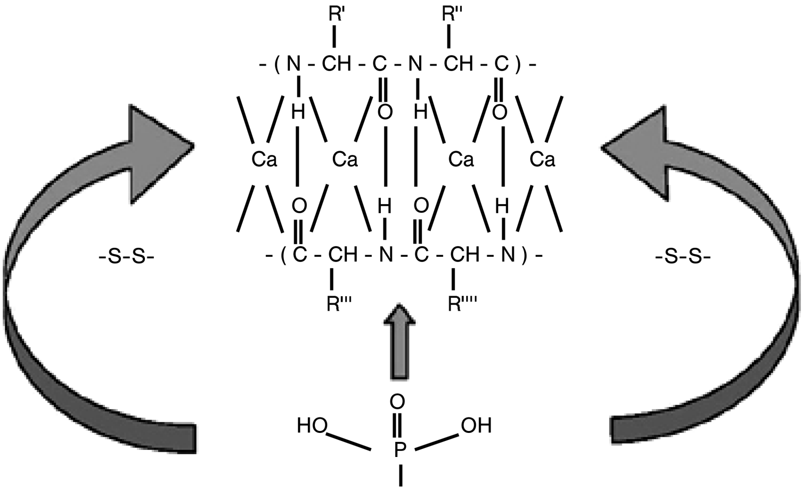


Figure 1.39 Peptide, phosphoryl, and sulfhydryl groups cause proteins to be precipitants

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.

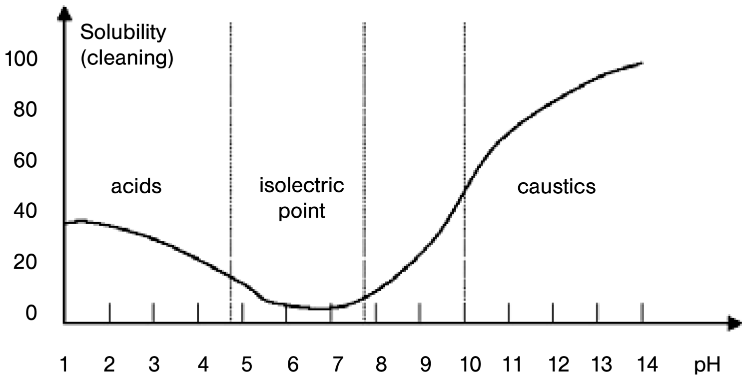


Figure 1.40 Proteins are stable at the isoelectric point.

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

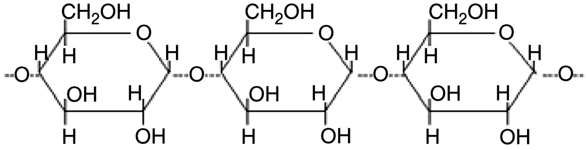


Figure 1.41 Starch chain.

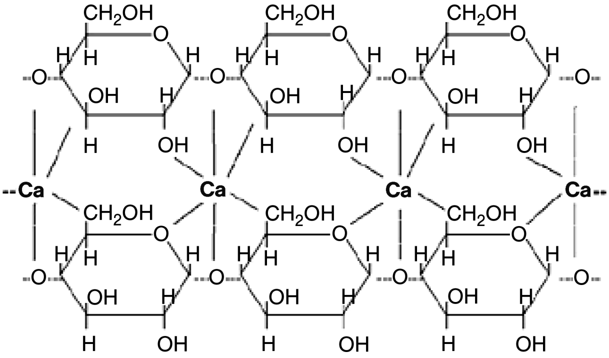


Figure 1.42 Starches behave as precipitants.

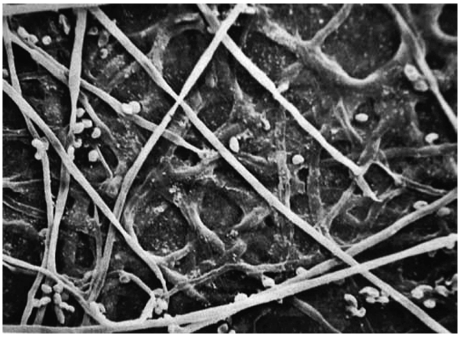


Figure 1.43 Mold adhering to surface with mucopolysaccharides and glycoproteins (courtesy of JohnsonDiversey; adapted from Ref. [87].).

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 bottlewashing. Milkstone in milking machines usually originates from the growth of mold spores (see Section 13.3).

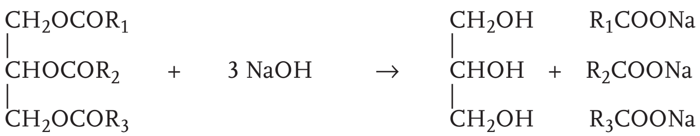
Pectins, alginates, and gums (e.g., carrageenan, tragacanth) form the group of carbohydrates present as deposits in fruit and vegetable processing. However, many industries make considerable use of them as additives to foods (e.g., ice cream, cheese, mayonnaise, jam, pudding, jelly...) and clarifiers 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 sequestrant 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.



$$\begin{array}{lcccll} \mathrm{CH_2OCOR_1} & & & & \mathrm{CH_2OH} & \mathrm{R_1COONa} \\ | & & & & | & \\ \mathrm{CHOCOR_2} & + & 3\,\mathrm{NaOH} & \rightarrow & \mathrm{CHOH}\ + & \mathrm{R_2COONa} \\ | & & & & | & \\ \mathrm{CH_2OCOR_3} & & & & \mathrm{CH_2OH} & \mathrm{R_3COONa} \end{array}$$

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,

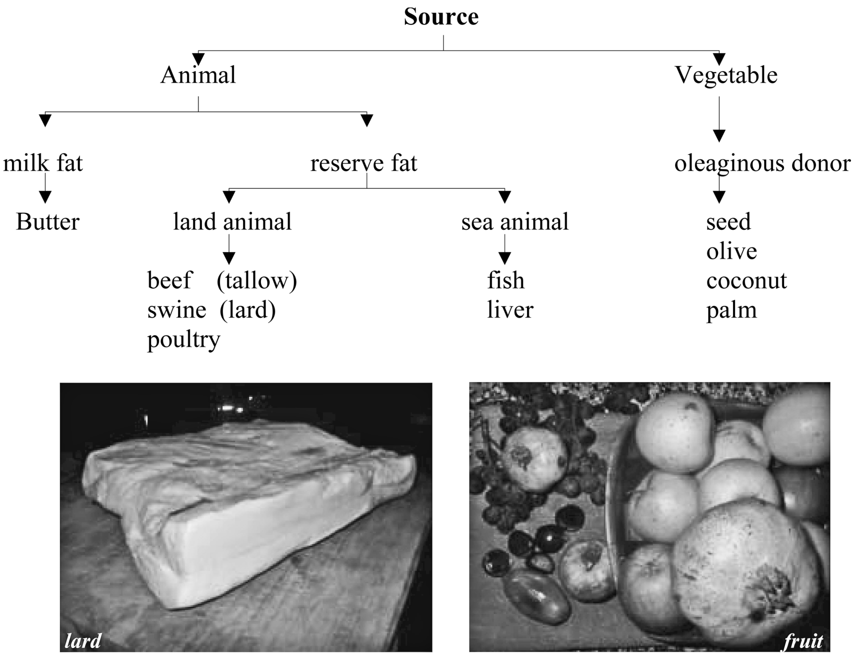


Figure 1.44 Sources of fatty material.

$$\text{(A)}\ \left[\begin{array}{ll}1 & \text{S}\\ 2 & \text{P}\\ 3 & \text{S}\end{array}\right.\quad \textit{(assigned to lard)}\qquad \text{(B)}\ \left[\begin{array}{ll}1 & \text{P}\\ 2 & \text{S}\\ 3 & \text{S}\end{array}\right.\quad \textit{(assigned to tallow)}$$

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:

$$R_1{-}COO{-}Ca{-}OOC{-}R_2$$

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]:

$$R{-}COOH \xrightarrow{R{-}NH_2} R{-}COO^{-+}NH_3{-}R' \xrightarrow[\text{heat}]{-H_2O} R{-}CONH{-}R'$$

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

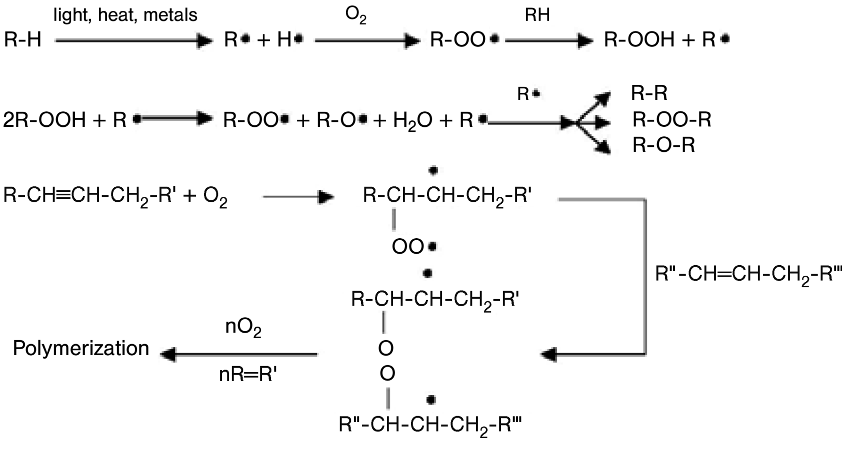


Figure 1.45 Scheme of radical reaction.

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 COO–Ca–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, laurylether 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 bottlewashing.
- 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 beween 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 mg L^{-1} 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.

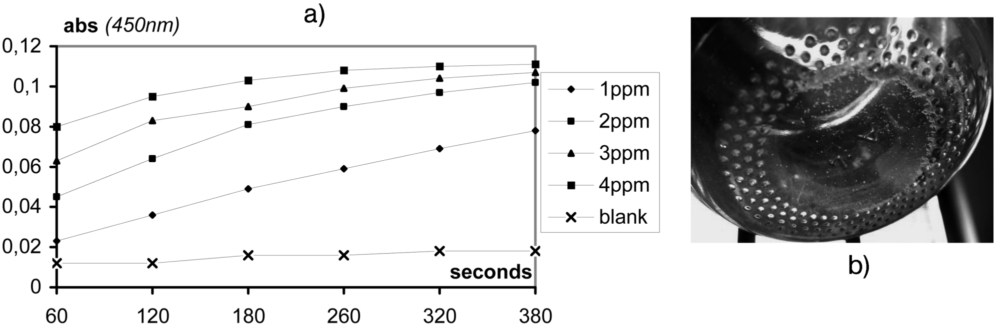


Figure 1.48 Chlorine destabilizing colloids a) and coagulated colloids in bottle b).

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:

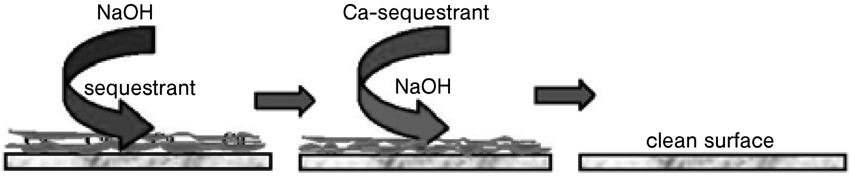


Figure 1.49 Carrier activity of sequestrants in the cleaning process.

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 °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 saucepans).

Hydrogen peroxide replaces chlorine for several reasons. Chorine 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

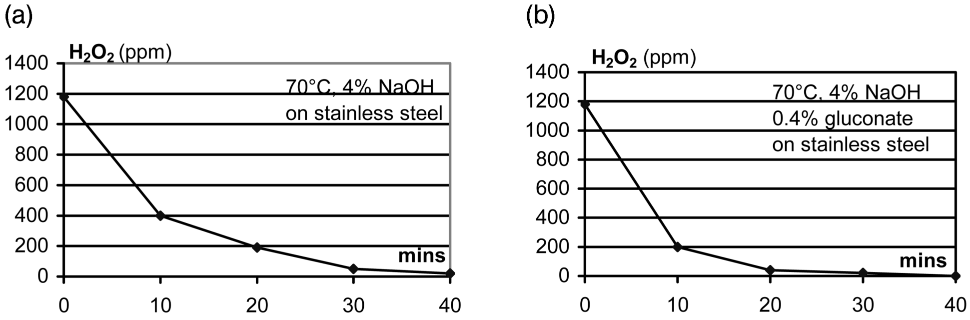


Figure 1.50 (a) Alkalinity and (b) temperature destabilize hydrogen peroxide.

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

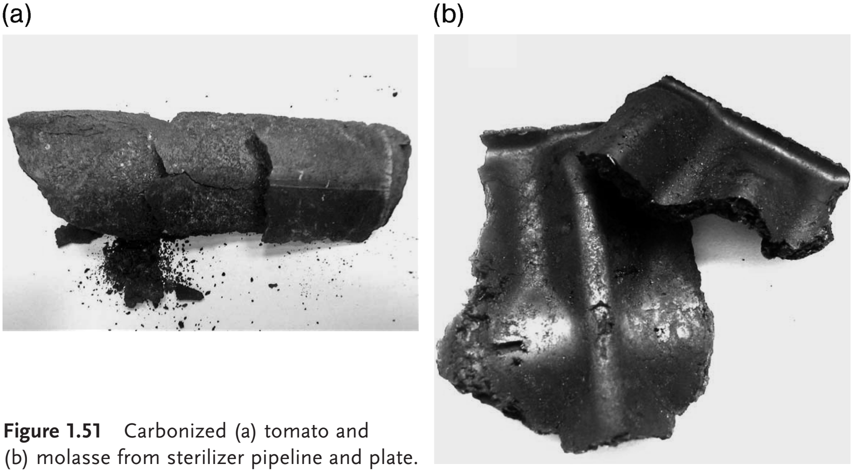


Figure 1.51 Carbonized (a) tomato and (b) molasse from sterilizer pipeline and plate.

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

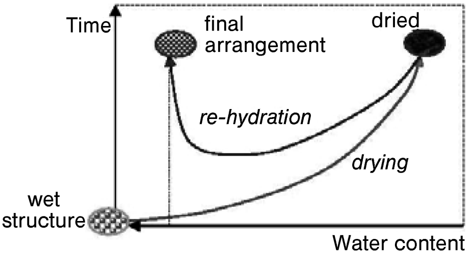


Figure 1.52 Irreversible modification of the food structure by drying.

- 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.

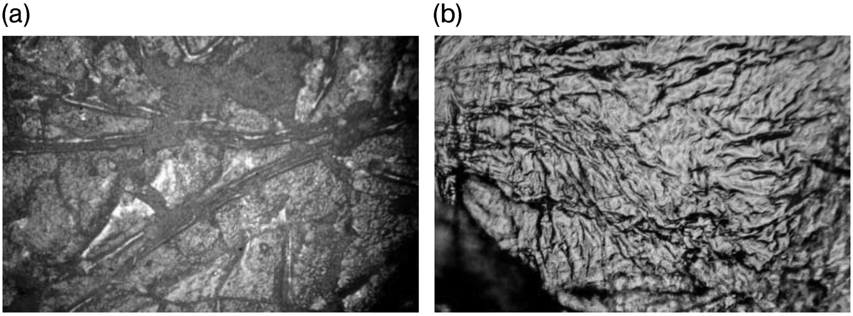


Figure 1.53 (a) Glass-like organic matter deposit on membrane used for microfiltration of apple juice, and (b) fatty amines in a lubricant solution insolubilized and polymerized to give a plastic-like film (photomicrograph).

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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