COMMON FOULANTS IN DESALINATION: INORGANIC SALTS

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Contents

1. Description and Overview (relative occurrence)
2. Calcium Carbonate
3. Calcium Sulfate
4. Magnesium Hydroxide
5. Silica and Silicates
6. Phosphates
7. Others
  7.1. Manganese
  7.2. Calcium fluoride (CaF₂)
  7.3. Barium and Strontium sulfates
Glossary
Bibliography and Suggestions for further study

Summary

Regardless of the method used for the production of potable water, the formation of solutions supersaturated with respect to various sparingly soluble inorganic salts, is possible. The thermodynamic driving force depends on the solution speciation which may be calculated from analytical data obtained from the physicochemical characterization of the treated water supplies. In addition, kinetics measurements are needed to model the fouling process. Calcium carbonate, a commonly encountered foulant, is characterized by polymorphism. Depending on the solution conditions (supersaturation, temperature and pH) the thermodynamically least stable vaterite may be stabilized. Surface diffusion-controlled crystal growth is reported for most cases of calcium carbonate fouling, while mass transport control mechanisms have also been proposed to explain fouling of tubes under flow conditions. The formation of calcium carbonates may be inhibited either by lowering supersaturation by acidification or by the use of water soluble inhibitors. Calcium sulfate is a salt often encountered in desalination processes where seawater is treated. Two hydrous and one anhydrous forms are known. The inhibition of calcium sulfates formation may be achieved by polyphosphates, phosphonates, synthetic polymers and proprietary formulated blends. Magnesium hydroxide scales are often found in boilers and are reduced or prevented by the formation of acidic conditions. Silica and silicates constitute a class of hard-to-deal-with foulants. They are formed through a rather complicated mechanism and may be prevented through the inhibition of silica polymerization or by the use of polymeric dispersants. Calcium phosphates is a large class of foulants involving several minerals. The thermodynamically most stable phase is hydroxyapatite which may form either
directly at low supersaturations or through the transformation of transient phases stabilized kinetically. Other less commonly encountered foulants include iron oxides, manganese oxides, calcium fluoride, barium and strontium sulfates.

1. Description and Overview (relative occurrence)

According to the water desalination act of 1996 of the U.S. Congress (U.S. Public Law 104-298) the terms "desalination" or "desalting" mean the use of any process or technique for the removal and when feasible, adaptation to beneficial use, of organic and inorganic elements and compounds from saline or biologically impaired waters, by itself or in conjunction with other processes. Under the same act saline water includes seawater, brackish water and other mineralized or chemically impaired water.

Water is the most valuable and essential resource, which is a prerequisite for the sustenance of life. The distribution of water on earth is: 97.23 per cent in the oceans, 2.14 per cent in ice caps and glaciers, 0.61 per cent in groundwater, 0.01 per cent in freshwater lakes and 0.01 per cent in various other formations. The structure of the water molecules makes it the excellent solvent it is, capable of dissolving practically everything it comes into contact with, including gaseous, solid and liquid materials. In our era of ever-increasing urbanization, good water quality becomes more precious as the increase of wastewater affects the environment and consequently the aquifers used for potable water. Increasing concern has turned attention towards the treatment of the effluents from municipal centers and industrial units so that the pollution of natural water resources is minimized. Sea and/or brackish waters, the most abundant water resource, is an attractive alternative for the coverage of needs in potable water. The high salts content of these waters may be eliminated by desalination to the extent that they may be converted into good quality water. Desalination processes are applied today on very large industrial scales in places depleted from water. Desalination plants may be distinguished in the major categories depending on the technology of separation of salts from saline water: Reverse Osmosis (RO) and distillation. Depending on the technology used the final water product is of high quality ranging from 1 to 500 ppm of total dissolved solids.

In the RO method, the saline water is forced through a semipermeable membrane, which restricts salts and other minerals but selectively allows the free passage of potable water. The principle of this method is based on the tendency for the flow of mass from a concentrated to a dilute solution with which it is in contact through a semipermeable membrane, so that the chemical potential of the dissolved species becomes equal on both sides of the membrane. The flow of mass to the equilibrium direction is called osmosis and the measure of the tendency of saline water to be diluted is the osmotic pressure. In the RO process, pressure is exerted on the saline water, in excess of the osmotic pressure, so that natural osmosis is reversed and water is forced to flow from the more to the less concentrated side. This process results in a 90-99 per cent reduction of the salts content of the feed water. The concentrate in which the salts are concentrated is rejected.

Distillation is the oldest desalination process whereby influent saltwater is heated until it boils. At this stage the dissolved minerals are separated resulting in a salt-free product,
which is captured in its gaseous state and then pumped out to the distribution system. Three main processes of distillation are employed: multistage flash distillation (MSF) in which the latent heat comes from the cooling of the liquid being evaporated; multiple effect distillation (MED) in which the latent heat comes from a solid surface; and vapour compression distillation (VC) in which the latent heat is obtained regeneratively (Van der Leeden, Troise and Todd 1990). In addition to the above, other methods are also applied including ion exchange, electrodialysis and vacuum freezing.

A common characteristic of all desalination methods is the production of a concentrated brine. The higher the concentration of salts in the brine, the more likely it becomes for scale development by precipitation. In the distillation and RO processes the major factor responsible for the deterioration of their performance is the deposition of solids on the heat exchangers and the RO membranes. The solids consist of various types of foulants. Fouling via deposition causes decreased production, unscheduled shutdowns, poor product water quality and premature equipment failure (Amjad 1993, 1996; Libutti, Knudsen and Mueller 1984).

Foulants in the desalination process fall into three categories: scale, suspended/colloidal matter and biological deposits. Scale consists of sparingly soluble salts which form

![Diagram of scale deposit formation](image)

Figure 1. Schematic outline of the stages involved in the formation of scale deposits.
during the desalination process because their solubility product is exceeded. Common scales encountered include calcium carbonate, calcium sulfate, silica, metal silicates, oxides/hydroxides of aluminium, iron and manganese. Other less commonly-encountered scales include calcium fluoride, barium sulfate, strontium sulfate and cupric sulfide. Soluble heavy metals are also responsible for fouling following oxidation provided that pH and dissolved oxygen conditions are suitable. Colloidal sulfur coming from oxidized hydrogen sulfide may cause severe fouling problems in water desalination systems. Moreover it should be noted that colloidal sulfur forms from the reaction of hydrogen sulfide with chlorine present in water. Iron and manganese are also important metals from the point of view of potential fouling since they form oxides under most desalination operational conditions which deposit on foreign surfaces. A common characteristic of the salts mentioned above is that their solubility decreases with increasing temperature. Deposits of this type form either when temperature or the salt concentration in water increases or when the solubility is exceeded and the solution becomes supersaturated. At this point nucleation of the salts forming scale deposits begins and may eventually lead to the formation of crystals which adhere on the surfaces with which water is in contact. In Figure 1, a schematic outline of the stages involved in scale formation is shown.

![Figure 1. Schematic outline of the stages involved in scale formation.](image)

**Figure 2. Solubility-supersolubility diagrams of a sparingly soluble salt with inverse solubility.**

As may be seen, of primary importance is the development of supersaturation which is the driving force for nucleation and provided that there is sufficient contact time with a foreign substrate, deposition may take place (Cowan and Weintritt 1976). Supersaturation is a measure of the deviation of a dissolved salt from its equilibrium value. In Figure 2 a typical solubility diagram for a sparingly soluble salt of inverse solubility is shown. The solid line corresponds to equilibrium. At point A the solute is in equilibrium with the corresponding solid salt. Any deviation from this equilibrium position may be effected either isothermally (line AB), at constant solute concentration, increasing the solution temperature (AC), or by varying both concentration and temperature (AD). A solution departing from equilibrium is bound to return to this state.
by the precipitation of the excess solute. However, for most of the scale-forming sparingly soluble salts, supersaturated solutions may be stable for practically infinite time periods. These solutions are metastable and may return to equilibrium only when a cause acts as e.g. the introduction of seed crystals of the salt corresponding to the supersaturated solution.

There is however a threshold to the extent of deviation from equilibrium marked by the dashed line in Figure 2, which if reached, results in spontaneous precipitation with or without induction time preceding precipitation. This range of supersaturations defines the labile region and the dashed line is known as the supersolubility curve. It should be noted that the supersolubility curve is not well defined and depends on several factors such as presence of foreign suspended particles, agitation, temperature, pH etc. The formation and subsequent deposition of solids occurs only when the solution conditions correspond to the metastable or the labile region. Below the solubility curve, fouling from scale deposits cannot take place. On the contrary, since at this range the solutions are undersaturated, dissolution is likely to take place should any crystals of the respective salt be present.

Supersaturation in solution can be developed in many ways including temperature fluctuation, pH change, mixing of incompatible waters, increasing the concentration by evaporation or solids dissolution etc. Although supersaturation is the driving force for the formation of a salt, the exact values in which precipitation occurs are quite different from salt to salt and as a rule, the degree of supersaturation needed for a sparingly soluble salt is in order of magnitude higher than the corresponding value for a soluble salt. Quantitatively, supersaturation may be expressed in several types of units (Myerson 1993). Thus supersaturation is often expressed as concentration difference:

\[ \Delta C = C - C_\infty \]  

(1)

where \( C \) and \( C_\infty \) are the solute concentration in solution and at equilibrium respectively. The supersaturation ratio \( S \) is defined as:

\[ S = \frac{C}{C_\infty} \]  

(2)

being a number >1 for supersaturated solutions. A related expression, the relative supersaturation, \( \sigma \), is defined as:

\[ \sigma = \frac{C - C_\infty}{C_\infty} \]  

(3)

and as may be seen from equations (2) and (3)

\[ \sigma = \frac{C}{C_\infty} - 1 = S - 1 \]  

(4)

For sparingly soluble salts \( M_vA_\nu \), the supersaturation ratio is defined as:
\[ S = \left( \frac{a_{\alpha+}}{a_{\alpha-}} \right)^{\frac{1}{\nu}} \left( \frac{a_{\alpha-}}{a_{\alpha+}} \right)^{-\frac{1}{\nu}} = \left( \frac{IP}{K_0^\alpha} \right)^{1/\nu} \]  

(5)

where subscripts \( s \) and \( \propto \) refer to solution and equilibrium conditions respectively, \( \alpha \) denotes the activities of the respective ions and \( \nu_+ + \nu_- = \nu \). \( IP \) and \( K_0^\alpha \)

are the ion products in the supersaturated solution and at equilibrium respectively.

The fundamental driving force for the formation of a salt from a supersaturated solution is the difference in chemical potential of the solute in the supersaturated solution from the respective value at equilibrium:

\[ \Delta \mu = \mu_\propto - \mu_s \]  

(6)

Since the chemical potential is expressed in terms of the standard potential and the activity, \( \alpha \), of the solute:

\[ \mu = \mu^0 + RT \ln \alpha \]  

(7)

where \( R \) and \( T \) are the gas constant and the absolute temperature respectively. Substitution of equation (7) to equation (6) gives the driving force for solid deposition (Mullin 1993):

\[ \frac{\Delta \mu}{RT} = \ln \left( \frac{a_\propto}{a_s} \right) = \ln S \]  

(8)

For electrolyte solutions the mean ionic activity is taken:

\[ \alpha = \alpha^\nu_+ (\nu_+ + \nu_-) \]  

(9)

and

\[ \frac{\Delta \mu}{RT} = \ln \left( \frac{a_\propto}{a_{s,\propto}} \right) = \ln S \]  

(10)

Nucleation takes place as soon as supersaturation is established. Although there is no general agreement on nucleation, primary defines nucleation which takes place in the absence of crystalline or any other type of suspended matter. When new crystals are generated in the neighbourhood of suspended crystallites or particles the nucleation is termed as secondary. Moreover, the primary nucleation may be further distinguished
into homogeneous and heterogeneous to denote situations in which it starts spontaneously or is catalyzed by the presence of foreign particles respectively. In primary nucleation, the corresponding rates strongly depend on supersaturation while in secondary nucleation the size of the crystallites present is reported to be very important (Cayes and Estrin 1967; Rousseau, Li and MacCabe 1976).

In the laboratory, secondary nucleation of scale-forming salts has been modelled by the use of mixed suspension mixed product removal crystallizer [MSMPR]. In this technique crystallization and nucleation occur simultaneously as the feed solutions consisting of the precipitating salt anionic and cationic components are introduced in the crystallizer. As the product is continuously removed a steady state is established. At this condition particle size analysis of samples can yield estimates for both nucleation and crystal growth rates (Garside and Davey 1980; Garside, Gibilaro and Tavare 1982). The nucleation process may be greatly influenced by the presence of impurities in the solutions which either suppress primary nucleation (Mullin, Chakraborty and Mehtak 1970) or promote secondary nucleation (Botsaris, Denk and Chua 1972).

Very often an induction time elapses between the achievement of supersaturation and the detection of the formation of the first crystals. This time, defined as the induction time, \( \tau \), is considered to correspond to the time needed for the development of supercritical nuclei. The induction time is inversely proportional to the rate of nucleation and according to the classical nucleation theory the following relationship may be written (Malollari, Klepetsanis and Koutsoukos 1995):

\[
\log \tau = A + \frac{B_{ss}^3}{(2.303kT)^3 \log S} \tag{11}
\]

Once stable, supercritical nuclei form in a supersaturated solution and grow into crystals of visible size. The rate of crystal growth may be defined as the displacement velocity of a crystal face relative to a fixed point of the crystal. This definition however cannot be easily applied to the formation of polycrystalline deposits such as those encountered in desalination fouling. In this case, the rates of growth may be expressed experimentally in terms of the molar rate deposition by equation 12:

\[
R_g = \frac{1}{A} \frac{dm}{dt} \tag{12}
\]

where \( m \) is the number of moles of the solid deposited on a substrate in contact with the supersaturated solution, e.g. RO membranes, pipes, exchangers or seed crystals, and \( A \), the surface area of the substrate. Very often, linear rates, \( \dot{r} \),

are used assuming the shape of the polycrystalline deposits being spherical, of equivalent mean radius

\( \bar{r} \).
\[
\dot{r} = \frac{d\bar{r}}{dt}
\]  

(13)

The molar is related with the linear rate with equation 14:

\[
\dot{r} = R \frac{M}{\rho}
\]  

(14)

where M is the molecular weight and \( \rho \) the density of the crystalline deposit.

The rate laws used to express the dependence of the rates as a function of the solution supersaturation provide mechanistic information for the fouling mechanism. At a microscopic scale the sequence of steps followed for the growth of crystals are shown in Figure 3:

![Figure 3. Model for the steps involved in the process of crystal growth of the supercritical nuclei.](image)

Bibliography and Suggestions for further study


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