

COMMON FOULANTS IN DESALINATION: INORGANIC SALTS

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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).

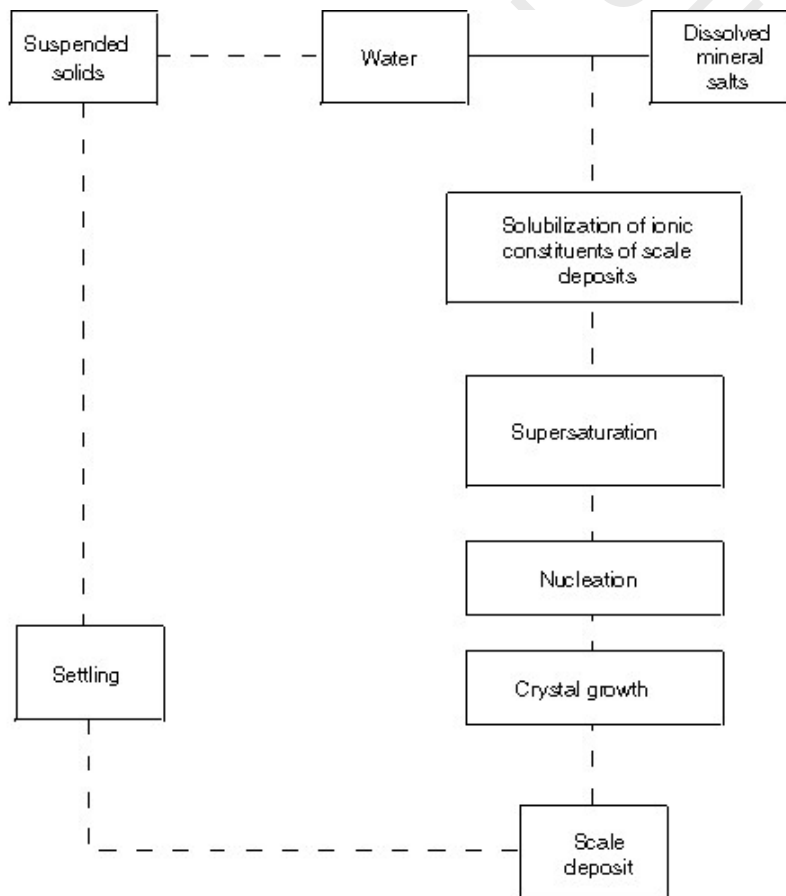


Figure 1. Schematic outline of the stages involved in the formation of scale deposits.

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

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.

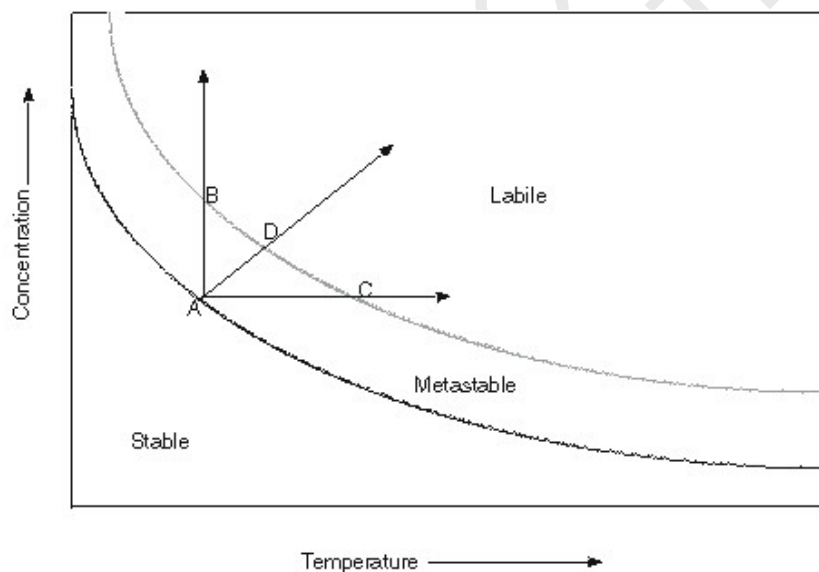


Figure 2. Solubility-supersolubility diagrams of a sparingly soluble salt with inverse solubility.

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:

$$\Delta C = C - C_{\infty} \quad (1)$$

where C and C_{∞} are the solute concentration in solution and at equilibrium respectively. The supersaturation ratio S is defined as:

$$S = \frac{C}{C_{\infty}} \quad (2)$$

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

$$\sigma = \frac{C - C_{\infty}}{C_{\infty}} \quad (3)$$

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

$$\sigma = \frac{C}{C_{\infty}} - 1 = S - 1 \quad (4)$$

For sparingly soluble salts $M_{\nu_+}A_{\nu_-}$ the supersaturation ratio is defined as:

$$S = \left\{ \frac{(\alpha_{M^{m+}})_s^{v+} (\alpha_{A^{a-}})_s^{v-}}{(\alpha_{M^{m+}})_\infty^{v+} (\alpha_{A^{a-}})_\infty^{v-}} \right\}^{1/v} = \left(\frac{IP}{K_s^0} \right)^{1/v} \quad (5)$$

where subscripts s and ∞ refer to solution and equilibrium conditions respectively, α denotes the activities of the respective ions and $v_+ + v_- = v$. IP and

$$K_s^0$$

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:

$$\Delta\mu = \mu_\infty - \mu_s \quad (6)$$

Since the chemical potential is expressed in terms of the standard potential and the activity, α , of the solute:

$$\mu = \mu^0 + RT \ln \alpha \quad (7)$$

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):

$$\frac{\Delta\mu}{RT} = \ln \left(\frac{\alpha_s}{\alpha_\infty} \right) = \ln S \quad (8)$$

For electrolyte solutions the mean ionic activity is taken:

$$\alpha = \alpha_\pm^v \quad (v_+ + v_-) \quad (9)$$

and

$$\frac{\Delta\mu}{RT} = \ln \left(\frac{\alpha_\pm}{\alpha_{\pm,\infty}} \right) = \ln S \quad (10)$$

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, τ , 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):

$$\log \tau = A + \frac{B_{\gamma S}^3}{(2.303kT)^3 \log S} \quad (11)$$

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:

$$R_g = \frac{1}{A} (dm/dt) \quad (12)$$

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} :

$$\dot{r} = \frac{d\bar{r}}{dt} \quad (13)$$

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

$$\dot{r} = R_g \frac{M}{\rho} \quad (14)$$

where M is the molecular weight and ρ 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:

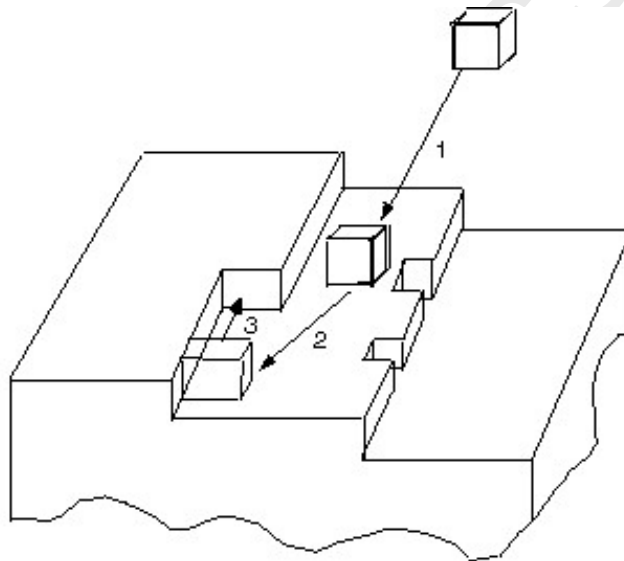


Figure 3. Model for the steps involved in the process of crystal growth of the supercritical nuclei.

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Bibliography and Suggestions for further study

Amjad Z (1988) Calcium sulfate dihydrate (gypsum) scale formation on heat exchanger surfaces: the influence of scale inhibitors. *J. Colloid and Interface Science* 123, 523-532.

Amjad Z (1988) Mechanisms of formation and inhibition of mineral scales in reverse osmosis systems, Ultrapure Water Expo 88, Philadelphia, PA.

Amjad Z (1988) Seeded growth of calcium containing scale forming minerals in the presence of additives. *Corrosion* 88, paper no. 421. NACE International, Houston, Texas.

Amjad Z (1991) Inhibition of calcium fluoride crystal growth by polyelectrolytes, *Langmuir* 7, 2405-2408.

Amjad Z (1996) Scale inhibition in desalination applications: an overview. In: *Corrosion 96*, NACE Int. Annual Conference Paper No. 230, Houston, Texas.

Amjad Z (ed.) (1993) *Reverse Osmosis: Membrane Technology Water Chemistry, and Industrial Application*. New York: Van Nostrand Reinhold Publ. Co.

Amjad Z and Hooley J P (1986) Influence of polyelectrolytes on the crystal growth of calcium sulfate dihydrate. *J. Colloid and Interface Science* 111, 496-503.

Amjad Z and Masler W F (1985) Inhibition of calcium sulfate dihydrate crystal growth by polyacrylates. *Corrosion* 88, paper no. 11. Nace International, Houston, Texas.

Amjad Z and Yorke M A (1985) Carboxylic functional polyampholytes as silica polymerization retardants and dispersants. US Patent No 4,510,0059.

Amjad Z, Pugh J and Reddy M M (1998) Kinetic inhibition of calcium carbonate crystal growth in the presence of natural and synthetic organic inhibitors, In: *Water Soluble Polymers. Solution Properties and Applications* (ed. Z Amjad), pp. 131-147. New York and London: Plenum Press.

Amjad Z, Zibrida J F and Zuhl R W (1997) A new antifoulant for controlling silica fouling in reverse osmosis systems. In: *World congress on desalination and water reuse*, Oct. 6-9 1997, pp. 1-22. Madrid, Spain.

Andritsos N, Kontopoulou M, Karabelas A J and Koutsoukos P G (1997) Calcium carbonate deposit formation under isothermal conditions. *Can J.Chem. Eng.* 74, 911-919.

Aronson S (1981) Mineral deposition from Icelandic geothermal waters: environmental and utilization problems. *J. Pet. Tech.* 181-187.

Austin A E, Miller J F, Vaughan D A and Kircher J F (1975) Chemical additives for calcium sulfate scale control. *Desalination* 16, 345-357.

Ball J W and Nordstrom D K (1991) WATEQ4F-User's manual with revised thermodynamic data base and test cases for calculating speciation of major, trace and redox elements in natural waters, U.S. Geological Survey Open File Report 90-129, 185 pp.

Barone J P and Nancollas G H (1977) The seeded growth of calcium phosphates. The effect of solid/solution ratio in controlling the nature of the grown phase. *J. Colloid and Interface Sci.* 62, 421-429.

Betts F and Posner A S (1974) An X-ray radial distribution study of amorphous calcium phosphate. *Mater. Res. Bull.* 9, 907-914.

Bianucci G (1963) The physical chemistry of seawater III. Calculation of the solubility and activity of calcium sulfate. *Ann. Idrol.* 1, 72-80.

Botsaris G D, Denk E G and Chua J (1972) Nucleation in an impurity concentration gradient. A new mechanism of secondary nucleation. *AIChE Symposium Series* No. 121, 68, 21-30.

Bradley R (1993) Design considerations for reverse osmosis systems. In: *Reverse Osmosis: Membrane Technology, Water Chemistry and Industrial Applications* (ed. Z Amjad), pp. 1-4-138. New York: Van Nostrand Reinhold Publ. Co.

Bradstreet S W (1950) Armour Research Foundation Final Report no. 90-501-G. U.S. Coast Guard.

Brown W E and Lehr J R (1959) *Application of phase rule to the chemical behaviour of monocalcium phosphate monohydrate*. *Soil Science American Proceedings* 23, 7-15.

Brown W E, Lehr J R, Smith J P and Frazier A W (1957) Crystallography of Octacalcium phosphate of J. *Amer. Chem. Soc.* 79, 5318-5319.

- Burton W K, Cabrera N and Frank F C (1951) The growth of crystals and the equilibrium structure of their surfaces. *Phil. Trans. Royal Society* (London), pp. 243, 299.
- Campbell A S and Fyla W S (1960) Hydroxyl ion catalysis of the hydrothermal crystallization of amorphous silica: a possible high temperature pH indicator. *Amer. Mineral* 45, 464-468.
- Carr R M and Fyfe W S (1958) Some observations on the crystallization of amorphous silica. *Amer. Mineral* 43, 908-916.
- Cayes N W and Estrin J (1967) Secondary nucleation in agitated $MgSO_4$ solutions. *Industrial and Engineering Chemistry Fundamentals* 6, 13-20.
- Chan S H (1989) A review on solubility and polymerization of silica. *Geothermics* 18, 49-56.
- Chan S H, Ram H, De Bellis C and Neusen K F (1988) Silica fouling of heat transfer equipment: experiments and model. *J. Heat Transfer* 110, 841-849.
- Chernov A A (1961) The spiral growth of crystals. *Soviet Physics Uspekhi* 4, 116-148.
- Corwin J F, Herzog A H, Owen G E, Yalmean R G and Swinnerton A C (1953) The mechanism of the hydrothermal transformation of silica glass to quartz under isothermal conditions. *J. Amer. Chem. Soc.* 75, 3933-3934.
- Cowan J C and Weintritt D J (1976) *Water Formed Scale Deposits*, pp. 204-206. Gulf Publ. Co. Houston, Texas.
- Dalas E and Koutsoukos P G (1988) Crystallization of calcite on collagen I. *Langmuir* 4, 907-1002.
- Dalas E and Koutsoukos P G (1989) Calcium carbonate formation on heated metal surfaces. *Geothermics* 18, 83-89.
- Dalas E, Kallitsis J and Koutsoukos P G (1988) The crystallization of calcium carbonate on polymeric substrates. *J. Crystal Growth* 89, 287-296.
- Dalas E, Kallitsis J and Koutsoukos P G (1991) Crystallization of hydroxyapatite on polymers. *Langmuir* 7, 1822-1826.
- Dalpi M, Karayanni E and Koutsoukos P G (1993) Inhibition of hydroxyapatite formation in aqueous solutions by zinc and 1,2-Dihydroxy-1,2-bis(dihydroxyphosphonyl)ethane. *J. Chem. Soc. Farad. Trans.* 89, 965-969.
- David Hasson (2001), Scale Formation and Prevention, In Galde, Heike, and Joachim Ulrich. Scaling in Seawater Desalination, Is Molecular Modeling the Tool to Overcome the Problem? Lutherstadt Wittenburg, Germany: ESF Exploratory Workshop,, pp. 49-68.
- Davies C W (1962) *Ion Association*. London: Butterworths, pp. 34-87.
- Davies C W and Jones A L (1949) The precipitation of silver chloride from aqueous solutions. Part I. *Discussions Farad. Soc.* 5, 103-111.
- Deliyianni E and Belessiotis B (1995) *Methods and Systems of Desalination*. 476 pp. Athens (in Greek).
- DeRooi J F, Heughebaert J C and Nancollas G H (1984) *J. Colloid Interface Science* 100, 350.
- Dubin L, Dammeier R L and Hart R A (1985) Deposit control in high silica water. *Corrosion* 85, Nace International, Paper No. 131, Houston, Texas.
- Eanes E A, Gillessen I H and Posner A S (1965) Intermediate stages in the precipitation of hydroxyapatite. *Nature* 208, 365-367.
- Eanes E D and Posner A (1968) Alkaline earth intermediate phases in the basic solution preparation of phosphates. *Calcif. Tiss. Res.* 2, 38-48.
- Ebrahim A, Hawaidi and Iqbal M. Mujtaba (2010), Sensitivity of Brine Heater Fouling on Optimization of Operation Parameters of MSF Desalination Process using gPROMS, 20th European Symposium on Computer Aided Process Engineering – ESCAPE20, S. Pierucci and G. Buzzi Ferraris (Editors)
- Feenstra T P and de Bruyn P L (1979) Formation of calcium phosphates in moderately supersaturated solutions. *J. Phys. Chem.* 83, 475-479.

- Flemming, Hans-Curt (1994) , Effects and Extent of Biofilm Accumulation in Membrane Systems, Chapter 5 in Geesey, Gill G., Zbigniew Lewandowski,
- Flesher P, Streatfield E L, Pearce A S and Hydes O D (1970) 3rd International symposium on fresh seawater 1, p. 493.
- Francis M D and Webb N C (1971) Hydroxyapatite formation from a hydrated calcium monohydrogen phosphate precursor. *Calcif. Tiss. Res.* 6, 335-342.
- Free D T (1993) Inhibition of silica and silicate deposition in cooling water systems. US Patent No 5, 271,862.
- Frondel C (1962) *Dana's System of Mineralogy*, vol III. 334 pp. New York: J Wiley.
- Furedi-Milhofer H and Sarig S (1996) Interactions between polyelectrolytes and sparingly soluble salts. *Prog. Crystal Growth and Charact.* 32, 45-74.
- Furedi-Milhofer H, Brecevic L and Purgaric B (1976) Crystal growth and phase transformation in the precipitation of calcium phosphates. *Faraday Discussions Chem. Soc.* 61, 184-193.
- Gardner G L (1978) Effect of pyrophosphate and phosphonate anions in the crystal growth kinetics of calcium oxalate hydrates. *J. Phys. Chem.* 82, 864-870.
- Garside J and Davey R J (1980) Secondary contact nucleation: kinetics, growth and scale-up. *Chem. Eng. Commun.* 4, 393-424.
- Garside J, Gibilaro L G and Tavare N S (1982) Evaluation of crystal growth kinetics from a desupersaturation curve using initial derivatives, *Chemical Engineering Science* 37, 1625-1628.
- Gates G L and Caraway W C (1965) Oil well scale formation in waterflood operations using ocean brines. Report R1 6658 Bureau of Mines, Wilmington CA., p. 28.
- Gazit E and Hasson D (1975) Scale deposition from an evaporating falling film. *Desalination* 17, 339-347.
- Giannimaras E K and Koutsoukos P G (1988) Precipitation of calcium carbonate in aqueous solutions in the presence of oxalate anions. *Langmuir* 4, 855-891.
- Gill G. Geesey (Editor), Hans-Curt Flemming, Zbigniew Lewandowski (1994) *Biofouling and Biocorrosion in Industrial Water Systems*, Publisher: CRC Press
- Glater J, York J L and Campbell K S (1980) *Principles of Desalination* (eds K S Spiegler and A K Laird), p. 627. New York: Academic Press.
- Gregory T M, Moreno E C, Patel J M and Brown W E (1974) Solubility of $\text{Ca}_3(\text{PO}_4)_2$ in the system $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ at 5, 15, 25 and 37°C. *J. Res. Nat. Bur. Stand.* 78A, 667-674.
- Griffith D W and Roberts S D (1979) Inhibition of calcium sulfate dihydrate crystal growth by phosphonic acids - Influence of inhibitor structure and solution pH. Paper No. SPE 7862, Society for Petroleum Engineers.
- Hann W F, Robertson S T and Bardsley J H (1993) Recent experience in controlling silica and magnesium silicate deposits with polymeric dispersants. Paper No 93-59 International Water Conference, Pittsburg PA.
- Hans-Curt Flemming (1997), Reverse osmosis membrane biofouling ,*Experimental Thermal and Fluid Science* ,Volume 14, Issue 4, 382-391
- Hasson D (1981) Precipitation fouling. In: *Fouling of heat transfer equipment* (eds E F C Somerscales and J G Knudsen), pp. 527-568. New York: Hemisphere Publ. Co.
- Hasson D and Zahavi J (1970) Mechanism of CaSO_4 scale deposition on heat transfer surfaces. *Industrial and Engineering Chemistry Fundamentals* 9, 1.
- Hasson D, Sherman H and Biton M (1978) Prediction of CaCO_3 scaling rates. In: *Proceedings of the 6th Int. Symposium of Fresh Water from the Sea* 2, 193-198.
- Hem J D (1967) Equilibrium chemistry of iron in groundwater. In: *Principles and Applications of Water*

- Chemistry* (eds S D Faust and J V Hunter), pp. 625-643. New York J.Wiley and Sons.
- Heughebaert J C and Nancollas G H (1984) Kinetics of crystallization of octacalcium phosphate. *J. Phys. Chem.* 10, 2423-2428.
- Heughebaert J C, Zawacki S J and Nancollas G H (1983) The growth of octacalcium phosphate on beta tricalcium phosphate. *Journal* 63, 83-90.
- Hirowatari K and Yamaguchi M (1990) Experimental study on a scale prevention method using exhausted gases from geothermal power stations. *Geothermal Resources Council Trans.* 14, Pt. II, pp. 1599-1602.
- Hohl H, Koutsoukos P G and Nancollas G H (1982) The crystallization of hydroxyapatite and dicalcium phosphate dihydrate. Representation of the growth curves. *J. Cryst. Growth* 57, 325-335.
- House W A (1981) Kinetics of crystallisation of calcite from calcium bicarbonate solutions. *J. Chem. Soc. Farad. Trans. I* 77, 341-359.
- Hurtado R and Mercado S (1990) Scale control studies at the cervo Prieto geothermal field. Geothermal resources council transactions 14, Pt I, pp. 1603-1610.
- Iler R K (1979) *The Chemistry of Silica Solubility, Polymerization, Colloid and Surface Properties and Biochemistry*, pp. 892. Chichester: J. Wiley and Sons Inc.
- Kastner M, Keene J B and Crieskes J M (1977) Diagenesis of siliceous oozes I. Chemical control on the rate of opal A to opal-CT transformation: an experimental study. *Geochim. Cosmochim. Acta* 41, 1041-1059.
- Kaup E C (1973) Design factors in reverse osmosis. *Chem. Eng.* 80, 40-65.
- Kazmierczak T F, Tomson M B and Nancollas G H (1982) Crystal growth of calcium carbonate. A controlled composition kinetic study. *J. Phys. Chem.* 77, 103-107.
- Kennedy G C (1950) A portion of the system silica-water, *Econ. Geol.* 45, 629-653.
- Kharin V M (1974) Kinetics of the crystallisation of polymorphic modifications of calcium carbonate russ. *J. Phys. Chem.* 48, 1018-1020.
- Kindle C H, Mercer B W, Elmore R P, Blair S C and Myers D A (1984) Geothermal injection treatment: process chemistry, field experiences and design options. Battelle Pacific Northwest Lab. PNL-4767 UC 66d.
- Kitano V (1962) Polymorphic formation of calcium carbonate in thermal springs with emphasis on the effect of temperature, *Bull. Chem. Soc. Japan* 35, 1973-1980.
- Klein C W (1995) Management of fluid injection in geothermal wells to avoid silica scaling at low levels of silica oversaturation. Proceedings of the World Geothermal Congress, vol. 4, pp. 2451-2456, Florence, Italy.
- Klein H A and Grabowski H A (1963) Experience with hydrogen damage in boilers. Paper presented at National Power Conference, Cincinnati, Ohio.
- Klepetsanis P G (1991) The formation of calcium sulfate in aqueous solutions. Doctorate thesis, 240 pp. University of Patras, Patras, Greece (in Greek).
- Klepetsanis P G, and Koutsoukos P G (1989) Spontaneous precipitation of calcium sulfate at constant calcium activity. *J. Crystal Growth* 98, 480-487.
- Klepetsanis P G, Drakia P and Koutsoukos P G (1995) The calcite-hydroxyapatite system. Crystal growth studies in aqueous solutions. In: *Mineral Scale Formation and Inhibition* (ed. Z Amjad), pp. 251-260. New York: Plenum Press.
- Klepetsanis P G, Koutsoukos P G, Chitanu G C and Carpov A A (1998) The inhibition of calcium carbonate formation by copolymers containing maleic acid. In: *Water Soluble Polymers. Solution Properties and Applications* (ed. Z Amjad), pp. 117-130. New York and London: Plenum Press.
- Koutsoukos P G (1998) Growth of calcium phosphates on different substrates: epitaxial considerations. In: *Calcium Phosphates in Biological and Industrial Systems* (ed. Z Amjad), pp. 41-66. Boston: Kluwer

Academic Publishers.

Koutsoukos P G and Kontoyannis C G (1984) The spontaneous precipitation of calcium carbonate in aqueous solutions. *J. Chem. Soc. Farad. Trans. 1* 80, 1181-1189.

Koutsoukos P G and Nancollas G H (1981) Crystal growth of calcium phosphates - Epitaxial considerations. *J. Crystal Growth* 53, 10-19.

Koutsoukos P G and Nancollas G H (1981) The influence of strontium ion on the crystallization of hydroxyapatite. *J. Phys Chem.* 85, 2403-2414.

Koutsoukos P G and Nancollas G H (1987) The mineralization of collagen *in vitro*. *Colloids and Surfaces* 28, 95-108.

Kralj D, Brecevic L and Nielsen A E (1990) Vaterite growth and dissolution in aqueous solution. I. Kinetics of crystal growth. *J. Cryst. Growth* 104, 793-800.

Langelier W F (1936) The analytical control of anti-corrosion water treatment. *J.A.W.W.A.* 28, 1500.

Langelier W F (1946) Chemical equilibria in water treatment. *J.A.W.W.A.* 38, 169.

LeGeros R Z and LeGeros J P (1984) Phosphate minerals in human tissues. In: *Phosphate Minerals* (J O Nriagu and P B Moore, eds), pp. 351-385. Berlin, Heidelberg: Springer Verlag.

LeGeros R Z, Shirra W P, Mirawite M A and LeGeros J P (1975) In: *Physico-Chimie et Cristallographie des Apatites d' Interêt Biologique*, pp. 105, 230. Paris: Colloque Internationaux.

LeGeros R Z, Taheri M H, Quirologico G B and LeGeros J P (1981) Formation and stability of apatites: effects of some cationic substituents. In: *Proceedings of the International Congress on Phosphorous Compounds IMPHOS*, Rabat, pp. 89-103.

Lehr J R, Brown W E and Brown E H (1959) Behavior of monocalcium phosphate monohydrate in soils. *Soil Science American Proc.* 23, 3-11.

Leung W H and Nancollas G H (1978) A kinetic study of the seeded growth of larium sulfate in the presence of additives. *J. Inorg. Nuclear Chemistry* 40, 1871-1875.

Libutti B L, Knudsen J G and Mueller R W (1984) The effects of antiscalants on fouling by cooling water. In: *Corrosion 84*, Nace Int. Annual Conference Paper No. 230, Houston, Texas.

Linnikov, Oleg D.,(2003) About seed concentration for prevention of scale ,*Desalination*, 157, 235-240, .

Liu S T and Nancollas G H (1970) The kinetics of crystal growth of calcium sulfate dihydrate. *J. Crystal Growth* 6, 281-289.

Liu S T and Nancollas G H (1973) The crystallization of magnesium hydroxide. *Desalination* 12, 75.

Liu S T and Nancollas G H (1975) Crystal growth and dissolution of barium sulfate in presence of additives. *J. Colloid and Interface Science* 44, 572-582.

Lone Star (2008),*Desalination: Is It Worth Its Salt? A Primer on Brackish and Seawater Desalination* ,<http://texas.sierraclub.org>

M. Esawy, M.R. Malayeri and H. Müller-Steinhagen(2009), Mechanism Of Crystallization Fouling During Pool, Boiling Of Finned Tubes,Thirteenth International Water Technology Conference, IWTC 13 , Hurghada, Egypt

Macek J, Zakarejsek S, Radkovic J and Bole V (1993) Crystallization of gypsum from batch chemical neutralization. *J. Crystal Growth* 132, 99-102.

Malollari I X, Klepetsanis P G and Koutsoukos P G (1995) Precipitation of strontium sulfate in aqueous solutions at 25°C. *J. Crystal Growth* 155, 240-246.

Marsh A R III, Klein G and Verneulen T (1975) Polymerization kinetics and equilibria of silica acid in aqueous solution. Lawrence Berkeley Laboratory Report LBL-4415, University of California.

McCartney E R and Alexander E A (1958) Effect of additives on crystallization. J Crystallization of CaSO₄ *J. Colloid Science* 13, 383-396.

- McCutchan J and Sieder E (1968) Scale control in saline water evaporators: a review of current status. *Water* 1968, AIChE Symp. Series Vol. 64, pp. 255-269.
- McDowell H (1968) Solubility of CaHPO_4 and ion pair formation, Ph.D. thesis. Washington, DC: Howard University.
- McDowell H, Gregory T M and Brown W E (1977) Solubility of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ in the system $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ at 5, 15, 25 and 37°C. *J. Res. Nat. Bur. Stand.* 81A, 273-281.
- Meier D and Dubin L (1987) A novel approach to silica inhibition. *Corrosion* 87, Nace International, Paper No. 334, Houston, Texas.
- Meijer J A, van Rosmalen G M, Veenman A W and van diesel C M (1980) Scale inhibition of calcium sulfate by a fluidized bed. *Desalination* 34, 217-232.
- Mizutani S (1977) Progressive ordering of cristobalitic silica in the early stages of diagenesis. *Contrib. Mineral Petrol.* 61, 129-140.
- Montel G, Bonel G, Heughebaert J C, Trombe J C and Rey C (1981) New concepts in the composition, crystallization and growth of the mineral component of calcified tissue. *J. Crystal Growth* 53, 74-99.
- Morel F M M (1983) *Principles of Aquatic Chemistry*, p. 243. New York: J. Wiley and Sons.
- Moreno E C and Varughese K J (1981) Crystal growth of apatites from dilute solutions. *Crystal Growth* 53, 20-30.
- Moreno E C, Brown W E and Osborn G (1960) Stability of dicalcium phosphate dihydrate in aqueous solutions and solubility of octacalcium phosphate. *Soil Sci.* 24, 99-102.
- Morse R W and Knudsen J W (1977) Effect of alkalinity on the scaling of simulated cooling tower water, *Canad. J. Chem. Eng.* 55, 272-281.
- Mroczek E K and McDowell G (1990) Silica scaling: field experiments. *Trans. Geoth. Res. Council* 14 Pt II, pp. 1619-1635.
- Mullin J W (1993) *Crystallization*, 3rd edn, pp. 118-122. Oxford: Butterworth-Heinemann.
- Mullin J W, Chakraborty M and Mehtak K (1970) Nucleation and growth of ammonium sulphate crystals. *J. Appl. Chem.* 13, 423-429.
- Muratore E (1970) Growth of calcium sulfate deposits on a heated surface. These de doctorat, University of Grenoble, France (in French).
- Myerson A S (1993) Solutions and solution properties. In: *Handbook of Industrial Crystallization* (ed. A S Myerson), pp. 1-31. Boston, MA: Butterworth-Heinemann.
- Nancollas G H (1965) *Interactions in Electrolyte Solutions*, Amsterdam: Elsevier.
- Nancollas G H (1979) The growth of crystals from solution. *Advances in Colloid and Interface Science* 10, 215-252.
- Nancollas G H (1989) *In vitro* studies of calcium phosphate crystallization. In: *Biom mineralization* (eds S Mann, J Weloto and R J P Williams), pp. 157-187. New York: VCH Publishing.
- Nancollas G H and Mohan M S (1970) The growth of hydroxyapatite crystals. *Archs. Oral. Biol.* 15, 731-745.
- Nancollas G H and Purdie N (1963) Crystallization of barium sulfate in aqueous solutions. *Trans. Farad. Soc.* 9, 735-742.
- Nancollas G H and Tomazic B (1974) Growth of calcium phosphate on hydroxyapatite crystals. Effect of supersaturation and ionic medium, *J. Phys. Chem.* 78, 2218-2225.
- Nancollas G H, White W, Tsai F and Maslow L (1979) The kinetics and mechanism of formation of calcium sulfate scale minerals. The influence of inhibitors. *Corrosion* 35, 304-308.
- Nancollas G N and Purdie N (1964) The kinetics of crystal growth. *Quart. Rev. (London) Chem. Soc.* 18, 1-20.

- Narasaraju T S B and Phebe D E (1996) Some physico-chemical aspects of hydroxyapatite. *J.Mater.Science* 31, 1-21.
- Nathan Y (1984) The mineralogy and geochemistry of phosphorites. In: *Phosphate Minerals* (eds J O Nriagu and P B Moore), pp. 275-291. Berlin, Heidelberg: Springer Verlag.
- Nawaf Naif Al-Mutairi (master degree thesis ,2007),Fouling Studies and Control in Heat Exchangers ,KING SAUD UNIVERSITY,COLLEGE OF ENGINEERING Chemical Engineering Department
- Newesely H (1966) Changes in crystal types of low solubility calcium phosphates in the presence of accompanying ions. *Arch. Oral Biol. Sp. Suppl.* 6, 174.
- Nielsen A E (1984) Electrolyte crystal growth mechanisms. *J. Crystal* 67, 289-310.
- Nielsen A E and Toft J M (1984) Electrolyte crystal growth kinetics. *J. Crystal Growth* 67, 278-288.
- NIST (1998) Critically selected stability constants of metal complexes. NIST Standard Reference Database 46, v.5.0, Database Software developed by R J Motekaitis.
- Nordstom D K, Plummer L N, Wigley T M L, Wolery T J, Ball J W, Jenne E A, Basset R L, Crerar D A, Florence T M, Fritz B, Hoffman M, Holdren G R, Lafon G M, Mattigod S V, McDuff R E, Morel F, Reddy M M, Sposito G and Thraillkill J (1979) A comparison of computerized chemical models for equilibrium calculations in aqueous systems. In: *Chemical Modelling in Aqueous Systems. Speciation, Solubility and Kinetics* (ed. E A Jenne), pp. 857-982. ACS Symposium Series No. 93, ACS, Washington DC.
- O'Hara M and Reid R C (1973) *Modelling Crystal Growth Rates from Solution*. New York: Prentice Hall.
- Okomoto G, Okura T and Goto K (1957) Properties of silica in water. *Geochim. Cosmochim. Acta* 12, 123-132.
- Osman A. Hamed, Khalid B. Mardouf, Adnan Al-Omran (2007),Impact of interruption of antiscalant dosing or cleaning balls circulation during MSF plant operation *Desalination*, Volume 208, Issues 1-3, Pages 192-203
- Papelis C, Hayes K F and Leckie J O (1988) HYDRAQL: A program for the computation of the chemical equilibrium composition of aqueous batch systems including surface complexation modelling of ion adsorption at the oxide/solution interface. Tech. report 306, Stanford University, Stanford, CA.
- Patel J M, Gregory T M and Brown W E (1974) Solubility of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in the quaternary system $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-NaCl-H}_2\text{O}$ at 25°C. *J. Res. Nat. Bur. Stand.* 78A, 675-681.
- Pitzer K S (1979) Theory-ion interaction approach. In: *Activity Coefficients in Electrolyte Solutions*, Vol. 1 (ed. R M Pytkowitz), pp. 157-208. Boca Raton, FL: CRC Press.
- Posner A S (1969) Crystal chemistry of bone mineral. *Physiol. Rev.* 49, 760-792.
- Posner A S, Blumenthal N C and Betts F (1984) Chemistry and structure of precipitated hydroxyapatites. In: *Phosphate Minerals* (eds J O Nriagu and P B Moore), pp. 330-350. Berlin, Heidelberg: Springer Verlag.
- Rahman A A, Salem M and Nancollas G H (1995) The influence of some phosphonic acids on the crystal growth of calcium fluoride. In: *Mineral Scale Formation and Inhibition* (ed. Z Amjad), pp. 121-129. New York: Plenum Press.
- Reddy M M and Nancollas G H (1973) Calcite crystal growth and inhibition by phosphonates. *Desalination* 12, 61-73.
- Reddy M M and Nancollas G H (1976) The crystallization of CaCO_3 . IV. The effects of magnesium, strontium and sulfate ions. *J. Cryst. Growth* 35, 33-38.
- Roques H and Girou A (1974) Kinetics of the formation conditions of carbonate tartars. *Water Res.* 8, 907.
- Rothbaum H P, Anderson B H, Harisson R F, Rohde A G and Slatter A (1979) Effect of silica polymerization and pH on geothermal scaling. *Geothermes* 8, 1-20.
- Rousseau R W, Li K K and MacCabe W L (1976) The influence of seed crystal size on nucleation rates.

AIChE Symposium Series No. 153, 72, 48-52.

Sabbides Th G and Koutsoukos P G (1993) The crystallization of calcium carbonate in artificial seawater; role of the substrate. *Journal of Crystal Growth* 133, 13-22.

Sarig S (1974) Crystal habit modification by water soluble polymers. *J. Crystal Growth* 24/25, 338-341.

Sexsmith D R and Petrey E (1973) Use of polyelectrolytes for scale control in seawater evaporators. *Desalination* 13, 89-92.

Shyu L (1982) The solid/solution interface: a kinetic study of the crystallization of calcium fluoride and phosphate salts, Ph.D. thesis, Sunyab, Buffalo, NY.

Sikes C S and Wierzbicki A (1995) Mechanisms of regulation of crystal growth in selected biological systems, In: *Mineral Scale Formation and Inhibition* (ed. Z Amjad), pp. 193-206. New York: Plenum Press.

Smith B and Alexander E A (1970) Effect of additives on the process of crystallisation II calcium sulfate. *J. Colloid and Interface Science* 34, 81-90.

Smith B R and Hulin Y (1992) Influence of various factors on the performance of gypsum scaling retardants. *Water treatment* 7, 51-66.

Smith B R and Sweet F. (1971) The crystallization of calcium sulfate dihydrate. *J. Colloid and Interface Science* 12, 75-82.

Smith C W (1993) Usage of a polymeric dispersant for control of silica industrial water treatment. Littleton, CO: Tall Oaks Publ. Inc.

Smith R M and Martell A E (1981) Critical stability constants, Vol. 4. *Inorganic Complexes*. New York: Plenum Press.

Söhnel O and Garside J (1992) *Precipitation, Basic Principles and Industrial Applications*, p. 342. Oxford: Butterworth-Heinemann.

Söhnel O and Haldirova M (1984) *Cryst. Res. Technol.* 19, 477.

Söhnel O, Haldirova M and Macenauer J (1990) Kinetics of growth of calcite in presence of ammonium ions. *Cryst. Res Technol.* 25, 1367-1373.

Sosman R B (1965) *The Phases of Silica*. 388 pp. New Brunswick, NJ: Rutgers Univ. Press.

Standiford F C and Sinek W L (1961) Stop scale in seawater evaporators. *Chem. Eng. Prog.* 57, 58.

Stumm W and Morgan J J (1981) *Aquatic Chemistry*, 2nd edn, p. 448. New York: J. Wiley and Sons.

Sulmont B (1974) Precipitation of $Mg(OH)_2$ in solution. Ph.D. thesis, Grenoble University, Grenoble, France.

Symeopoulos B D and Koutsoukos P G (1993) Radioanalytical monitoring of formation of barium sulfate in aqueous solutions. *J. Radioanal. Nucl. Chem.* 173, 23-26.

Symeopoulos B D and Koutsoukos P G (1993) The use of radianalytical methods in nucleation and crystal growth studies. *Appl. Rad. Isot.* 44, 894-896.

Tamim Younos, Kimberly E. Tulou(2005) ,Overview of Desalination Techniques, Journal Of Contemporary Water Research & Education Issue 132, Pages 3-10

The Nalco Water Handbook (1988) (ed. F N Lemmer), pp. 4-15. New York: McGraw Hill Co.

Thordarson H and Tomasson T (1989) Brine clarification at Svartsengi, Iceland. Effect of pH and temperature on the precipitation of silica and its properties. *Geothermics* 18, 287-294.

Tomson M B and Nancollas G H (1978) Mineralization kinetics: a constant composition approach. *Science* 200, 1059-1060.

Truesdell A H and Jones B F (1974) WATEQ, A computer program for calculating chemical equilibria of natural waters, *J.Res. U.S.G.S.* 2, 233-274.

Tsuge H, Sugino Y, Takeda M and Matsumura T (1981) The threshold scale inhibition of calcium sulfate.

- Proceedings of the 9th Annual NSWIA Conference, Washington DC.
- Tung M S and Brown W E (1977) *Calcif. Tiss. Res.* 35, 783.
- Van der Leeden F, Troise F L and Todd D K (1990) Geraghty and Miller Groundwater Series: *The Water Encyclopedia*, 2nd edn. Chelsea Mich. Lewis Publishers, Inc.
- van der Leeden M C (1991) The role of polyelectrolytes in barium sulfate precipitation, Ph.D. thesis, 246 pp. Technical University of Delft, Delft. The Netherlands.
- van Rosmalen G M and Bennema P (1990) Characterization of additive performance on crystallization: additive performance. *J. Crystal Growth* 99, 1053-1060.
- van Rosmalen G M, Daudey P J and Marchéé W G J (1981) An analysis of growth experiments on gypsum crystal in suspension. *J. Crystal Growth* 52, 801-811.
- Veres O A, Lee A and Tsao L (1982) Equations and type curves for predicting the polymerization of amorphous silica in geothermal brine. *J. Soc. Petrol. Eng.* 22, 9-16.
- Volmer M (1939) *Kinetic der Phasenbildung*. Leipzig: Steinkopff.
- Walton A G and Hlabse T (1963) Growth kinetics of barium sulfate suspensions. 29, 249-255.
- Walton A G, Badin W J, Furedi H and Schwarz A (1967) Nucleation of calcium phosphate from solution. *Canad. J. Chem.* 45, 2696-2701.
- Wannesson J (1963) Geochemical properties of silica. *Compt. Rend.* 256, 2888-90.
- Watkinson A P (1988) Water quality effects on fouling from hard waters. In: *Heat exchanger sourcebook* (ed. J W Palan), pp. 850-861. Washington, New York and London: Hemisphere Publ. Co.
- Watkinson A P and Martinez O (1975) Scaling of heat exchanger tubes by CaCO_3 , *Trans. ASME J. Heat Transfer* 97, 504-514.
- Weijnen M P C (1984) The influence of additives on the crystallization of gypsum. Ph.D. thesis, University of Delft, Delft, The Netherlands.
- Weijnen M P C and Van Rosmalen G M (1985) The influence of various polyelectrolytes on the precipitation of gypsum. *Desalination* 54, 239-261.
- Weijnen M P C and van Rosmalen G M (1986) Absorption of phosphonates on gypsum crystals. *J. Cryst. Growth* 79, 157-168.
- Weimarn P P (1926) The precipitation laws. *Chem. Reviews* 2, 217-242.
- Westall J, Zachary J L and Morel F (1976) MINEQL, a computer program for the calculation of chemical equilibrium composition of aqueous systems, Technical Note No. 18, Ralph Parsons Lab., MIT, Cambridge.
- Wiechers H N S, Sturrock P and Marais G V R (1975) CaCO_3 crystallization kinetics. *Water Res.* 9, 835-845.
- Xyla A G and Koutsoukos P G (1987) Effect of diphosphonates on the precipitation of calcium carbonate in aqueous solutions. *J. Chem. Soc. Farad. I* 83, 1477-1485.
- Xyla A G and Koutsoukos P G (1988) Spontaneous precipitation of calcium carbonate in aqueous solutions at sustained supersaturation In: *Proceedings of Jigastock '88*, Vol. 2, p. 693-697, Versailles, France.
- Xyla A G and Koutsoukos P G (1989) Quantitative analysis of calcium carbonate polymorphs by IR spectroscopy. *J. Chem. Soc. Farad. I* 85, 3165-3172.
- York S A and Schorle E S (1966) *Principles of Desalination* (ed. K D Spiegler), Ch. 10, pp. 627-676.
- Zawacki S J, Koutsoukos P G, Salimi M H and Nancollas G H (1986) The growth of calcium phosphates In: *Geochemical Processes at Mineral Surfaces*, ACS Special Publication series No. 323 (eds J Adavis and K F Hayes), pp. 650-662. Washington DC: American Chemical Society.