Nucleation and Kinetics of Mixed Salts in Scaling

Roya Sheikholeslami
School of Chemical Engineering and Industrial Chemistry, The University of New South Wales,
Sydney, 2052 Australia

During membrane and thermal desalination, the saline solution becomes supersaturated. Once the solution becomes unstable, nucleation and crystallization of the salts occur resulting in a buildup of an unwanted deposit layer on transfer surfaces and increasing the mass- or heat-transfer resistance of the system and the energy input for producing water. Due to the process complexity, research focused primarily on single salt fouling and applying the nucleation and kinetics of a single system in developing physical models for precipitation (crystallization) fouling. This article demonstrates that single salt nucleation and crystallization kinetics applied so far to crystallization fouling cannot be extended to real situations when a combination of various salts and solutes are present. Other noncrystallizing species, if present, may affect the surface energy of a crystal and alter the Gibbs free energy for homogeneous nucleation. Other crystallizing species may also act as a nucleus initiating nonhomogeneous nucleation with a lower Gibbs free energy and promoting nucleation. The presence and catalytic and inhibitory effects of dissolved and solid species on metastability of the solution should be considered in kinetic analysis of crystallization fouling. Kinetic relationships developed take into account the kinetics of coprecipitating salts with and without a common ion and in the presence of other soluble species. They can be easily extended to multiprecipitating systems, but further advances in experimental techniques are necessary to integrate the kinetic analysis and experimental data.

Introduction

Fouling stages and mechanisms are classified by Epstein (1983) in terms of a 5×5 matrix of which induction, transport, attachment, aging, and removal are five stages of fouling. Crystallization/precipitation fouling (scaling), particulate fouling, biological fouling, corrosion fouling, and chemical reaction fouling are five different mechanisms of fouling. Scaling is one of the major and undesirable phenomena in the operation of reverse osmosis membranes and thermal desalination systems. Although crystallization is the underlying mechanism for scale formation, the process of scale formation in heat exchangers and membranes is quite different from that in industrial crystallizers. Once the salt concentration exceeds its saturation limit, it promotes fouling that is the accumulation of undesired solid materials at the phase interfaces and increases the resistance to heat or mass transfer. For precipitation to occur next to the heat- and mass-transfer surface, the solution has to become supersaturated, but not necessarily all supersaturated solutions will precipitate. Solutions can remain supersaturated for a long time or infinitely and this condition is called metastability, where the solution is supersaturated, but nucleation does not take place. Once the nucleation starts, the solution is called unstable. Of course, it should be noted that metastability in batch or continuous crystallization is not the same as that for scaling. In the operation of reverse osmosis and thermal desalination units, the solution becomes concentrated and the main limiting factor is the degree of supersaturation that the solution can tolerate before becoming unstable. Also, once the nucleation occurs, it is desirable to limit and reduce the rate of precipitation. Therefore, it is of paramount importance to the operation of reverse osmosis and thermal desalination units to assess the time that the solution remains metastable, as well as the nucleation rate and the precipitation kinetics.

Modeling crystallization fouling is different from that in industrial crystallizers. This article intends to address issues of concern to crystallization fouling, not industrial crystalliza-

---

Correspondence concerning this article should be addressed to R. Sheikholeslami.

tion. The application of the population balance method, as is done in industrial crystallizers, has been investigated in bulk precipitation resulting in particulate deposition (Kostoglou and Karabelas, 1998) and its use is not relevant in the case of wall crystallization fouling. In analysis and modeling crystallization fouling, kinetics is incorporated in the attachment stage, usually in terms of an elementary reaction; as such, there are no granular aspects. Also, there are no stirring effects, as one would expect in industrial crystallizers; in scaling, velocity effects and flow hydrodynamics are incorporated in the transport and removal stages. The effect of crystal structure and strength is incorporated in the removal stage of fouling. Therefore, the reader should bear in mind that although in scaling one would talk about the crystallization kinetics, it is not in the same context as it is in industrial crystallizers.

Due to the complexity of the fouling process, it is customary, but with little success, to use the single salt nucleation and kinetics for sparingly soluble salts in assessing the scaling condition in real waters where mixtures of precipitating and nonprecipitating salts are present; recent investigations (Sudmalis and Sheikholeslami, 2000; Chong and Sheikholeslami, 2001; Sheikholeslami and Ng, 2001; and Yu et al., 2002) show that the presence of other soluble or precipitating salts affect the precipitation of other salts and single salt data and are not applicable to solution mixtures. To mitigate fouling, it is very important to predict the solution metastabilty, nucleation rate and kinetics of precipitation in real feedwater and to modify and optimize the process accordingly.

It should be emphasized that the subject of industrial crystallization, its kinetics and effect of various parameters including impurities on it is well studied (Mullin, 1972, 1993; Nyvlt et al., 1985; Davey, 1979; Davey and Garside, 2000; Sohnel and Garside, 1992; Sangwal, 1999; Furedi-Milhofer and Sarig, 1996; Buckley, 1951). However, Hasson (1981, 1999) reviewed the research work on crystallization fouling (scaling) in the last 20 years and established that almost all the work has been done when a single foulant is present and as well as the fact that there are contradictory results under seemingly similar conditions. Recent works of the author's (Sudmalis and Sheikholeslami, 2001; Chong and Sheikholeslami, 2001; Sheikholeslami and Ng, 2001; Yu et al., 2001, 2002) on co-precipitation and composite scale formation address solubility effects, rate data, crystal structure and strength, and also dynamic effects. Mixed salt investigations are of importance because first the mechanism of fouling might be different for different salts (Gill and Sheikholeslami, 1997) and second as referenced above the single salt data might not be applicable to the condition when the salts co-exist.

Scale formation is usually due to the presence of ionic solutes and reactions, however, there are cases where deposit/scale formation is due to a nonionic reaction (such as silica polymerization) in an aqueous solution that usually contains ionic compounds. However, there is ample evidence (Krauskopf, 1956; Iler, 1979; Marshall and Warakomski, 1980; Chen and Marshall, 1982; Chan et al., 1987) that the presence of ions and the type of ions affect the rate of polymerization, no systematic assessments of the nucleation and polymerization in the presence of other ionic species has been carried out.

Systematic approaches are necessary to incorporate the effect of the presence of other soluble or precipitating salts in scaling from mixed salt solutions. Recent publications of the author's (Chong and Sheikholeslami, 2001; Sheikholeslami and Ng, 2001; Sheikholeslami, 2001, 2002) show the effect of the presence of other ions and salts on the morphology and crystal structure and propose systematic approaches to examine the thermodynamics of co-precipitation. This article establishes that single salt nucleation and kinetics for sparingly soluble salts based on Nancollas' approach (1971) that have been normally applied to scaling are not applicable to mixed salt solutions and proposes strategies to assess nucleation and kinetics of scaling in the presence of other ionic, nonionic and precipitating species; our investigations clearly support that a basic approach considering the nucleation and reaction kinetics in mixed solutions is necessary for the assessment of scaling in feedwater when mixed species are present.

Experimental Methods

Mixed salt experiments were carried out with various model systems using different compounds, concentrations, temperatures, pH values, stirring rates, and in batch constant volume reactors and in dynamic systems. A dynamic system refers to either a continuously operating reverse osmosis unit or a heat exchanger unit in which crystallization fouling is being investigated, while occurring on the membrane or on the heat exchanger surface. Solution matrices were mixtures of calcium carbonate and calcium sulfate at various proportions and degrees of dominance, of calcium oxalate and silica, and also of silica in the presence of noncrystallizing and crystallizing salts. As mentioned earlier, some of the experiments were carried out in constant volume batch reactors, others in dynamic systems either in heat exchangers under thermal gradients or in reverse osmosis units. The solutions were prepared with analytical grade chemicals and with microfiltered (with 0.22 μm Millipore filter) distilled water. The specifics of solution preparation, analytical techniques, and the batch and dynamic setups are discussed in detail elsewhere (Sudmalis and Sheikholeslami, 2000; Chong and Sheikholeslami, 2001; Sheikholeslami and Ng, 2001; Yu et al., 2001, 2002; Sheikholeslami et al., 1999; Koo and Sheikholeslami, 2001; Sheikholeslami and Zhou, 2000; Sheikholeslami and Tan, 1999). As mentioned earlier, effect of various parameters were investigated, however, the results discussed in this article only compare the effect of foulant species under otherwise identical conditions. The results were reproducible.

Results and Discussion

In the model solutions components were used such as $CaCO_3$, $CaSO_4$, CaC_2O_4, and SiO_2 that are commonly found in scale deposits. Some solutions also contained nonprecipitating soluble salts that are commonly found in feedwater supplies, and the results, both in batch and dynamic systems, showed that the existence of soluble salts and also crystallization of one salt clearly affected crystallization of the other salt. Alteration of the induction period, metastability of the solution, nucleation, and kinetics of precipitation of one salt in the presence of other soluble or crystallizing salts will be discussed in the following section.

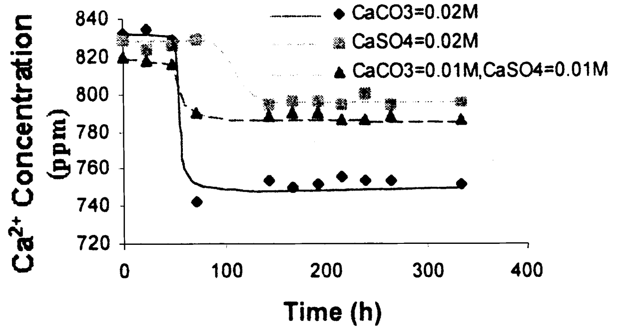


Figure 1a. Effect of composition on the induction for 0.002 M Ca in pure and mixed solutions (Sudmalis and Sheikholeslami, 2000).

Nucleation

The most common mechanism by which a solid will precipitate out of a solution is crystallization. Supersaturation is a prerequisite for the formation of a nucleus leading to precipitation or crystal formation. Once the solution becomes supersaturated, nucleation may not occur immediately and the solution may remain supersaturated without the formation of crystals; this supersaturated solution is called a metastable solution. The metastability will usually persist for a period of time called the induction period before nucleation and crystal formation occurs. The induction period is salt specific. For example, the induction period for $CaSO_4$ is much longer than that of $CaCO_3$ in single salt crystallization. It also depends on the degree of supersaturation of the precipitating salt. Our experiments have shown that the presence of other soluble and crystallizing species does indeed affect the induction period. Detailed discussions of various systems are provided elsewhere (Sudmalis and Sheikholeslami, 2000; Chong and Sheikholeslami, 2001; Sheikholeslami and Ng, 2001; Yu et al., 2002; Koo and Sheikholeslami, 2001; Sheikholeslami et al., 2001), but some representative results are presented and discussed here.

Representative results for two precipitating salts (calcium carbonate and calcium sulfate) are shown in Figure 1. Induction periods for mixed solutions are compared with those of pure salts for solutions with a total Ca content of 0.01 M (Figure 1a) and 0.02 M (Figure 1b); the induction period in the mixed solutions followed the same time pattern as that observed in pure $CaCO_3$ solutions. It suggests that, once the $CaCO_3$ is formed, it then acts as a nuclei for the formation of $CaSO_4$. Figure 2 shows the effect of a neutral nonprecipitating salt, and, therefore, only the ionic strength on the induction period of a precipitating salt ($CaSO_4$). The induction period of $CaSO_4$ is investigated by monitoring the depletion of both precipitating ionic species (Figures 2a and 2b). The results indicated the induction period for precipitation from 0.05 M solutions of $CaSO_4$ to increase from 8 h to 20 h, and to 100 h, for, respectively, 0.1 M, 0.2 M and for 0.5 M NaCl solutions. The effect of crystallizing and noncrystallizing species on the induction period of silica polymerization are, respectively, shown in Figures 3 and 4. Silica solution of approximately 400 ppm was metastable for up to approximately 250 h; however, the presence of 200 ppm of crystallizing calcium oxalate monohydrate (COM) induced polymerization almost instantaneously (Figure 3). Another investigation (Figure 4) showed the effect of dissolved salts on the induction period of 360 ppm of silica solution. The induction period decreased from 45 h for 400 ppm of $CaCl_2$ to 30 h for 400 ppm of $MgCl_2$, and further to 10 h in the presence of 400 ppm of $CaCO_3$. These results can be explained in terms of the thermodynamics of crystallization.

Crystallization is generally considered to be a three step process: nucleation, growth, and recrystallization; however, this is a simplification of the actual situation, as these three steps may greatly overlap during the crystallization process. The nucleation itself is subdivided to primary and secondary nucleation. In the case of sparingly soluble salts, primary nucleation is the main mechanism. Primary nucleation can be homogeneous where the crystals are formed without the aid of foreign bodies or surfaces, or heterogeneous where other substances aid the nucleus formation. The Gibbs free energy of formation is less for heterogeneous nucleation than that of homogeneous nucleation.

For a supersaturated solution, the chemical potential of the crystallizing compound in the solution (state 1) is higher than that in the solid phase (state 2) or that at saturation, and

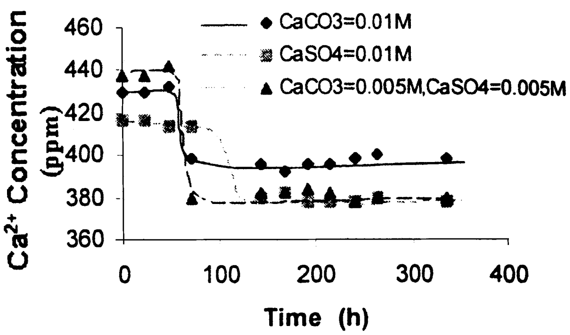


Figure 1b. Effect of composition on the induction for 0.001 M Ca in pure and mixed solutions (Sudmalis and Sheikholeslami, 2000).

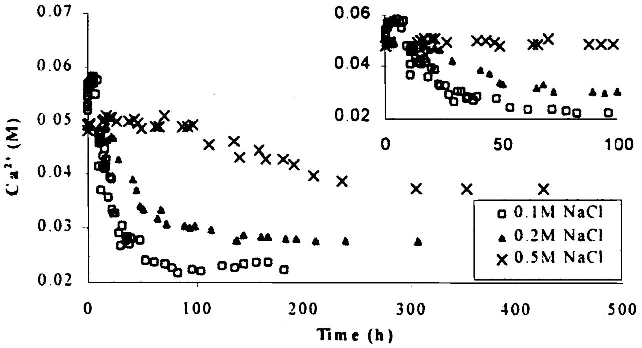


Figure 2a. Precipitation of $CaSO_4$ in the presence of NaCl as monitored by reduction in calcium ion concentration.

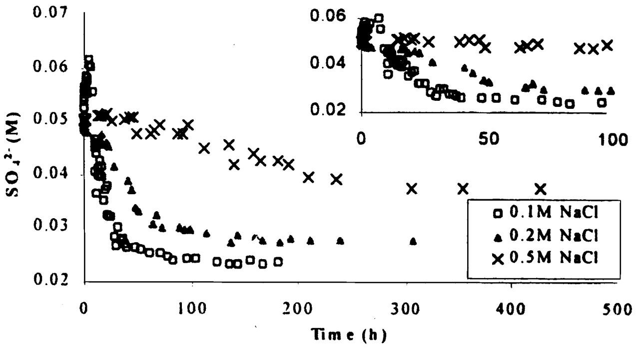


Figure 2b. Precipitation of $CaSO_4$ in the presence of NaCl as monitored by reduction in sulfate ion concentration.

there is a driving force for the formation of the nuclei and, thus, bringing the system into equilibrium; this would involve the release of energy. However, energy is required for the formation of the solid phase and a surface and net rate of change in the Gibbs free energy of the system is shown in Eq. 1

$$\Delta G_{\text{homo}} = +\Delta G_{\text{surface}} - \Delta G_{\text{supsat'n}} = +\sigma A_n - n(\mu_1 - \mu_2) \tag{1}$$

Replacing the relationship (Atkins, 1995) for chemical potential μ in Eq. 1 would result in Gibbs free energy for homogeneous nucleation in terms of activity a, the number of molecules in the nucleus n, the surface area of nucleus A_n, the surface energy σ (J/m^2), the volume of nucleus V, volume of a single crystal V_m (m^3/molecule), the Avagadro number ($N = 6.023 \times 10^{23}$ molecules/mol), and the Boltzmann constant ($k = R/N$)

$$\Delta G_{\text{homo}} = +\sigma A_n - \frac{V}{V_m}\frac{1}{N} RT \ln\left(\frac{a_1}{a_2}\right) \tag{2}$$

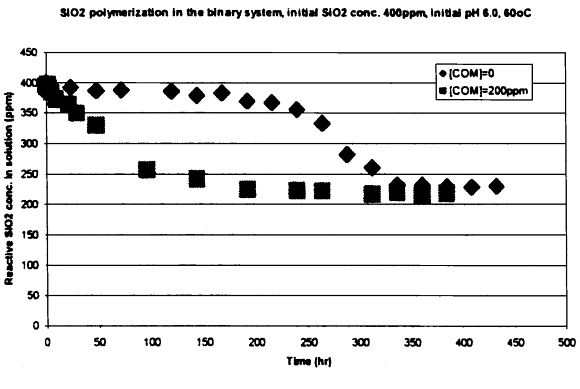


Figure 3. Polymerization of silica in the presence and absence of COM precipitation.

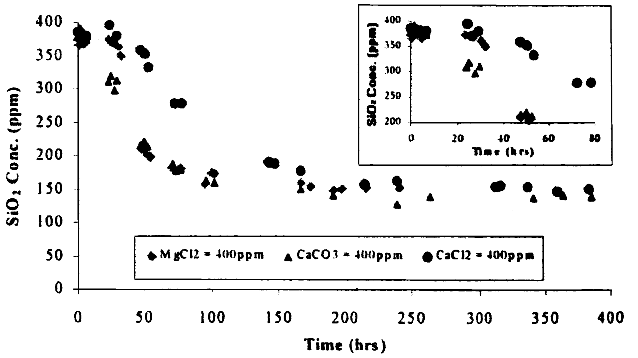


Figure 4. Polymerization of silica in the presence of dissolved salts.

Activity can be related through the activity coefficient γ to concentration c for a nonelectrolyte by Eq. 3 and for an electrolyte such as A_xM_y, there will be x cations and y anions produced in the solution ($A_xM_y \rightleftharpoons xA^{z+} + yM^{z-}$) by Eq. 4

$$a = c\gamma \tag{3}$$

$$a = \left\{(x^x y^y)^{1/(x+y)} c\gamma_{\pm}\right\}^{(x+y)} \tag{4}$$

Replacing activity from Eq. 4 for an electrolyte in Eq. 2 will result

$$\Delta G_{\text{homo}} = +\sigma A_n - \frac{V}{V_m}\frac{1}{N}(x+y) RT \ln\left(\frac{c_1\gamma_{\pm,1}}{c_2\gamma_{\pm,2}}\right) \tag{5}$$

The parentheses in Eq. 5 is supersaturation S. Mostly, it is assumed that the ratio of activity coefficients for supersaturated ($\gamma_{\pm,1}$) and saturated ($\gamma_{\pm,2}$) states are unity, and, therefore, the concentration and activity ratios would be the same. When the concentration ratio is less than unity, the solution is not supersaturated and there is no chemical potential and no driving force for the formation of a nuclei. When the concentration ratio is above unity, there is a chemical potential for the formation of a nuclei, but the energy required for the formation of the surface should be overcome before a nucleus could be formed. Once the energy for the formation of the surface is overcome, ΔG_{homo} becomes positive and the nucleus will form, but it may redissolve. The ΔG_{homo} increases from zero to a maximum until it reaches a critical value (ΔG^*_{homo}) at which the nuclei will not redissolve. So, if the radii of a nucleus is less than r^*, it will have to either continue to grow toward the critical radius or to dissociate into its component molecules. This will continue until the size of the nucleus (or the number of molecules in the nucleus) reaches a critical value. After that point, an increase in the nucleus size will be more effective in increasing the right term $\Delta G_{\text{supsat'n}}$ in Eq. 2 and, therefore, the ΔG_{homo} decreases. The energy barrier for nucleation corresponds to the value of ΔG_{homo} for critical nucleus size ΔG^*_{homo}. Therefore, the rate of nucleation can be defined by an Arrhenius relationship shown by Eq. 6

$$J_{\text{homo}} = \Omega \cdot \exp(-\Delta G^*_{\text{homo}}/kT) \tag{6}$$

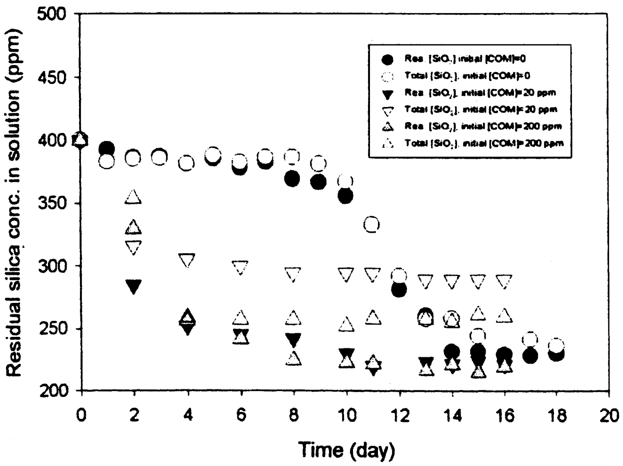


Figure 5a. Effect of COM on the kinetics of SiO_2 polymerization (Yu et al., 2001).

"Rea" stands for reactive.

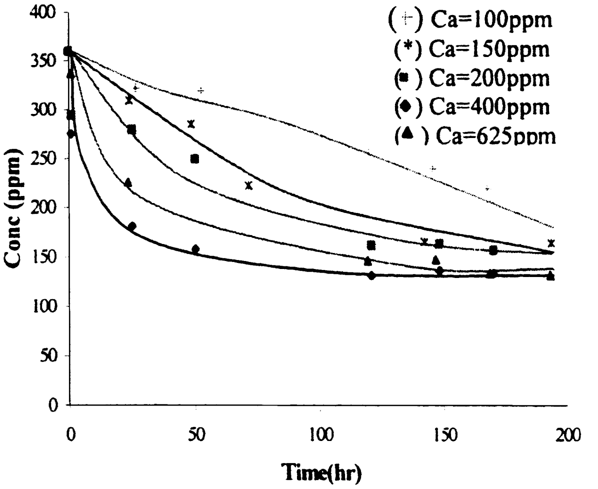


Figure 6. Effect of $CaCl_2$ concentration (as $CaCO_3$) on silica polymerization from solutions with initial $SiO_2 = 360$ ppm (Sheikholeslami et al., 1999).

where $\Omega(s^{-1} \cdot m^{-3})$ is the preexponential term (a function of diffusivity and interplanar distance in crystal lattice), and k is the Boltzmann constant and T is the temperature. Considering a spherical nucleus, ΔG^*_{homo} can be determined by replacing A with $k_a r^2$ and V with $k_v r^3$ in Eq. 2 and then differentiating with respect to r and equating it with zero, obtaining r^* and then replacing that in Eq. 2

$$r^* = \frac{2k_a V_m \sigma}{3k_v[kT(x+y)\ln(S)]} \tag{7}$$

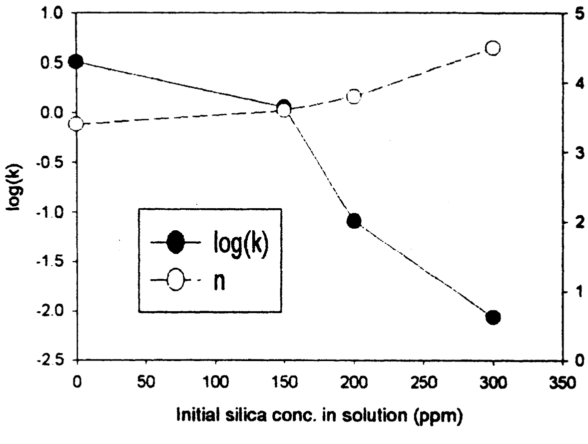


Figure 5b. Changes in the rate constant (k) and order of reaction (n) for COM precipitation in binary systems as a function of initial silica conc., at initial COM conc. 150 ppm, pH 8.0 and at 60°C (Yu et al., 2001).

$$\Delta G^*_{\text{homo}} = A_n \cdot \sigma - \frac{V^*}{V_m} kT(x+y)\ln(S) = \frac{\beta V_m^2 \sigma^3}{[kT\nu \ln(S)]^2} \tag{8}$$

Where $\beta = (4k_a^3/27k_v^2)$ is the geometric factor and values are available in the literature (Nyvlt et al., 1985) for different crystallites, and ν is the total number of ions $(x+y)$ produced when the solute is dissociated (that is, $\nu = 2$ for $CaCO_3$), and, therefore, it would be unity for nonelectrolytes. The induction time for nucleation is inversely related to the rate of nucleation (Mullin, 2001) and the B (m^{-3}) is the proportionality constant and k (J/K) the Boltzmann constant.

$$t_{\text{ind}} = \frac{B}{J} = B\Omega^{-1} \exp\left(\frac{\Delta G^*_{\text{homo}}}{kT}\right) \tag{9}$$

$$\ln t_{\text{ind}} = A' + B' \frac{\sigma^3}{T^3 \nu^2 (\ln S)^2} \tag{10}$$

where $A' = \ln B\Omega^{-1}$ and $B' = (\beta V_m^2/k^3)$. In practice, homogenous nucleation is virtually impossible to attain. Melia (1965) reported many cases of spontaneous nucleation and upon further examination concluded that nucleation had been induced in some way. Since heterogenous nucleation takes place at a lower critical supersaturation than homogenous nucleation, the overall free energy change is less. Mathematically, a constant less than unity (ϕ) can relate the Gibbs free energies for homogeneous and heterogeneous nucleation (Mullin, 2001). Sohnel and Garside (1992) provide a relationship for ϕ as a function of the wetting angle (Θ) of the foreign solid phase by the liquid. Therefore, the above homogeneous thermodynamic analysis is extended to heterogeneous nucleation by Eq. 11

$$\Delta G^*_{\text{hetro}} = \phi \cdot \Delta G^*_{\text{homo}} = \frac{(2 - 3\cos\Theta + \cos^3\Theta)}{4} \Delta G^*_{\text{homo}} \tag{11}$$

In the case of species that coprecipitate, three possibilities may exist. One is that the first precipitating salt can act as a foreign matter and reduce the energy barrier, and, therefore, the induction time for the formation of the other precipitating species as seen in Figures 1 and 3. The second is that final precipitate obtained from two coprecipitating salts will have a morphology and structure different from that in pure condition (Sudmalis and Sheikholeslami, 2000; Chong and Sheikholeslami, 2001; Sheikholeslami and Ng, 2001; Yu et al., 2002; Sheikholeslami, 2002; and Sheikholeslami et al., 2002). Also, altering the crystal structure affects the interplanar distance in the crystal lattice, and, hence, the preexponential term in Eq. 6 and, hence, change the rate of nucleation and the induction time. The third is that the presence of one precipitating salt affects the solution thermodynamics and, as such, the induction time period. The effect of coprecipitating salts on the induction has been experimentally seen (Sodmalis and Sheikholeslami, 2000; Chong and Sheikholeslami, 2001; Sheikholeslami and Ng, 2001; Yu et al., 2002 and Sheikholeslami, 2002) and very few results are shown in Figures 1a, 1b, and 3.

In case the other species present in the solution remain soluble, their mere presence may affect the induction period and nucleation through their effect on:

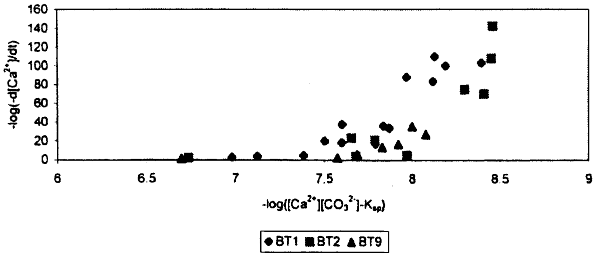
(1) The supersaturation (S) as seen for precipitation of ionic salts in the presence of soluble ionic species with and without a common ion. The representative results for the condition without a common ion are shown in Figures 2a and 2b.

(2) The surface energy σ for the formation of crystal, and, hence, the critical Gibbs free energy for nucleation as seen in the precipitation of ionic salts in the presence of soluble nonionic species such as the case with antiscalants.

In the case of silica polymerization in the presence of soluble ionic species (Figure 4), a combination of both (1) and (2) above may take part as the ionic species attract some of the water molecules due to hydration, and, therefore, reduce the amount of the effective available solute and, as such, increase the effective supersaturation. The soluble salts may also reduce the critical Gibbs free energy by catalytic effects (Sheikholeslami et al., 1999; Sheikholeslami and Tan, 1999) and, therefore, reduce the observed induction period.

Growth and kinetic analysis

Two mechanisms of diffusion and surface integration (2-D nucleation such as mononuclear and polynuclear nucleation, and screw dislocation) have been proposed and discussed in detail by Sohnel and Garside (1992) for growth. Reddy and Nancollas (1971a,b) proposed growth governed by a chemical reaction for sparingly soluble salts. These techniques were employed and discussed in detail (Chong and Sheikholeslami, 2001; Sheikholeslami and Ng, 2001; Yu et al., 2002; Sheikholeslami and Tan, 1999; Koo and Sheikholeslami, 2000; Sheikholeslami et al., 2000) in kinetic analysis of the mixed systems; the results indicate that the presence and precipitation of one salt clearly affected the rate and order of reaction of the second salt. Even the presence of soluble ionic species was shown to affect the kinetics of scale formation by changing both the order and the rate of reaction (Koo and Sheikholeslami, 2000; Sheikholeslami et al., 2001). Some of the results are shown in Figures 5 to 8. The presence of COM not only reduced the induction period in silica polymerization, as discussed previously, but also increased the rate of polymerization of silica (Figure 5a); the presence of silica reduced the rate constant for surface integration, while increasing the order of reaction (Figure 5b). The kinetics of silica polymerization in the presence of dissolved soluble species of $CaCl_2$ is shown in Figure 6 indicating the polymerization rate to generally increase with increases in calcium content.


(a) Including the initial surge

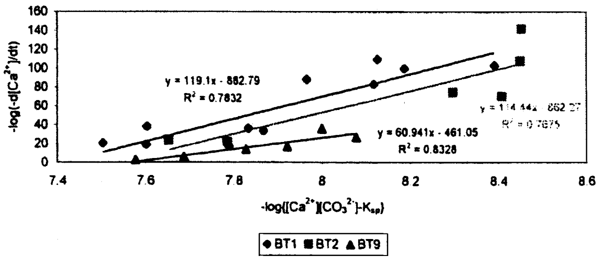

(b) Excluding the initial surge

Figure 7. Assessment of rate of precipitation for calcium carbonate in presence of calcium sulfate (■ at 60°C, ◆ at 70°C, and ▲ at 80°C).

(a) Including the initial surge; (b) excluding the initial surge (Chong and Sheikholeslami, 2001).

The Reddy and Nancollas (1971a,b) approach was applied to mixtures of calcium carbonate and calcium sulfate in solutions with varying degrees of dominance of each salt. In a predominantly $CaCO_3$ solution (Figure 7), the mixtures did not obey the Reddy and Nancollas (1971a,b) approach and no linear relationship with a slope of unity was obtained either when the initial surge period (period of very rapid nucleation) was included (Figure 7a) or even when it was excluded (Figure 7b). In mixed solutions where $CaSO_4$ was dominant (Figure 8), only the rate of depletion of total calcium could be approximated as a second order (Figure 8a) and the rate of consumption of sulfate was only a second order when the solution was purely calcium sulfate or had only minute amounts (0.002 M) of calcium carbonate (Figure 8b).

It has long been recognized that kinetics of nucleation depends on the presence of foreign bodies and seeds, thus causing catalytic effects. However, when one comes to assess the kinetics of scale forming salts, it is still customary to apply the single salt precipitation to that when mixed species are present. The authors work has clearly shown that kinetics of single salt data are not extendable to mixed systems and, as

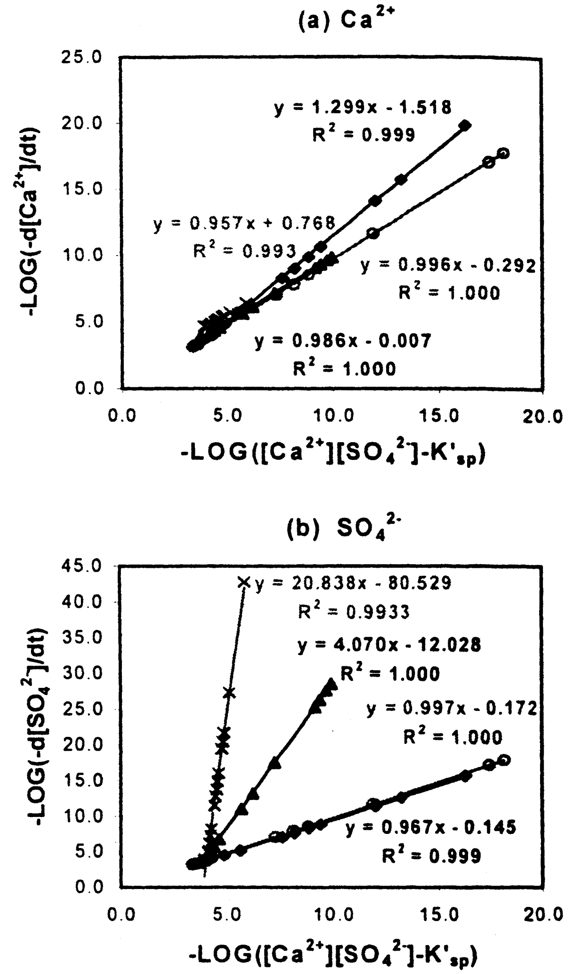


Figure 8. Assessment of rate of precipitation using Nancollas method (◆ for pure $CaSO_4$, ○ with 0.002 M $CaCO_3$, ▲ with 0.008 M $CaCO_3$, × with 0.01 M of $CaCO_3$; all solutions with total Ca of 0.03 M.

(a) Based on Ca; (b) based on sulfate depletion (Sheikholeslami and Ng, 2001).

such, development of a general approach for kinetics of precipitation in mixed salt solution is necessary.

To obtain a method of kinetic analysis for solutions containing mixed crystallizing ionic species, the author proposes to extend the general approach for kinetics of reaction crystallization, which was originally proposed by Klein and David (1995) for a single salt to encompass co-precipitating solutions. The basic chemical reaction crystallization leading to the formation of an insoluble material can be expressed (Klein and David, 1995) in terms of the stoichiometric equation

$$S_A A + s_B B \underset{k_d}{\overset{k_r}{\rightleftharpoons}} s_s S + s_n N \tag{12}$$

where A and B are the reactants, S is the solid product, N is the nonsolid byproduct, s represents the stoichiometric number for each component, and k_r and k_d are the rate constants for reaction (formation) and dissolution. The kinetics of the previous reaction in a batch reactor can be defined in terms of the reaction extent χ according to Eqs. 13 to 16

$$n_A = n_A^0 - s_A \chi \tag{13}$$

$$n_B = n_B^0 - s_B \chi \tag{14}$$

$$n_S = n_S^0 + s_S \chi \tag{15}$$

$$n_N = n_N^0 + s_N \chi \tag{16}$$

where n^0 and n, respectively, represent the number of moles of each substance at time zero and at any given point in time. The rate of reaction r is the variation of the reaction extent χ per unit time t per volume V as shown by Eq. 17

$$r = \frac{1}{V}\frac{d\chi}{dt} = k_0 \exp\left(\frac{-E}{RT}\right) C_A^{\alpha} C_B^{\beta} C_S^{\delta} C_N^{\eta} C_{OS}^{\nu s} C_{ON}^{\nu n} \tag{17}$$

where $k_r = k_0$ exp$(-E/RT)$ is the temperature-dependent reaction constant, C represents the concentration of each substance, and the exponents are the reaction partial orders. In the above equation, C_{OS} and C_{ON}, respectively, represent the concentration of other solid and other nonsolid species present, and if they are catalytic to the reaction, νs and νn are positive and if inhibitory, then the exponents are negative. If δ and η are negative, the reaction is auto inhibitory, if they are positive, the reaction is auto catalyzing and if they are equal to zero the reaction is neither auto inhibited nor is it auto catalytic. For the last case where neither catalytic and nor inhibitory effects are present, Eq. 17 can be further simplified to

$$r = k_r C_A^{\alpha} C_B^{\beta} \tag{18}$$

The net rate of crystallization is the rate of reaction for solid formation less of dissolution and, therefore, is shown by Eq. 19

$$R_{\text{cryt. growth}} = k_r \left[C_A^{\alpha} C_B^{\beta} - K_{SP} \right] \tag{19}$$

where K_{SP} is the concentration product at equilibrium. In the case of coprecipitating salts, Eq. 17 can be written for each salt, but it cannot be simplified to Eq. 18 because the presence of one salt might have a catalytic or inhibitory effect on the other. This is actually the case used in the author's studies (Chong and Sheikholeslami, 2001; Sheikholeslami and Ng, 2001; Yu et al., 2001 and Sheikholeslami et al., 2001). Therefore, Eq. 19 that usually is used for precipitation of a single sparingly soluble salt cannot be employed in the case of coprecipitating salts.

Applying the same procedure that was described earlier for single solid phase precipitation, and for a simple case when the stoichiometric numbers are unity, one can write the relationships for coprecipitation. Therefore, Eqs. 23–32 would describe the relationship when there is a common ion, while Eqs. 35–45 are used when coprecipitation does not involve a common ion. In these equations, S_1 and S_2 represent solids coprecipitating with each other, and $X_1 = \chi_1/n_A^0$ and $X_2 = \chi_2/n_C^0$. The rates of formation for S_1 and S_2 are shown, respectively, by r_1 and r_2. It can safely be considered that the reactions are not autoinhibitory or autocatalytic but the effect of the second solid phase and, in some cases, the effect of soluble material, cannot be ignored. Therefore, the rate equations for formation can only be simplified partially, as shown by Eqs. 33, 34, 44, and 45. The exponent describing the catalytic effect of the second solid phase νs can be defined as a function of the wetting angle Θ of the second solid phase, and, therefore, ϕ, as shown in Eq. 11 and it can be approximated by equating the rate of nucleation and growth for each of the homogeneous (Eq. 20) and nonhomogeneous (Eq. 21) conditions, taking their ratio and replacing ΔG^*_{homo} from Eq. 8

$$J_{\text{homo}} = k_r C_A^{\alpha} C_B^{\beta} = \Omega \exp\left[\frac{-\Delta G^*_{\text{homo}}}{kT}\right] \tag{20}$$

$$J_{\text{nonhomo}} = k_r C_A^{\alpha} C_B^{\beta} C_s^{\nu s} = \Omega \exp\left[\frac{-\phi \Delta G^*_{\text{homo}}}{kT}\right] \tag{21}$$

$$\nu s = \frac{\beta V_m^2 \sigma^3}{kT[kT\nu \ln(S)]^2 \ln C_S}(1-\phi) \tag{22}$$

The dissolution rates can be incorporated and subtracted from the crystal formation rates in order to obtain the net rate of crystallization. Therefore, to obtain the rate of crystallization and the partial order with respect to all the components, one should know the instantaneous concentrations for ions and the solid phases in the solution, as well as the solubility constants of the salts when they co-exist. Hence, this is the information required in order to be able to determine coprecipitation kinetics. The discussion earlier can be expanded to multiprecipitating species. The only challenge is the determination of instantaneous solid properties and concentration that will become practical with future advances in optical measurement.

Reactions for Coprecipitation in Mixed Salt Solutions

Without Common Ion

$$s_A A + s_B B \rightleftharpoons s_{S1} S_1 + s_{N1} N_1 \tag{23}$$

$$s_C C + s_D D \rightleftharpoons s_{S2} S_2 + s_{N2} N_2 \tag{24}$$

$$n_A = n_A^0(1 - X_1) \tag{25}$$

$$n_C = n_C^0(1 - X_2) \tag{26}$$

$$n_B = n_B^0(1 - X_1) \tag{27}$$

$$n_D = n_D^0(1 - X_2) \tag{28}$$

$$n_{S1} = n_A^0 X_1 \tag{29}$$

$$n_{S2} = n_C^0 X_2 \tag{30}$$

$$r_1 = \frac{1}{V}\frac{d\chi_1}{dt} = k_{r1} C_A^{\alpha} C_B^{\beta} C_{S1}^{\delta 1} C_{N1}^{\eta 1} C_{S2}^{\nu s1} C_{\text{ON}}^{\nu n1} \tag{31}$$

$$r_2 = \frac{1}{V}\frac{d\chi_2}{dt} = k_{r2} C_C^{\lambda} C_D^{\pi} C_{S2}^{\delta 2} C_{N2}^{\eta 2} C_{S1}^{\nu s2} C_{\text{ON}}^{\nu n2} \tag{32}$$

$$r_1 = \frac{1}{V}\frac{d\chi_1}{dt} = k_{r1} C_A^{\alpha} C_B^{\beta} C_{S2}^{\nu 1} C_{\text{ON}}^{\nu n1} \tag{33}$$

$$r_2 = \frac{1}{V}\frac{d\chi_2}{dt} = k_{r2} C_C^{\lambda} C_D^{\pi} C_{S1}^{\nu 2} C_{\text{ON}}^{\nu n2} \tag{34}$$

With Common Ion

$$s_A A + s_{B1} B \rightleftharpoons s_{S1} S_1 + s_{N1} N_1 \tag{35}$$

$$s_C C + s_{B2} B \rightleftharpoons s_{S2} S_2 + s_{N2} N_2 \tag{36}$$

$$n_A = n_A^0(1 - X_1) \tag{37}$$

$$n_C = n_C^0(1 - X_2) \tag{38}$$

$$n_B = n_B^0 - n_A^0 X_1 - n_c^0 X_2 \tag{39}$$

$$n_{S1} = n_A^0 X_1 \tag{40}$$

$$n_{S2} = n_C^0 X_2 \tag{41}$$

$$r_1 = \frac{1}{V}\frac{d\chi_1}{dt} = k_{r1} C_A^{\alpha} C_B^{\beta 1} C_{S1}^{\delta 1} C_{N1}^{\eta 1} C_{S2}^{\nu s1} C_{\text{ON}}^{\nu n1} \tag{42}$$

$$r_2 = \frac{1}{V}\frac{d\chi_2}{dt} = k_{r2} C_C^{\lambda} C_B^{\beta 2} C_{S2}^{\delta 2} C_{N2}^{\eta 2} C_{S1}^{\nu s2} C_{\text{ON}}^{\nu n2} \tag{43}$$

$$r_1 = \frac{1}{V}\frac{d\chi_1}{dt} = k_{r1} C_A^{\alpha} C_B^{\beta 1} C_{S2}^{\nu 1} C_{\text{ON}}^{\nu n1} \tag{44}$$

$$r_2 = \frac{1}{V}\frac{d\chi_2}{dt} = k_{r2} C_C^{\lambda} C_B^{\beta 2} C_{\text{ON}}^{\nu n^2} \tag{45}$$

Conclusions

Assessing the induction periods, growth and kinetics of crystallization in mixed salt solutions is important in determining the rate of scale formation in desalination, as well as in other chemical applications. Experiments have shown that the presence of other cations or anions that may form a particulate matter plays a significant role in promoting precipitation of a salt solution due to the affinity that the salt has to precipitate on other particulate matter; the species will tend to do this long before homogeneous nucleation becomes a viable option. Nevertheless, work has mainly been in the absence of other precipitating species and correlations, and have been established where nucleation has been achieved homogeneously.

This article clearly demonstrates the effect of one salt/species on the nucleation, growth, and kinetics of salt crystallization. The single salt kinetics data are not applicable to situations where other salts/species are present, specifically, in the case of coprecipitating salts. The effect of a common ion, as well as the catalytic and inhibitory effect of other salts/species cannot be ignored. The effects of other species on nucleation, solution metastability and kinetics have been theoretically explained. A comprehensive and systematic approach to kinetics of coprecipitation is proposed, which takes into account the effects of soluble salts and coprecipitating salts both with and without common ion. The approach can be easily extended to multiprecipitating systems.

Literature Cited

Atkins, P. W., *Physical Chemistry*, Oxford University Press, U.K. (1995).

Buckley, H. E., *Crystal Growth*, Wiley, New York (1951).

Chan, S. H., K. F. Neusen, and C. T. Chang, "The Solubility of Polymerisation of Amorphous Silica in Geothermal Energy Applications," ASME-JSME Thermal Eng. Conf., ASME (1987).

Chen, C. T. A., and W. L. Marshall, "Amorphous Silica Solubilities IV. Behaviour in Pure Water and Aqueous Sodium Chloride, Sodium Sulfate, Magnesium Chloride, and Magnesium Sulfate Solutions up to 350°C," *Geochim. Cosmochim. Acta*, **46**, 279 (1982).

Chong, T., and R. Sheikholeslami, "Thermodynamics and Kinetics for Mixed Calcium Carbonate and Calcium Sulfate Precipitation," *Chem. Eng. Sci.*, **56**, 5391 (2001).

Davey, R. J., *Industrial Crystallization*, Vol. 78, E. J. de Jong and S. J. Jancic, eds., North Holland, Amsterdam, 169 (1979).

Davey, R. J., and J. Garside, *From Molecules to Crystallizers*, Oxford Science Publications, Oxford (2000).

Epstein, N., "Thinking about Heat Transfer Fouling: A 5×5 Matrix," *Heat Transfer Eng.*, **4**, 43 (1983).

Furedi-Milhofer, H., and S. Sarig, *Prog. Cryst. Growth Charact.*, **32**, 45 (1996).

Gill, M., and R. Sheikholeslami, "A Preliminary Study to Estimate the Combined Effects of Precipitation and Particulate Fouling of $CaSO_4$," Chemeca'97, New Zealand, The Society of Chemical Engineers, NZ (1997).

Hasson, D., "Precipitation Fouling—a Review," *Fouling of Heat Transfer Equipment*, E. F. C. Somerscales and J. G. Knudsen, eds., Hemisphere, New York, 527 (1981).

Hasson, D., "Progress in Precipitation Fouling Research, A Review," *Proceedings of Eng. Found. Conf., Understanding Heat Exchanger Fouling and its Mitigation*, R. Bott, ed., Begell House, New York, 67 (1999).

Iler, R. K., *The Chemistry of Silica*, Wiley, New York (1979).

Klein, J. P., and R. David, "Reaction Crystallization," *Crystallization Technology Handbook*, A. Mersmann, ed., Marcel Dekker, New York, 359 (1995).

Koo, T., and R. Sheikholeslami, "Study of Silica Fouling in Reverse Osmosis Membranes," World Cong. in Chem. Eng., Melbourne, Australia, Institution of Engineers, Australia (2001).

Kostoglou, M., and A. J. Karabelas, "Comprehensive Modeling of Precipitation and Fouling in Turbulent Pipe Flow," *Ind. & Eng. Chem. Res.*, **37**, 1536 (1998).

Krauskopf, K. B., "Dissolution and Precipitation of Silica at Low Temperature," *Geochim et Cosmochim Acta*, **10**, 1 (1956).

Koo, T., and R. Sheikholeslami, "The Effect of Silica Polymerisation in the Presence of Polyvalent Ions in Batch Tests," Chemeca, Perth, Australia (2000).

Melia, T. P., "Crystal Nucleation from Aqueous Solution," *J. of Appl. Chemistry*, **15**, 345 (1965).

Mullin, J. W., *Crystallization*, Butterworths, London (1972).

Mullin, J. W., *Crystallization*, 3rd ed., Butterworths-Heinemann, Oxford (1993).

Mullin, J. W., *Crystallization*, 4th ed., Butterworths-Heinemann, Oxford (2001).

Marshall, W. L., and J. M. Warakomski, "Amorphous Silica Solubilities—II. Effect of Aqueous Salt Solutions at 25°," *Geochim. Cosmochim. Acta*, **44**, 915 (1980).

Nancollas, G. H., and M. M. Reddy, "The Crystallization of Calcium Carbonate II. Calcite Growth Mechanism," *J. Colloid Interf. Sci.*, **37**, 824 (1971).

Nyvlt, J., O. Sohnel, M. Matuchova, and M. Broul, *The Kinetics of Industrial Crystallization*, Elsevier, Amsterdam (1985).

Reddy, M. M., and G. H. Nancollas, "The Crystallization Calcium Carbonate, I. Isotopic Exchange and Kinetics," *J. Colloid Interf. Sci.*, **36**, 166 (1971a).

Reddy, M. N., and G. H. Nancollas, "The Crystallization of Calcium Carbonate II. Calcite Growth Mechanism," *J. Colloid Interf. Sci.*, **37**, 824 (1971b).

Sangwal, K., "Kinetic Effects of Impurities on the Growth of Single Crystals from Solutions," *J. of Crystal Growth*, **203**, 197 (1999).

Sheikholeslami, R., "Strategies and Future Directions for Systematic Characterization of Feed Water and Determination of Scaling Limits and Rates for Process Assessment and Optimization," International Desalination Association, MA (2001).

Sheikholeslami, R., "Mixed Salts—Scaling Limits and Propensity," *Desalination*, in press (2002).

Sheikholeslami, R., I. S. Al-Mutaz, T. Koo, and A. Young, "Pretreatment and the Effect of Cations and Anions on Prevention of Silica Fouling," *Desalination*, **139**, 83 (2001).

Sheikholeslami, R., I. S. Al-Mutaz, S. Tan, and S. D. Tan, "Silica Fouling—Effect of Ca, Mg, and Pretreatment by Sodium Aluminate and Softeners," 6th World Cong. in Chemical Engineering, Melbourne, Australia (2001).

Sheikholeslami, R., D. Hasson, and R. Semiat, "Final Progress Report on Study of The Formation and Inhibition of Silica Scales in RO Desalting," The University of New South Wales, Progress Report Final Report (May, 1998–July, 2000), MEDReC PROJECT 97-A-004D (2000).

Sheikholeslami, R., and M. Ng, "Calcium Sulfate Precipitation in Presence of Non-dominant Calcium Carbonate: Thermodynamics and Kinetics," *Ind. Eng. Chem. Res.*, **40**, 3570 (2001).

Sheikholeslami, R., and S. Tan, "Effects of Water Quality on Silica Fouling of Desalination Plants," *Desalination*, **126**, 267 (1999).

Sheikholeslami, R., A. Yeung, T. Koo, and P. K. R. Yadem, "Silica Fouling of Reverse Osmosis Membranes—Batch and Dynamic Investigations," Chemeca, Newcastle, Australia, Institution of Engineers, Australia (1999).

Sheikholeslami, R., and S. Zhou, "Performance of RO Membranes in Silica Bearing Waters," *Desalination*, **132**, 337 (2000).

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

Sudmalis, M., and R. Sheikholeslami, "Precipitation and Co-precipitation of $CaCO_3$ and $CaSO_4$," *Can. J. Chem. Eng.*, **78**, 21 (2000).

Yu, H., R. Sheikholeslami, and B. Doherty, "Preliminary Study of the Mechanisms of Composite Fouling of Amorphous Silica and Calcium Oxalate in Cane Sugar Mill Evaporators," Int. World Cong. in Chem. Eng., Melbourne, Australia, Institution of Engineers, Australia (2001).

Yu, H., R. Sheikholeslami, and W. O. S. Doherty, "Mechanisms, Thermodynamics and Kinetics of Composite Fouling of Calcium Oxalate and Amorphous Silica in Sugar Mill Evaporators—A Preliminary Study," *Chem. Eng. Sci.*, in press (2002).

Manuscript received Oct. 12, 2001, and revision received Mar. 8, 2002.