

Coprecipitation of CaCO_3 and CaSO_4

Michael Sudmalis and Roya Sheikholeslami*

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

Precipitation is of great importance in a number of industrial problems. The most common mechanism by which a solid will precipitate out of solution is crystallization. Combinations of various salts, including sparingly soluble salts, are present in industrial water systems. Due to complexity of the fouling process, research has concentrated mostly on studying single salt crystallization. This paper is an attempt to study the effect of co-precipitation of two salts with a common ion.

Crystallization has been studied for many years. Therefore, an immense body of information is available in this area. It is beneficial to first briefly discuss the available information and then point out some of the information still lacking in this area. Various studies have quantified thermodynamic data such as K_{sp} values, heat of precipitation, and temperature and pH effects on solubility for single salts (Plummer and Busenberg, 1982; Hardie, 1967; Gujon and Mutaftschiev, 1976; Partridge and White, 1929; Khamskii, 1969). The significant effect that neglecting the existence of an ion-pair can have on K_{sp} values has also been investigated (eg., Reardon and Langmuir, 1974; Plummer and Busenberg, 1982). Salinity effects have been quantified by incorporating the ionic strength in predictive relationships (eg., Power and Fabauss, 1964; Moller and Rajagopalan, 1975; Harned and Davis, 1943). In addition, there has been numerous studies on assessment and development of inhibitors (eg., Amjad, 1989; Reddy and Nancollas, 1973; Gill and Yorke, 1995; Weijnen and van Rosmalen, 1985; van der Leeden and van Rosmalen, 1987).

On the kinetic side, rate constants, activation energies and temperature effects have been studied (eg., Turner and Smith, 1998; Kazmierczak et al., 1982; Kharin, 1974; Kharin et al., 1980; Neilsen, 1964; Strickland-Constable, 1968; Reddy and Nancollas, 1971). Empirical and theoretical relationships for and the effect of operating variables on the germination time and velocity have been determined (eg., Volmer, 1939; Becker and Doring, 1935; Roques and Girou, 1974). On the physical and chemical sides, the structure, crystal lattice, and hydration water have been determined for various salts (Hill, 1937; Plummer and Busenberg, 1982; Keysar et al., 1994). Also, there has been work determining which polymorph is kinetically favoured and which one is thermodynamically stable (Kahlweit, 1960; Hill, 1937; Kharin, 1974; Plummer and Busenberg, 1982). All these known, there is still an abundance of data missing. One such an area is the interactive effect of coprecipitating salts with or without common ions. These include solubility effects, rate data, crystal structure and strength, inhibitor effects and also dynamic effects.

Significance and Application of Coprecipitation Studies

Coprecipitation occurs in all industrial water systems involving heat exchanger equipments and membrane systems. This includes recirculating

Coprecipitation characteristics of CaCO_3 and CaSO_4 were studied under various operating conditions. The investigations were carried out in temperature-controlled batch tests. Coprecipitation results were compared with our experimental results of a single salt crystallization. It was found that the induction period and kinetics of coprecipitation of these two salts follow that of pure CaCO_3 . However, thermodynamic concentrations of Ca in coprecipitation followed that of pure CaSO_4 at all times. The relationship between the thermodynamic concentrations of Ca for pure CaCO_3 and CaSO_4 solutions depended on the pH of the CaCO_3 solution. CaSO_4 precipitated in form of gypsum and had a needle shape structure; CaCO_3 had a spiral growth and precipitated in form of calcite. The precipitate structure was affected by the co-existence of salts; the co-precipitation resulted in CaCO_3 crystals interwoven by CaSO_4 crystals. This tends to result in a co-precipitate that is stronger than pure CaSO_4 and weaker than pure CaCO_3 precipitate.

On a étudié les caractéristiques de coprécipitation de CaCO_3 et de CaSO_4 dans diverses conditions de fonctionnement. Les études ont été réalisées au moyen d'essais discontinus à température contrôlée. Les résultats de coprécipitation ont été comparés à nos résultats expérimentaux portant sur la cristallisation d'un sel unique. Il s'avère que la période d'induction et la cinétique de coprécipitation de deux sels suivent celle du CaCO_3 pur. Cependant, les concentrations thermodynamiques du Ca en coprécipitation suivent celles du CaSO_4 pur en tout temps. La relation entre les concentrations thermodynamiques du Ca pour des solutions de CaCO_3 et CaSO_4 purs dépend du pH de la solution de CaCO_3 . Le CaSO_4 se précipite sous forme de gypse et a une structure en forme d'aiguille; le CaCO_3 a une croissance en spirale et se précipite sous forme de calcite. La structure du précipité est influencée par la coexistence des sels; la coprécipitation donne des cristaux de CaCO_3 entrelacés de cristaux de CaSO_4 . Cela tend à produire un coprécipité plus fort qu'un précipité de CaSO_4 pur et plus faible qu'un précipité de CaCO_3 pur.

Keywords: precipitation, crystallization, coprecipitation, calcium carbonate, calcium sulfate.

*Author to whom correspondence may be addressed. E-mail address: r.sheikholeslami@unsw.edu.au

cooling water systems, and desalination, power generation, waste-water treatment, and water purification plants. This study is significant and necessary because it advances the understanding and facilitates

quantification of the kinetics and thermodynamics of coprecipitation that is imperative in various areas. These are: a) developing effective additives and inhibitors for industrial water systems; b) employing proper pre-treatment steps; c) developing mathematical models to predict fouling propensities; d) choice of cleaning technologies; and e) setting up safe operating envelopes in industrial plants.

Background Theory

This paper looks at quantitative and some qualitative analysis of coprecipitation of CaCO_3 and CaSO_4 from kinetics, thermodynamics and structural points of view. To be able to discuss and explain some of the results and observations, crystallization in general and that of pure CaCO_3 and CaSO_4 in particular are briefly discussed first.

Crystallization has been the subject of many papers and research over the last seventy years (Hasson, 1981, 1999). Crystallization is generally considered to be a three step process: nucleation, growth and recrystallization (Davis et al., 1995; Buckley, 1951; Van Hook, 1961; Nielson, 1964; Strickland-Constable, 1968; and Mullin, 1972). However, this is a simplification of the actual situation, as these three steps have a great deal of overlap. In addition, the co-presence of salts in a solution can further complicate the crystallization process.

Nucleation

In order for crystallization to occur, the dissolved species must be in a supersaturated state. In addition, there is a requirement for centres of crystallization that can take various forms such as seeds, embryos or foreign matter present in the solution. Nucleation follows the following steps:

1. Formation of ion-pairs by electrostatic interactions between dissolved cations and anions;
2. Aggregation of ion-pairs to form pre-nucleation entities (aggregates) which are in dynamic equilibrium with solution; and
3. Growth of aggregates to a critical size which results in nucleation of solid state particles. These nucleated particles do not readily re-dissolve.

Nucleation can be either primary or secondary. It is called secondary when a nucleus is formed on the existing crystal (e.g., seeded crystallization). Primary nucleation is subdivided into heterogeneous or homogenous nucleation. The former is dependent on foreign bodies (surfaces) in the solution and uses the foreign substances as sources of growth until a nucleus has formed. The latter can only occur in the bulk when the difference in chemical potential between solid and dissolved states could overcome and is far less common and virtually impossible to attain (Melia, 1965) in practical situations. The greater the degree of supersaturation, the higher the chemical potential of the dissolved state and, therefore, homogenous nucleation will dominate. The number of pre-nucleation aggregates that is required varies from as little as ten up to many thousands, depending on the degree of supersaturation and the species involved.

Classical theory of nucleation treats homogeneous nucleation in terms of Gibbs free energy and is derived from the work of Gibbs (1928), Volmer (1939) and Becker and Doring (1935):

$$\Delta G = \Delta G (\text{surface}) + \Delta G (\text{bulk}) = \sigma A - n (\mu_1 - \mu_2) \quad (1)$$

$$\Delta G = 4 \pi r^2 \sigma - (4 \pi r^3 / (3 V_m)) K T \ln (C_{\text{solution}} / C_{\text{solid}}) \quad (2)$$

When the solution is not supersaturated ($\Delta G \geq 0$), all the nuclei that may form will dissolve. If r is sufficiently large (r^3 will dominate) or when the concentration ratio is large (for highly supersaturated solutions), ΔG will become negative and the solution will nucleate. Therefore, there is a critical ΔG^* which represents an energy barrier for nucleation. Heterogeneous nucleation takes place at lower critical supersaturation (lower ΔG^*) and its critical free energy is approximated by:

$$\Delta G_{\text{het}}^* = \phi \Delta G^* \quad (3)$$

The corresponding critical radius and the number of molecules in a critical radius are r^* , n^* (Equations 4 and 5). In simple terms, if the growing nucleus coagulates to a point where the radius reaches r^* , then this nucleus will not dissociate into its component molecules. Alternatively, if the radii of a nucleus is less than r^* , the nucleus will have to either continue to grow toward the critical radius or to dissociate into its component molecules.

$$r^* = 2 V_m \frac{\sigma}{K T \ln (C_{\text{solution}} / C_{\text{solid}})} \quad (4)$$

$$n^* = 2 \beta V_m^2 \left[\frac{\sigma}{K T \ln (C_{\text{solution}} / C_{\text{solid}})} \right]^3 \quad (5)$$

The first rate equation for nucleation was described by Volmer and Weber (1922; 1929) and subsequent work was done by Becker and Doring (1935), Kahlweit (1960) and Neilson (1964):

$$J = A_1 \exp \left[\frac{-\Delta G^*}{K T} \right] = A_1 \exp \frac{-\beta V_m^2 \sigma^3}{(K T)^3 [\ln (C_{\text{solution}} / C_{\text{solid}})]} \quad (6)$$

Christiansen and Neilson (1951) used a more empirical approach, by analogy with polymerization:

$$J = k_1 C^n \quad (7)$$

$$\theta_{\text{ind}} = k_2 C_{\text{in}}^{1-n^*} \quad (8)$$

Growth

Various theories exist for crystal growth (Neilsen, 1982). Brice (1986) suggests the crystal growth can follow either of the following possible mechanisms:

- a) direct ion incorporation into crystal lattice;
- b) nucleation at the surface of crystallite which is also called secondary nucleation; and
- c) particle agglomeration.

Re-crystallization

Comprised of any changes and transitions in the solid-state phase. That includes dehydration; for example, since the dehydration step is slow, a hydrated and amorphous form of CaCO_3 that is kinetically favoured is formed first and at a later stage transforms to calcite and aragonite which are thermodynamically stable (Plummer and Busenberg, 1982). This usually happens at high supersaturations of in excess of 5. Also, the crystal structure can change to transform from one polymorph

to another. The solid phase transition is another complicating factor during the growth process.

Calcium Carbonate Precipitation

Calcium carbonate is a sparingly soluble salt and its solubility in water is determined by:

$$K_{sp} = \{Ca^{2+}\} \{CO_3^{2-}\} \quad (9)$$

The aqueous system that is formed contains other cations and anions, which are all in dynamic equilibrium with each other with the position of equilibrium being a function of temperature, pressure, ionic strength and pH. The carbonate ion is the key, which can further dissociate as determined by the carbonic series in water which was studied in great detail in both closed and open systems by Stumm and Morgan (1970), and Loewenthal and Marais (1976). Distribution factors in a closed system are:

$$\alpha_{H_2CO_3} = \{1 + (K_1/[H^+]) + (K_1 K_2/[H^+]^2)\}^{-1} \quad (10)$$

$$\alpha_{HCO_3^-} = \{1 + ([H^+]/K_1) + K_2/[H^+]\}^{-1} \quad (11)$$

$$\alpha_{CO_3^{2-}} = \{1 + ([H^+]/K_2) + ([H^+]^2/(K_1 K_2))\}^{-1} \quad (12)$$

Open systems that provide a venue for exchange of CO_2 between the gaseous and liquid phase further complicate the analysis.

In all the studies reported in the literature, the rate of nucleation was measured in terms of an experimentally measured induction period. Roques and Girou (1974) correlated V_G (Equation 13), which was derived from work of Volmer (1939), and Becker and Dorring (1935):

$$V_G = 1.22 \times 10^{-2} V_o^{0.88} \quad (13)$$

$$\log \theta_G = \{\log^2 \{[(C - C_o)/C_o]\}\}^{-1} \quad (14)$$

Germination velocity, V_G , can be thought of as the nucleation velocity, whereby a constant number of micronuclei are formed with every passing minute, whereas the germination (induction) period, θ_G , is simply the time taken until the onset of nuclei formation. Stirring and agitation (mainly in the form of the bubbled gas) influenced both V_G and θ_G . Under the effect of stirring or agitation, germination times were found to be less (up to 10 times) than that for unagitated conditions; this is believed to favour heterogeneous nucleation. This partially explains the variation in some experimental results (see Results and Discussion).

Wiechers et al. (1975) studied the kinetics of $CaCO_3$ precipitation. Sohnel and Mullin (1978, 1982) used various methods as simple as observations and as elaborate as a stopped-flow method to measure induction period for $CaCO_3$. With the stopped-flow method, which utilizes the solutions conductivity, they could measure induction times as short as 5 ms and therefore were able to perform experiments at very high supersaturations, at which heterogeneous nucleation is negligible and obtained correlations for induction period and interfacial energy Sohnel and Mullin (1978, 1982).

Calcium Sulfate Deposition

Much research has been performed in an attempt to analyze the mechanism for deposition of $CaSO_4$, which may precipitate

in three forms, namely gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$) and hemihydrate ($CaSO_4 \cdot 1/2H_2O$). Within industry, gypsum and anhydrite are the predominant forms as they precipitate below $100^\circ C$; hemihydrate dominates at temperatures above $102^\circ C$.

A large amount of solubility work has been performed on gypsum and anhydrite, with accurate K_{sp} correlations available in the literature (Marshall and Slusher, 1968; Nordstrom et al., 1990; Electric Power Research Institute, 1982) all of which may be adjusted for the appropriate temperature.

Literature (Ritter, 1983; Bramson et al., 1996) indicates that any correlation for calcium sulfate precipitation is most accurate when both mass transfer and supersaturation effects are incorporated. The effect of water quality is of great importance on induction times and precipitation of calcium sulfate. Also, excess of cations (or other ions) plays an ever-increasing role due to the affinity that calcium sulfate has with precipitating on other particulate matter in preference to, say, the heat transfer surface. 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 have been established where nucleation has been achieved homogeneously. A correlation for the $CaSO_4$ induction time was proposed by Hasson and Zahavi (1970).

Previous Work on Coprecipitation

The reviewed literature on crystallization (Hasson 1981, 1999) indicate that very little study has been devoted to the study of the coprecipitation phenomenon. There has been some qualitative research by Hasson and Karmon (1984), whereby conditions were sought that created a tenacious calcium sulfate scale layer. A major factor affecting scale tenacity was the purity of the deposit, where the higher the impurities, the greater the strength of the scale. However, with calcium carbonate, adhesive strength was seen to decrease with increasing impurities. They found that the scales of impure $CaCO_3$ deposits are weaker than homogenous and heterogenous deposits. The most difficult deposit to remove from heat transfer surfaces was this scale with impurities measuring less than 5% by mass. The analytical results indicate that for aggressive scale, the main constituent was calcium carbonate; this agrees with results of Morse and Knudsen (1977).

In further studies, Bramson et al. (1996) qualitatively examined the crystals of coprecipitated calcium carbonate and sulfate. Pure calcium sulfate deposits were found to be far less adherent than deposits containing coprecipitated calcium carbonate. The coprecipitated calcium carbonate seems to act as bonding cement, enhancing considerably the strength of calcium sulfate scale layer.

Scope of This Paper

This paper is aimed to look at the kinetic and thermodynamic characteristics of coprecipitation of calcium carbonate and calcium sulfate by using a concentration matrix (Table 1) for experimentation. All the runs were used for thermodynamic studies while the ones identified by asterisks were monitored for kinetic analysis.

This setup has great application in comparing and contrasting results. It enables analysis of increasing sulfate concentration at constant carbonate molarity and vice-versa. Also, comparisons can be made from solutions containing the same amount of total calcium, such as 0.02 M $CaSO_4$, 0.02 M $CaCO_3$ and 0.01 M

Table 1. Solution concentration matrix.

		CaCO ₃ (M)					
		0	0.005	0.01	0.015	0.02	0.03
CaSO ₄ (M)	0		1	2*	3	4*	5
	0.005	6	7*	8	9		
	0.01	10*	11	12*	13		
	0.015	14	15	16	17		
	0.02	18*					
	0.03	19					

*Runs involved in kinetic analysis.

CaSO₄ with 0.01 M CaCO₃. Relative characteristics of precipitates were determined using SEM analysis.

Though the data are extensive and include some quantitative analysis, the scope of this paper tends to be more qualitative than quantitative. Additional data are required for comprehensive quantification of results.

Experimental Procedure

Solution Preparation

All the chemicals and reagents used in this study were of analytical grade. All the test tubes that were used in the calcium experiments were scrubbed and rinsed using concentrated hydrochloric acid, and then thoroughly washed with distilled water. The water that was used in the experimentation was triple-distilled for purity. The supersaturated solution of calcium sulfate (CaSO₄) and calcium carbonate (CaCO₃) was prepared by adding equimolar amounts of Na₂SO₄ and CaCl₂, and CaCl₂ and NaHCO₃, respectively. Other ions present (i.e., Na⁺, Cl⁻, ...) will contribute to the ionic strength of solution and will be affecting the solubility as they influence the Gibbs free energy. This effect will be taken into account in quantitative analysis but in comparative studies this effect would not interfere with our analysis.

For supersaturation values that resulted in spontaneous precipitation of CaCO₃, hydrochloric acid was used to adjust pH and subsequently dissolve all of the particulate CaCO₃. Three hours later, 4.1 mL of concentrated NaOH were added to the solution to bring the solution to metastable supersaturation. This would have affected the salinity of the solution and therefore its solubility. However, in this instance the effect of salinity on solubility would not interfere with our comparative precipitation and coprecipitation results as the same CaCO₃ solution was used for both pure precipitation and coprecipitation tests. Using this method, salt-supersaturation of up to 2.5 were prepared. The solution pH was about 7.5 ± 0.5; however, in the comparative runs the solution pH was the same.

Sampling and Analysis

Mixtures as indicated in Table 1 were created and placed into baths that were maintained at constant temperatures of 60°C, 70°C, and 80°C. The mixtures that were only involved in thermodynamic analyses were simply placed in the baths and were untouched until the kinetic analyses on selected runs (identified by asterisks) were concluded. The samples were left untouched during the experimental runs to insure the absence of mixing and therefore a higher possibility of homogeneous nucleation.

For kinetic analysis, sampling was taken on irregular intervals; on any sampling day the solutions were analyzed for calcium by atomic absorption. When it was clear that the samples were at thermodynamic equilibrium, all solutions were analyzed for all interacting species. The final solutions were filtered, and the liquid split into three parts. One was diluted with distilled water to double its volume for atomic absorption analysis. Another one was sent to ICP for sulfur readings, and a third one was sent for total carbon analysis.

The solid calcium precipitates were left on their filter paper and dried in an oven for three days at temperatures between 55°C to 65°C. These dried solid samples were then taken to the scanning electron microscope unit and covered in a thin layer of gold and photographed.

Results and Discussion

Pure CaCO₃ and CaSO₄

The induction period for CaCO₃ is much less than that of CaSO₄ and supports the experimental data of previous investigators. Comparing this result with Equation (5), suggests that the number of critical nuclei, n^* , needed for CaSO₄ nucleation is much larger than that for CaCO₃ nucleation. In turn, this would suggest that the geometric shape factor, β , for CaSO₄ is greater than that of CaCO₃. The reported data for various geometries show that β decreases when the roundness increases (i.e., from 16.76 for spheres to 55.34 for tetrahedrons) (Gibbs, 1928; Volmer, 1939; Becker and Doring, 1935). Therefore, the experimental results concur with the literature, as the experiments also show that CaSO₄ precipitates are needle-shaped while CaCO₃ precipitates are cubic calcite. The above comparisons can be made only if we consider that nucleation is homogeneous otherwise we should take into account the effect of foreign bodies and the ϕ factor.

Roques and Girou (1974) reported that truly homogeneous nucleation of calcium carbonate is probably never observed but under very high supersaturations, the influence of heteronuclei can be reduced to a minimum and the nucleation process is approximately homogeneous. This is true of CaSO₄ as well. Therefore, we have assumed that under the supersaturations used in this study, the effect of heteronuclei is not significant.

Even though this study was intended to be only qualitative and comparative with respect to salt composition, the solubility data for pure salts were compared with those found in the literature. The results indicated that our experimental data and the literature values were in good agreement for unseeded precipitation.

Effect of Temperature

Figures 1 and 2 show the change in calcium concentration as a function of time at three different temperatures for both pure and mixed solutions having total calcium content of 0.02 M and 0.01 M, respectively. Figures 1a and 2a and 1b and 2b are, respectively, for pure calcium carbonate and calcium sulphate and Figures 1c and 2c are for a mixture of both.

When we compare runs at different temperatures but otherwise identical conditions, it seems that temperature does not affect induction times for pure CaSO₄ (Figures 1b and 2b) and is only marginally shorter for CaCO₃ at 80°C (Figures 1a and 2a). The same trend exists for coprecipitation (Figures 1c and 2c).

Temperature affects the final Ca concentration for all samples when it is raised to 80°C (Figures 1 and 2). Except for pure CaCO₃ at total calcium concentration of 0.02 M (Figure 1a), there is no significant difference between the equilibrium

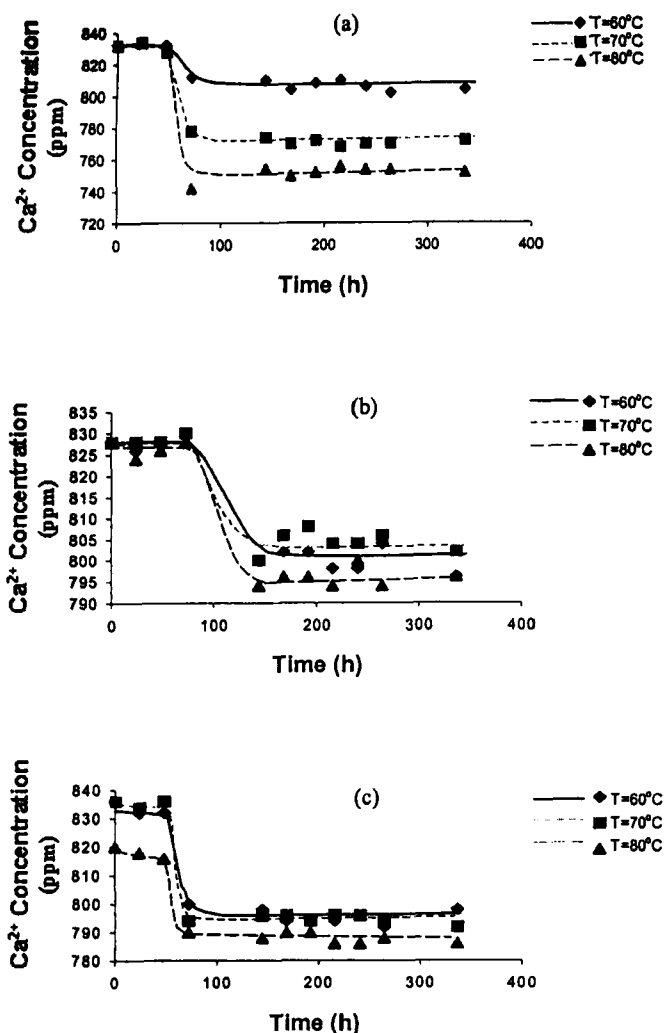


Figure 1. Comparison of the effect of temperature at given solution composition for 0.02 M total Ca^{2+} concentration: (a) CaCO_3 ; (b) CaSO_4 ; (c) 0.01 M of CaCO_3 plus 0.01 M of CaSO_4 .

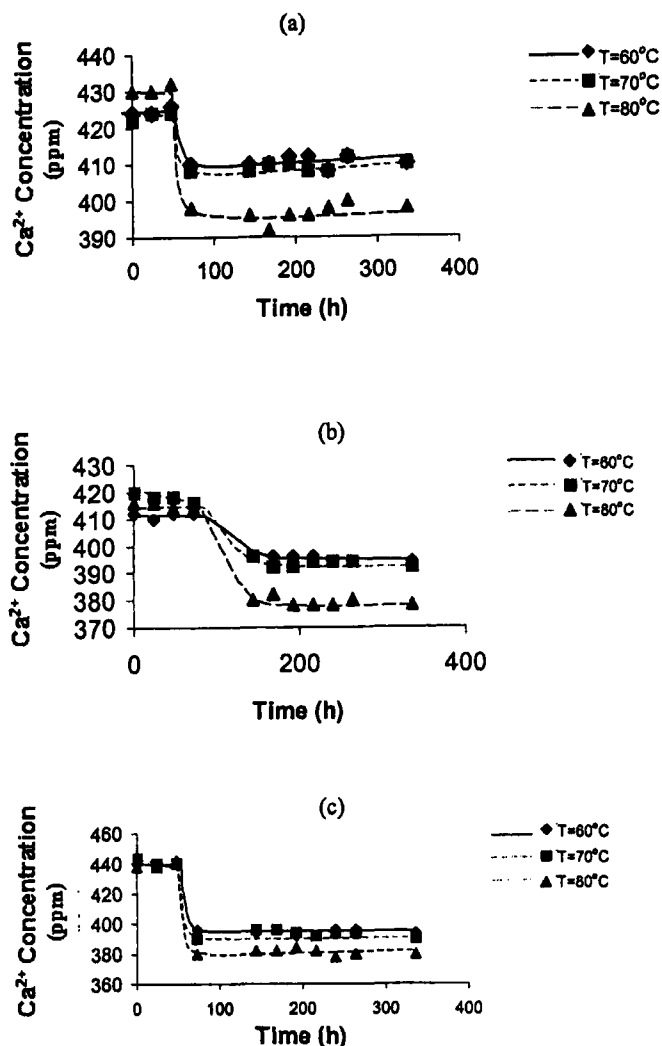


Figure 2. Comparison of the effect of temperature at given solution composition for 0.01 M total Ca^{2+} concentration: (a) CaCO_3 ; (b) CaSO_4 ; (c) 0.005 M of CaCO_3 plus 0.005 M of CaSO_4 .

calcium concentration at 60°C and 70°C (Figures 1 and 2). Final Ca concentrations for mixed solutions (Figures 1c and 2c) follow the same trends as those of pure CaSO_4 .

For pure CaCO_3 (Figures 1a and 2a) the rate of reaction increases with temperature; the effect is, however, more pronounced for higher initial concentration of 0.02 M (Figure 1a). For 0.01 M pure CaCO_3 , temperature effects are not noticeable between 60°C and 70°C (Figure 2a). For pure CaSO_4 (Figures 1b and 2b), the temperature effect is noticeable only at 80°C. This can indicate that the deposit tends to be gypsum rather than anhydrite as the slope of solubility curve versus temperature within that range is steep for anhydrite but not for gypsum.

Effect of Initial Concentration

Increasing the initial calcium concentration from 0.01 M to 0.02 M reduces the induction period for pure CaCO_3 from about 65 h to 50 h (Figures 1a and 2a). For pure CaSO_4 and mixed solutions, the effect of concentration increase on the induction time is not noticeable. The precipitation rate decreases with decreases in concentration. However, insufficient data during the initial period precludes determining rate constants either for pure or for mixed solutions. In addition, due

to variation of pH in the runs, K_{sp} values were not determined. Therefore, as mentioned previously, the results in this study should be treated from qualitative rather than quantitative point of view.

Effect of Solution Composition

Figures 3 and 4 show the effect of solution composition at given temperatures of 60°C, 70°C and 80°C. The induction period for CaCO_3 is half that of CaSO_4 and the induction period for the mixture follows that of CaCO_3 irrespective of the solution temperature and initial Ca concentration (Figures 3 and 4). However, the solubility concentration of the mixture follows that of CaSO_4 and again the same trends exist for all operating temperatures and initial calcium concentrations.

The interesting point is that not only does the solubility of the mixture follow that of CaSO_4 , it does it irrespective of whether equilibrium calcium concentration of pure CaSO_4 is above or below that of pure CaCO_3 . As we see from the figures, in some cases the equilibrium concentration of pure CaCO_3 is above that of pure CaSO_4 and while the relationship is reversed for others. This was due to the fact that the CaCO_3 solubility is pH dependent (Equations 9 and 12) while CaSO_4 solubility is independent of pH for $\text{pH} > 3$; since pH was not the same for all

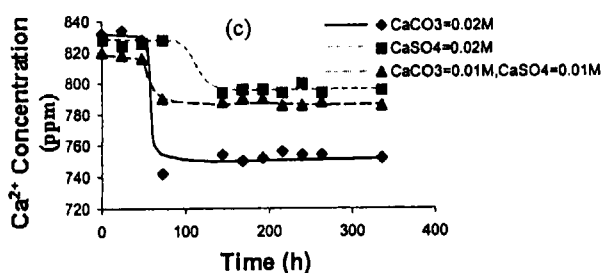
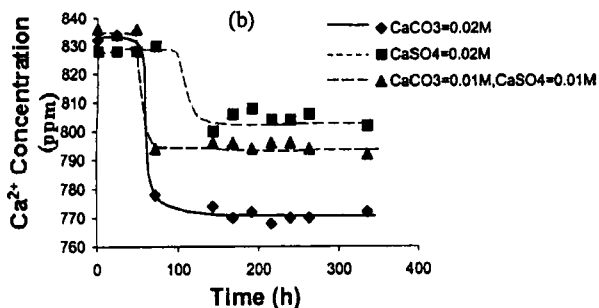
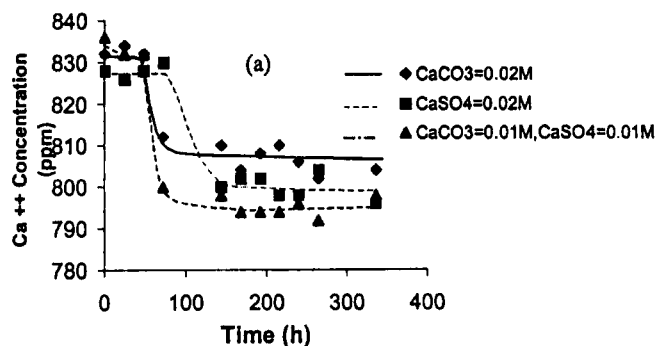


Figure 3. Comparison of the effect of composition at given temperatures for 0.02 M total Ca^{++} of Pure and mixed solutions: (a) 60°C; (b) 70°C; and (c) 80°C.

pure CaCO_3 solutions, it resulted in variation in relative solubility with respect to CaSO_4 . Despite this fact, the equilibrium solubility of the mixture followed that of pure CaSO_4 for all cases (Figures 3 and 4). This indicates that the usual practice of determining hardness and setting operating condition based on that, without considering the effect of co-existence of anions on K_{sp} , is not accurate. Therefore, the effect of co-existence of anions, which precipitate calcium, cannot be neglected.

Figures 3 and 4 show that consistently in all the runs the induction period for CaCO_3 is almost half that of CaSO_4 . It should be noted, however, that the literature reported induction times between calcium carbonate and sulfate are markedly different. Also, literature usually indicates a much shorter induction period for CaCO_3 than what is observed here. The induction times for calcium sulfate can be up to 100 h, whereas the times for carbonate are much less (as little as 4 h or less under some conditions) (Hasson and Zahavi, 1970; Gill and Sheikholeslami, 1997). The difference between the reported induction times

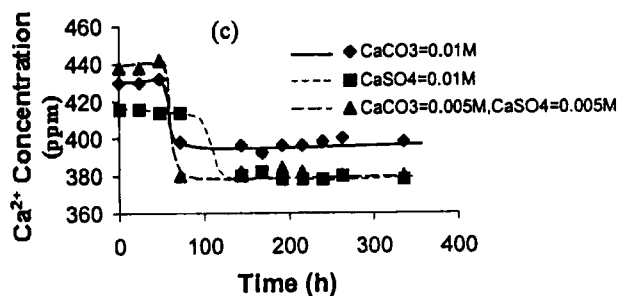
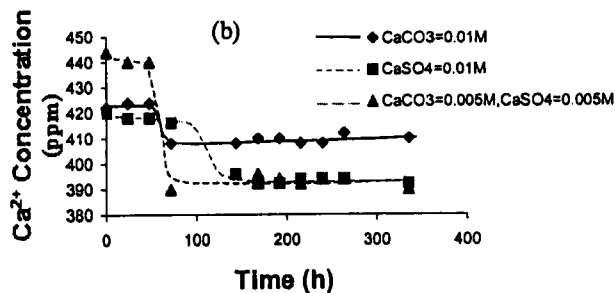
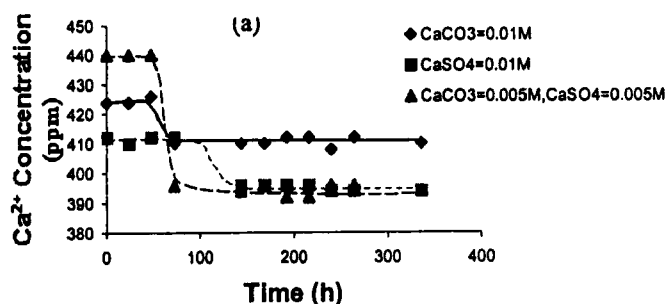


Figure 4. Comparison of the effect of composition at given temperatures for 0.01 M total Ca^{++} of pure and mixed solutions: (a) 60°C; (b) 70°C; and (c) 80°C.

(4 hrs) for CaCO_3 and those of this study might suggest that reported literature values were obtained under heterogeneous nucleation while the condition of this experiment favours homogeneous nucleation. This seems to be the case as the crystallization took place in test tubes without any mixing.

Deposit Structure

Deposits were analyzed by Scanning Electron Microscopy (SEM) with 5 kV of electron beam energy and some of the results are presented in Figures 5 to 10. Figure 5 shows the results for pure (0.01 M) CaSO_4 at various temperatures; Figure 6 shows that of 0.02 M CaSO_4 . Calcium sulfate crystals were of needle shape and the size and density of particles increased with increasing temperature and concentration (Figures 5 and 6). The increase in particle density suggests that crystal growth cannot be due to, or at least only due to ion incorporation into the crystal lattice. The effect of temperature was not as significant as that of concentration. However, the temperature effect was more important at lower concentrations (lower supersaturations,

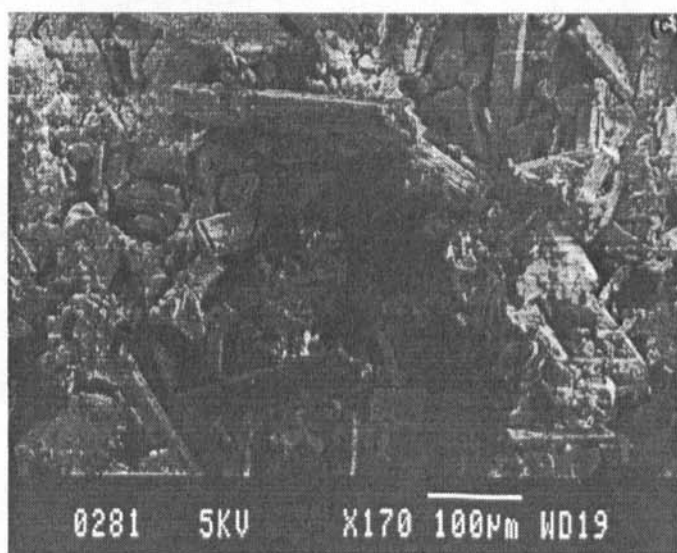
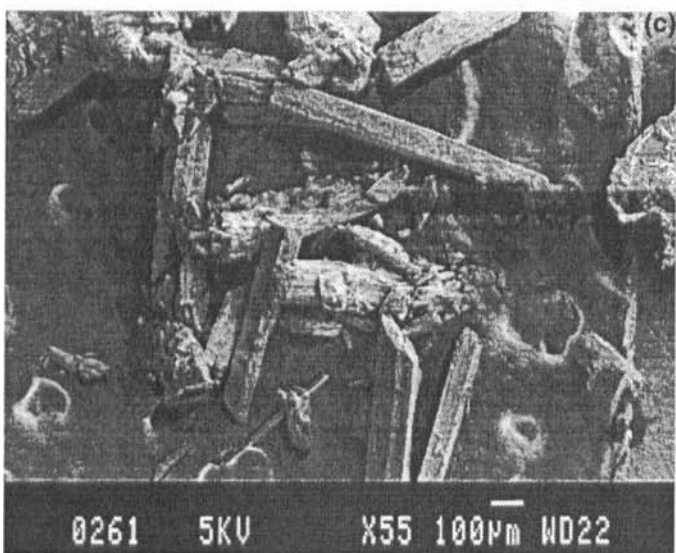
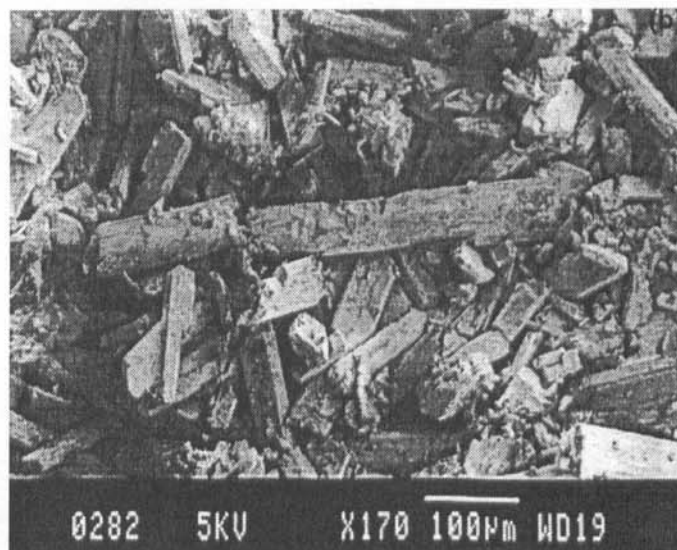
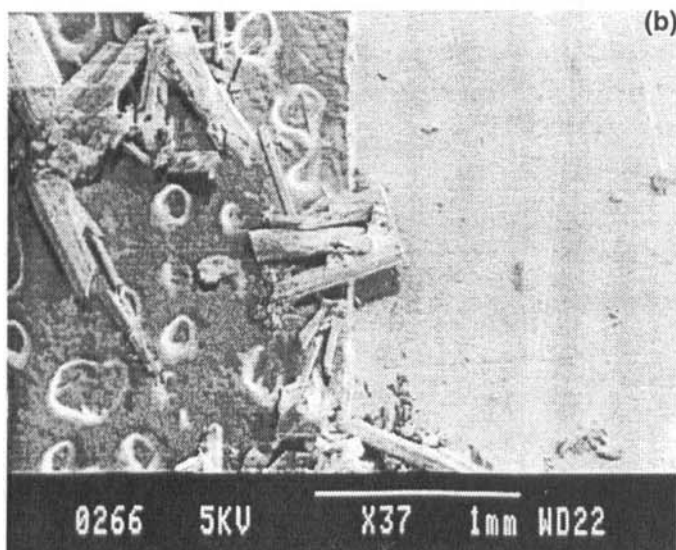
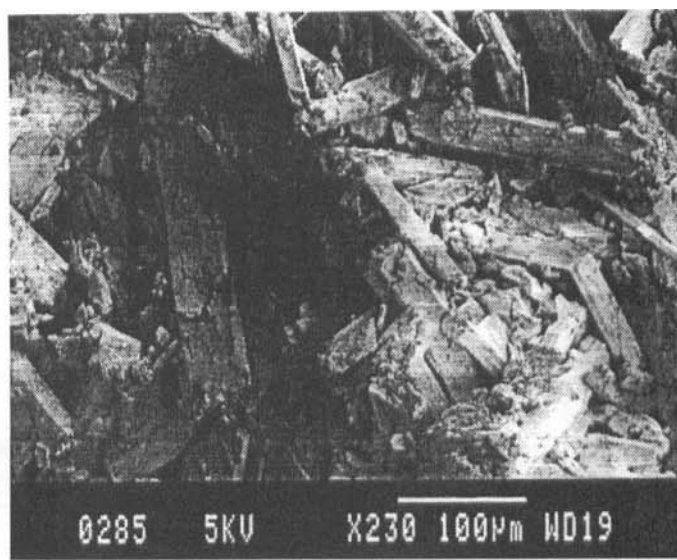
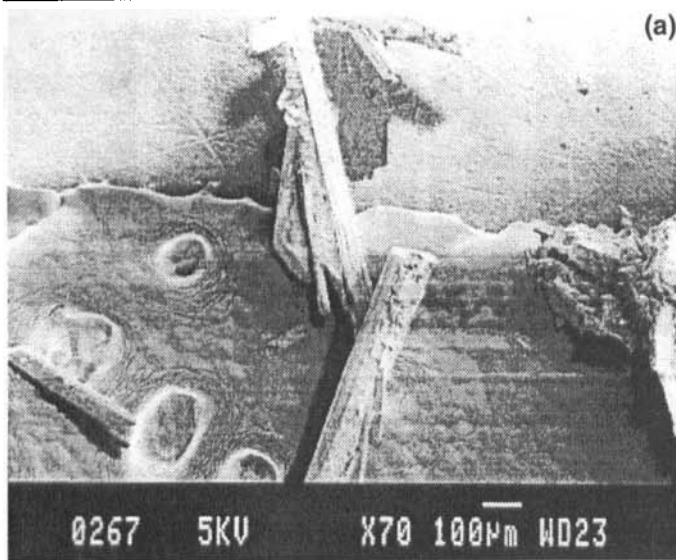
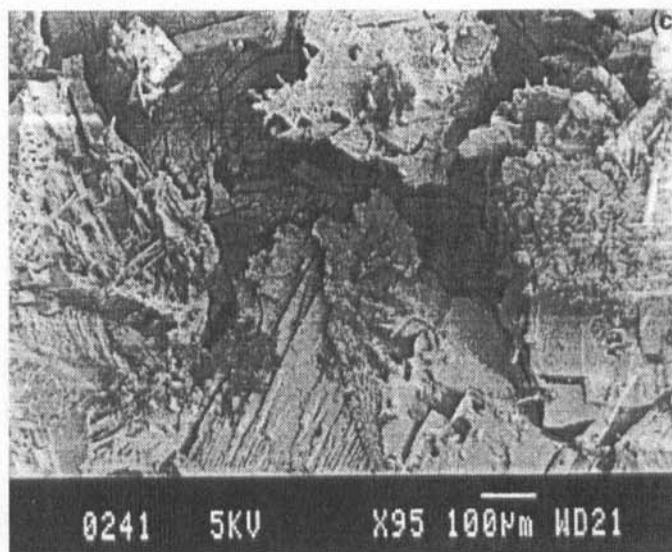
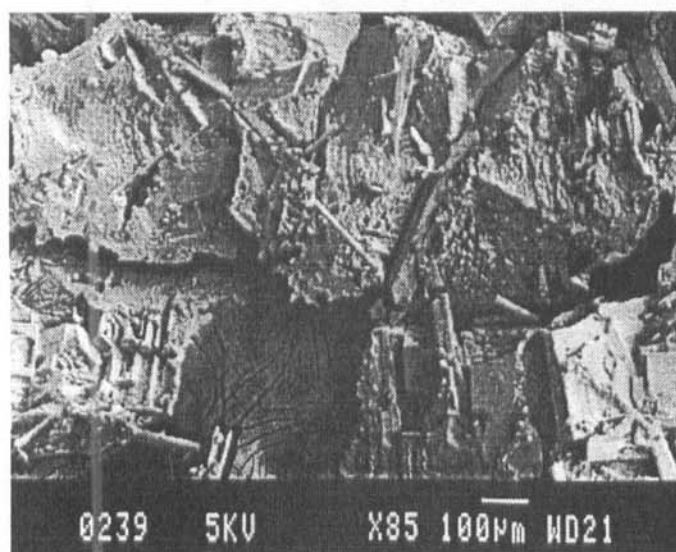
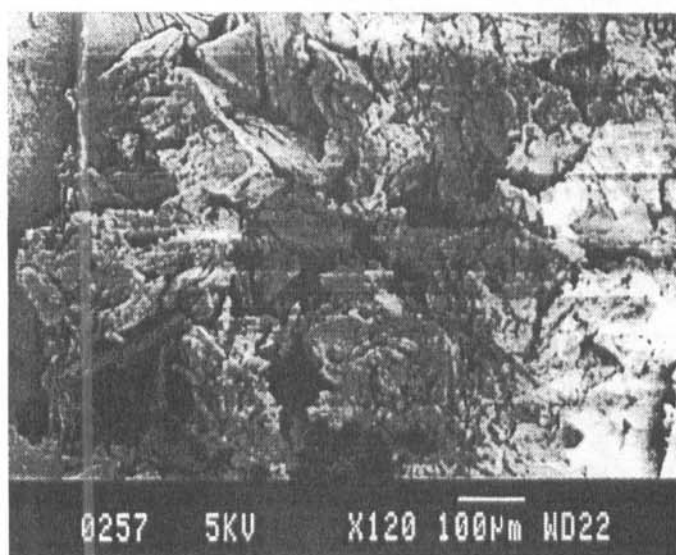
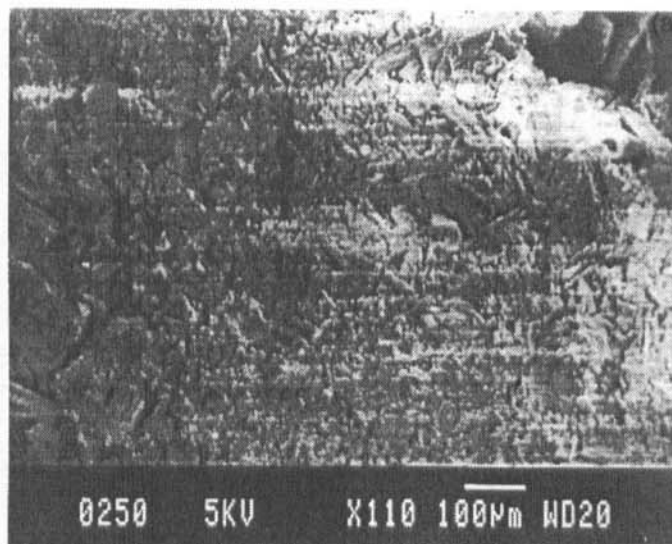
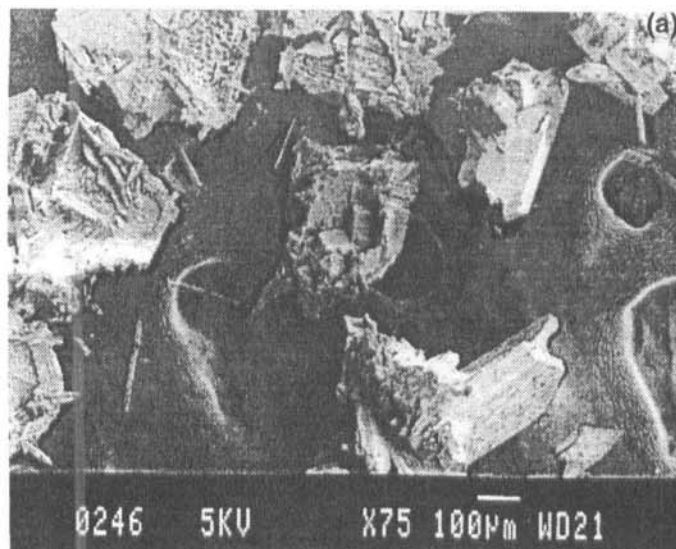


Figure 5. SEMs for 0.01 M CaSO_4 at: (a) 60°C; (b) 70°C; and (c) 80°C.

Figure 6. SEMs for 0.02 M CaSO_4 at: (a) 60°C; (b) 70°C; and (c) 80°C.

Figure 5) than that at higher ones (Figure 6). The effect of concentration increase (from 0.01 M to 0.03 M) at a given temperature of 80°C can be seen by comparing Figures 5c, 6c

and 9a. This comparison confirms the increase in particle size and density with increases in concentration; however, the effect is much more pronounced between 0.01 M and 0.02 M than



between 0.02 M and 0.03 M. Therefore, in general at higher supersaturations crystal density and size are less affected by operational changes.

Comparing respective runs (Figures 5 and 7 and Figures 6 and 8), it is evident that the effect of temperature is much more significant for CaCO_3 than CaSO_4 . Spiral growth is evident for

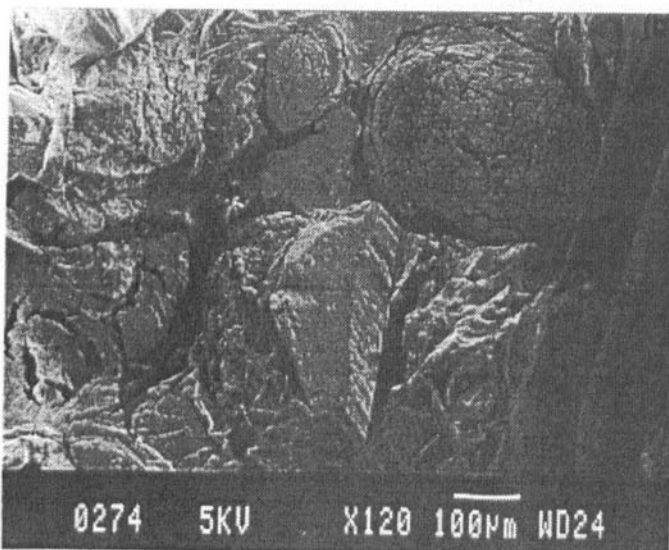
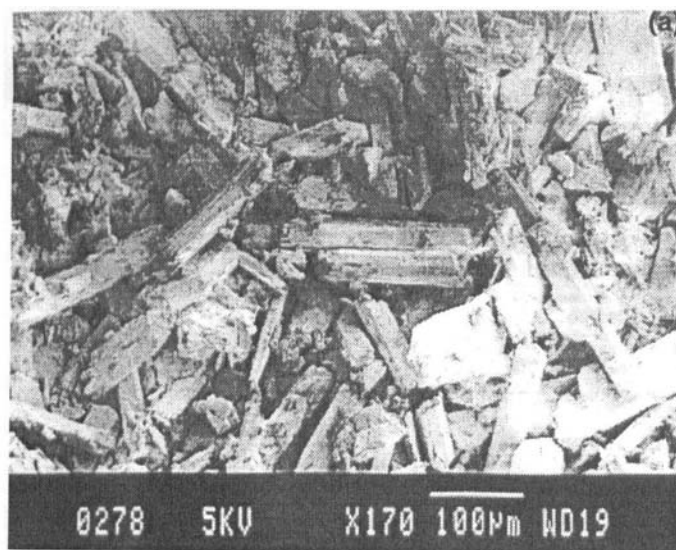


Figure 9. SEMs for 0.03 M: (a) CaSO_4 ; and (b) CaCO_3 at 80°C .

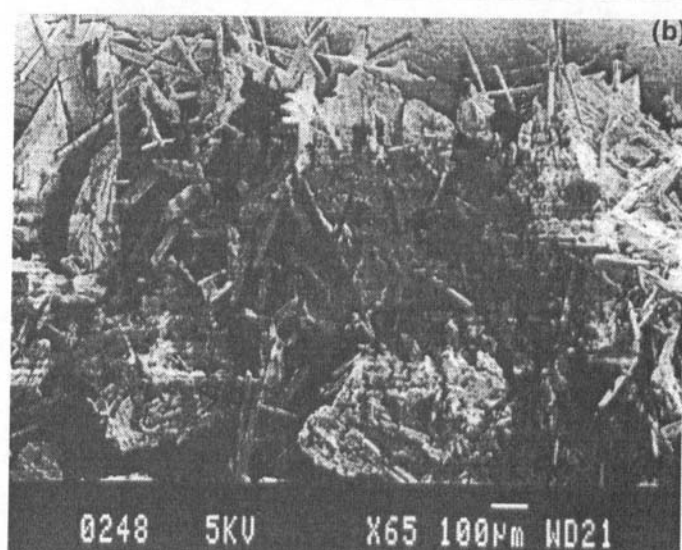
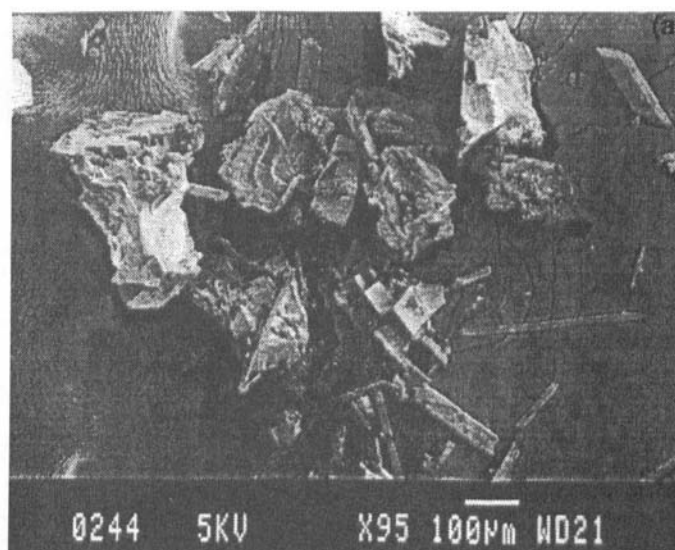


Figure 10. SEMs for equimolar mixed solutions of CaSO_4 and CaCO_3 of: (a) 0.01 M; and (b) 0.02 M at 70°C .

CaCO_3 ; this concurs with the results of Sohnle and Mollin (1982), who believed that under their experimental conditions a spiral growth mechanism for CaCO_3 was more likely. Comparing Figures 9a and 9b suggests that spiral growth is not evident for CaSO_4 . This has important implications; for example, it suggests that some predictive models that are based on spiral growth are only applicable to CaCO_3 not to CaSO_4 . Therefore, in general, the usual practice of developing a mathematical model and substantiating it with experimental results for a given salt and then extending the model to other salts becomes questionable.

Figures 5 to 8 show that temperature, within the experimental region, did not affect the crystal structure for either of the salts; needle-shaped gypsum was formed for CaSO_4 while calcite was formed for CaCO_3 . Figures 10a and b show the effect of solution concentration on the particle density and size for mixed solutions. Again, we see the same trends as that of pure solutions. A comparison between Figures 10a and 10b suggests that CaCO_3 is formed first and CaSO_4 is nucleated subsequently extending from the CaCO_3 crystal. This results in a mixed precipitate that seems to be oriented as CaCO_3 joined and interwoven by CaSO_4 crystals (Figure 10b). It seems that coprecipitation reduces

particle size for both salts (Figures 6b, 8b and 10b; all at 0.02 M) but more noticeably for CaSO_4 (Figures 6b and 10b). Comparing Figures 5b, 7b and 10a, it seems that coprecipitation has reduced the size and particle density more significantly for 0.01 M solutions. The influence of coprecipitation on the structural deposits, which were formed at identical initial Ca concentration, suggests that the practice of considering hardness, without paying any attention to the specific types of anions present, as a measure of scaling propensity of water is questionable.

Crystal structures were compared to understand why some investigators (Bramson et al., 1995, 1996) observed that presence of small amounts of CaCO_3 strengthened the normally weak CaSO_4 scale. Figure 6b shows the structure for a porous and loose precipitate. Under the same temperature and concentration, CaCO_3 produces a dense scale (Figure 8b). It seems that coprecipitation reduces the deposit strength from that of pure CaCO_3 (Figures 8b and 10b) while the presence of CaCO_3 seems to strengthen the loosely structured pure CaSO_4 scale (Figures 6b and 10b). The scale in coprecipitation (Figure 10b) has a non-uniform structure in comparison to those of pure precipitation (Figures 6b and 8b).

Conclusions

Coprecipitation occurs in all industrial water systems and its qualitative and quantitative understanding is necessary in various areas, eg., developing effective additives, employing proper pre-treatment steps, developing predictive models, etc.

A series of batch tests (a total of 57 runs) were carried out at three different temperatures to characterize the precipitation and coprecipitation characteristics of CaCO_3 and CaSO_4 . The duration of each run was about 350 h to insure thermodynamic equilibrium. Routine sampling and determination of Ca concentration for designated runs provided data for kinetic analysis. Concentrations of calcium, sulfate and carbonate and the deposit structure were determined at the end of the test for all runs. However, the results are more of a qualitative nature than a quantitative one.

It was found that induction period and kinetics of coprecipitation of these two salts follow that of pure CaCO_3 . However, thermodynamic concentrations of Ca in coprecipitation followed that of pure CaSO_4 irrespective of the fact whether equilibrium calcium concentration of Ca is above or below that of CaCO_3 . The precipitate structure is affected by co-existence of salts and tends to result in a coprecipitate that is stronger than pure CaSO_4 and weaker than pure CaCO_3 precipitate. The results also suggested that the crystal growth stage cannot be due to or at least only due to ion incorporation into the crystal lattice.

Since coprecipitation affects the structure, the application of a predictive model developed for a pure salt is questionable when coprecipitation exists. Also the practice of considering hardness, as a measure of scaling propensity of water, without paying any attention to the specific types of anions present is questionable.

The future studies will include quantification of results; all the constituents of the solution need to be monitored with time for this purpose. More frequent sampling is required during the initial period to quantify kinetic data and rate constants. In addition, the solution pH should not vary between the runs and should be monitored during the runs to quantify K_{sp} values. Also of interests are the determination of crystal structure with XRD analysis and examination of coprecipitation with one dominant salt and the other in minute quantities to study interactive effects.

Nomenclature

A	surface area, (m^2)
A_1	constant in Equation (6)
C, C_0	solution and equilibrium concentrations, respectively (Equation 14), (mol/L)
J	rate of nucleation, (# nuclei/ $\text{cm}\cdot\text{s}$)
k_1 and k_2	constants in Equations (7) and (8), respectively
K	Boltzmann constant, (1.380662×10^{-23} J/K $^{-1}$)
K_{sp}	the solubility product, (mol^2/L^2)
K_1, K_2	first and second dissociation constants of carbonic acid, (mol/L)
n, n^*	number of molecules, respectively, in a nucleus and in a critical nucleus
N_A	Avagadro's number
r	the radius of the nucleus, (m)
S	$(C - C_0)/C_0$, degree of supersaturation
T	the absolute temperature, (K)
V_G	germination velocity, (# nuclei formed/min)
V_m	the mean molecular volume of the crystal, (m^3)

Greek Letters

α	distribution factor, ($0 < \alpha < 1$)
β	geometrical shape factor
ΔG and ΔG^*	Gibbs free and critical free energies, respectively, (J)
θ_G	the latency time or germination period, (s)
θ_{ind}	induction time, (s)
σ	solid-liquid interfacial surface energy, (J/ m^2)
μ_1, μ_2	chemical potential in the dissolved and solid states, respectively, (J/mol)
ϕ	factor less than unity relating homogeneous and heterogeneous nucleation

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Manuscript received January 22, 1999; revised manuscript received January 12, 2000; accepted for publication January 13, 2000.