Coprecipitation of CaCO$_3$ and CaSO$_4$

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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; Khamski, 1969). The significant effect that neglecting the existence of an ion-pair can have on $K_{sp}$ values has also been investigated (e.g., Reardon and Langmuir, 1974; Plummer and Busenberg, 1982). Salinity effects have been quantified by incorporating the ionic strength in predictive relationships (e.g., Power and Fabaus, 1964; Moller and Rajagopalan, 1975; Harned and Davis, 1943). In addition, there has been numerous studies on assessment and development of inhibitors (e.g., 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 (e.g., Turner and Smith, 1998; Kazmierczak et al., 1982; Kharin, 1974; Kharin et al., 1980; Nielsen, 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 (e.g., 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 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

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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 CaCO₃ and CaSO₄ 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 CaCO₃ and CaSO₄ 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):

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

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

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), $\Delta G$ will become negative and the solution will nucleate. Therefore, there is a critical $\Delta G^*$ which represents an energy barrier for nucleation. Heterogeneous nucleation takes place at lower critical supersaturation (lower $\Delta G^*$) and its critical free energy is approximated by:

$$
\Delta G_{\text{het}}^* = \phi \Delta G^*
$$

The corresponding critical radius and the number of molecules in a critical radius are $r^*$ and $n^*$ (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.

$$
r^* = \frac{2 V_m \sigma}{k T \ln \left( C_{\text{solution}}/C_{\text{solid}} \right)}
$$

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

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):

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

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

$$
J = k_1 C_{\text{in}}^m
$$

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

Growth

Various theories exist for crystal growth (Neilson, 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 CaCO₃ 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:

\[ K_{sp} = [Ca^{2+}][CO_3^{2-}] \]  

(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 Loewenthall and Marais (1976). Distribution factors in a closed system are:

\[ a_{HCO_3} = [1 + (K_1/[H^+]) + (K_2/[H^+]^2)]^{-1} \]  

(10)

\[ a_{HCO_3^-} = [1 + ([H^+]K_1) + K_2/[H^+]^2]^{-1} \]  

(11)

\[ a_{CO_3^{2-}} = [1 + ([H^+]K_2) + ([H^+]^2)/(K_1 K_2)]^{-1} \]  

(12)

Open systems that provide a venue for exchange of CO₂ 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 \( V_C \) (Equation 13), which was derived from work of Volmer (1939), and Becker and Dorr ing (1935):

\[ V_C = 1.22 \times 10^{-2} V_0^{0.88} \]  

(13)

\[ \log \theta_C = \log \left( \frac{([C - C_0]/C_0) \times [C]}{C_0} \right) \]  

(14)

Germination velocity, \( V_C \), 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, \( \theta_C \), is simply the time taken until the onset of nuclei formation. Stirring and agitation (mainly in the form of the bubbled gas) influenced both \( V_C \) and \( \theta_C \). 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 CaCO₃ 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 CaCO₃. 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 CaSO₄, which may precipitate in three forms, namely gypsum (CaSO₄·2H₂O), anhydrite (CaSO₄) and hemihydrate (CaSO₄·1/2H₂O). Within industry, gypsum and anhydrite are the predominant forms as they precipitate below 100°C; hemihydrate dominates at temperatures above 102°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 CaSO₄ 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 CaCO₃ 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 CaSO₄, 0.02 M CaCO₃ and 0.01 M
Table 1. Solution concentration matrix.

<table>
<thead>
<tr>
<th>CaCO₃ (M)</th>
<th>0</th>
<th>0.005</th>
<th>0.01</th>
<th>0.015</th>
<th>0.02</th>
<th>0.03</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>2*</td>
<td>3</td>
<td>4*</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>6</td>
<td>7*</td>
<td>8</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaSO₄</td>
<td>0.01</td>
<td>10*</td>
<td>11</td>
<td>12*</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>(M)</td>
<td>0.015</td>
<td>14</td>
<td>15</td>
<td>16</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>18*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Runs involved in kinetic analysis.

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.

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.

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
Effect of Initial Concentration
Increasing the initial calcium concentration from 0.01 M to 0.02 M reduces the induction period for pure CaCO₃ from about 65 h to 50 h (Figures 1a and 2a). For pure CaSO₄ 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 CaCO₃ is half that of CaSO₄ and the induction period for the mixture follows that of CaCO₃ irrespective of the solution temperature and initial Ca concentration (Figures 3 and 4). However, the solubility concentration of the mixture follows that of CaSO₄ 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 CaSO₄, it does irrespective of whether equilibrium calcium concentration of pure CaSO₄ is above or below that of pure CaCO₃. As we see from the figures, in some cases the equilibrium concentration of pure CaCO₃ is above that of pure CaSO₄ and while the relationship is reversed for others. This was due to the fact that the CaCO₃ solubility is pH dependent (Equations 9 and 12) while CaSO₄ solubility is independent of pH for pH>3; since pH was not the same for all
pure CaCO₃ solutions, it resulted in variation in relative solubility with respect to CaSO₄. Despite this fact, the equilibrium solubility of the mixture followed that of pure CaSO₄ 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 coexistence of anions, which precipitate calcium, cannot be neglected.

Figures 3 and 4 show that consistently in all the runs the induction period for CaCO₃ is almost half that of CaSO₄. 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 CaCO₃ 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 (4 hrs) for CaCO₃ 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) CaSO₄ at various temperatures; Figure 6 shows that of 0.02 M CaSO₄. 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 CaSO₄ at: (a) 60°C; (b) 70°C; and (c) 80°C.

Figure 6. SEMs for 0.02 M CaSO₄ 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
CaCO$_3$; this concurs with the results of Sohnel 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 where 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, e.g., 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 CaCO₃ and CaSO₄. 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 CaCO₃. However, thermodynamic concentrations of Ca in coprecipitation of CaCO₃ follow that of pure CaSO₄, irrespective of the fact whether equilibrium calcium concentration of Ca is above or below that of CaCO₃. The precipitate structure is affected by co-existence of salts and tends to result in a coprecipitate that is stronger than pure CaSO₄ and weaker than pure CaCO₃ 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 Kₛ 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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, A₁</td>
<td>surface area, (m²)</td>
</tr>
<tr>
<td>C, C₀</td>
<td>solution and equilibrium concentrations, respectively (Equation 14), (mol/L)</td>
</tr>
<tr>
<td>J</td>
<td>rate of nucleation, (# nuclei/cm²-s)</td>
</tr>
<tr>
<td>k₁, k₂</td>
<td>constants in Equations (7) and (8), respectively</td>
</tr>
<tr>
<td>K</td>
<td>Boltzmann constant, (1.380662 × 10⁻²² J K⁻¹)</td>
</tr>
<tr>
<td>KₛP</td>
<td>the solubility product, (mol²/L²)</td>
</tr>
<tr>
<td>K₁, K₂</td>
<td>first and second dissociation constants of carbonic acid, (mol/L)</td>
</tr>
<tr>
<td>n, n*</td>
<td>number of molecules, respectively, in a nucleus and in a critical nucleus</td>
</tr>
<tr>
<td>Nₐ</td>
<td>Avogadro’s number</td>
</tr>
<tr>
<td>r</td>
<td>the radius of the nucleus, (m)</td>
</tr>
<tr>
<td>S</td>
<td>degree of supersaturation</td>
</tr>
<tr>
<td>T</td>
<td>the absolute temperature, (K)</td>
</tr>
<tr>
<td>Vₑ</td>
<td>germination velocity, (# nuclei formed/min)</td>
</tr>
<tr>
<td>Vₘ</td>
<td>the mean molecular volume of the crystal, (m³)</td>
</tr>
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</table>

Greek Letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>distribution factor, (0&lt;α&lt;1)</td>
</tr>
<tr>
<td>β</td>
<td>geometrical shape factor</td>
</tr>
<tr>
<td>ΔG and ΔC</td>
<td>Gibbs free and critical free energies, respectively, (J)</td>
</tr>
<tr>
<td>θₑ</td>
<td>the latency time or germination period, (s)</td>
</tr>
<tr>
<td>ηₑ</td>
<td>induction time, (s)</td>
</tr>
<tr>
<td>σ</td>
<td>solid-liquid interfacial surface energy, (J/m²)</td>
</tr>
<tr>
<td>μ₁, μ₂</td>
<td>chemical potential in the dissolved and solid states, respectively, (J/mol)</td>
</tr>
<tr>
<td>φ</td>
<td>factor less than unity relating homogeneous and heterogeneous nucleation</td>
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References


Buckley, H.E., Crystal Growth, John Wiley and Sons Ltd., New York, NY (1951).


