



Influence of additives on the precipitation of gypsum in sodium chloride solutions

S.K. Hamdona^{a*}, O.A. Al Hadad^b

^aNational Institute of Oceanography and Fisheries, Alexandria, Egypt
Tel./Fax: +20 (3) 545-0652; email: hamza_hamdona0@yahoo.com

^bA Girls College, Prescience Agency Management of Education, Madina Monawara, Kingdom of Saudia Arabia

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Abstract

The kinetic of precipitation of calcium sulfate dihydrate (gypsum) in sodium chloride solutions was investigated at various supersaturation from 1.05–2.49, pH = 8.50, 25°C and ionic strength 0.5 M. The rate of precipitation showed a quadratic dependence upon the relative supersaturation which suggests a surface-controlled growth mechanism. Influence of a number of amino acids on the rate of reaction has been studied at several additive concentrations. The addition of amino acids even at relatively low concentration (10^{-6} mol l⁻¹) markedly retard the rates of precipitation. Moreover, the effect was enhanced as the relative supersaturations decreased. Additionally the synergistic effect of one amino acid and other inhibitors was studied. The retardation effect of these additives has been attributed to the blocking of active sites by adsorption of these additives at the crystal surfaces. Inhibition of crystallization of gypsum by amino acids can be interpreted in terms of a Langmuir adsorption isotherm. This research will help to understand the usefulness of these compounds for industrial applications such as the control of scale.

Keywords: Gypsum; Additives; Precipitation; Amino acids

1. Introduction

The precipitation of alkaline earths sulfate and carbonate scales in geothermal applications, evaporative desalination plants, cooling towers, and petroleum engineering is a persistent problem

[1–4]. The formation of mineral scales is an economic barrier to recovery of potable water from sea or brackish water as well as on the industrial utilization of many natural waters. Scales deposition occurs when natural waters are heated or concentrated beyond certain limit. The formation of scales on heat transfer surface in sea water distillation plants represents a limit on the

*Corresponding author.

temperature at which they can be operated and the brine concentration factors that can be tolerated. Such factors limit the economics that can be achieved in a given distillation plant designs for instance. If in expensive methods could be found for preventing the formation of scale on plant heat transfer surfaces, there would be immediate economic benefits [5–10].

The crystallization of calcium sulfate scales has been recognized to be strongly dependent on kinetic factors, especially the degree of saturation, ionic strength and temperature. The influence of foreign substance is also needs to be considered.

Additives play an important part in the theory of crystallization in supersaturated solutions. The factors that govern the mechanism of precipitation of these sulfate salts are therefore of considerable interest, especially the influence of foreign substance which may exert a marked effect on the rates of precipitation either through adsorption at surface of crystals or by lattice substitution. Unfortunately, no satisfactory way of effectively preventing this type of scale has been discovered. As a result, a variety of commercial products appears in the water-treatment market, and research continues to develop method that is satisfactory both in economical and environmental terms.

Recently, it is found that the presence of metal ions in the reaction medium was inhibited the rate of precipitation of calcium sulfate dehydrate (gypsum). Precipitation is inhibited and a precipitation rate is following order: $Cd > Cu > Fe > Cr$. Complete inhibition of gypsum was not found in any concentration of these metal ions and degree of saturations [11]. Lioliou et al. found that the polymeric molecules on the growing supercritical gypsum nuclei showed different affinity for the polymers tested in agreement with the respective inhibition efficiency, in the order: $PAA1 > PAA2 > PSA > PAA3$. The presence of polymers in the supersaturated solutions resulted

in modification of the precipitated gypsum crystal morphology [12].

In the present work precipitation and crystal growth of gypsum from seeded supersaturated calcium sulfate dihydrate solutions has been investigated. The influence of some amino acids; glycine (Gly), serine (Ser), aspartic acid (Asp) and arginine (Arg) upon the rate of precipitation has been studied. Inhibition of the crystal growth rates in the presence of mixed additive from arginine, poly(acrylamid carboxyl) (MW-200,000) (PAAC); arginine, H_3PO_4 and arginine-cadmium, are determined to illustrate the synergistic effect.

2. Materials and methods

2.1. Analytical grade chemicals

Grade A glassware and doubly distilled deionized water were used. Calcium chloride solutions were standardized by ethylendiaminetetra acetic acid (EDTA) titration after careful filtration. Sodium sulfate and sodium chloride solutions were filtered by using 0.22 μm Millipore filters and standardized by passing through a cation-exchange resin (Dowex 50) in the hydrogen form and titrating the eluted acid with standardized sodium hydroxide.

2.2. Calcium sulfate dihydrate crystals

These were prepared by precipitation from calcium chloride and sodium sulfate solutions, as described previously by Lui and Nancollas [13]. The crystals were aged at least one month before being filtered to obtain the dry crystals that were used in crystal growth experiments. The crystals were confirmed as gypsum by x-ray powder diffraction (Shimadzu XD-3 diffractometer) and by scanning electron microscopy. The specific surface area (SSA) of the crystals, measured using a single point nitrogen adsorption apparatus

was $0.35 \text{ m}^2\text{g}^{-1}$. All experiments were done in a thermostatted double walled pyrex glass vessel of 500 ml capacity and were adjusted to the required temperatures by circulating thermostatted water through the outer jacket. Stemming was effected using a variable-space magnetic stirrer with a Teflon stirring bar. Nitrogen gas was first bubbled into a solution of the electrolyte at the temperature of the reaction for saturation with water vapor, and then into the reaction vessel throughout the duration of the experiment.

2.3. Supersaturated solutions

These were prepared by the addition of thermostatted known volumes of calcium chloride solutions followed by careful addition of the appropriate amounts of sodium sulfate solutions in the cell which adjusted to the required ionic strength (0.5 M) with sodium chloride solutions. The reaction vessel was fitted with a Teflon cover with holes for the electrodes and sampling. At the beginning of the experiment, the pH of the supersaturated solutions was adjusted to the desired value (8.50) by the controlled addition of sodium hydroxide standard solutions. The pH of solutions was measured using a combination electrode (9100 Herisau) standardized before and after each experiment with NBS primary standard buffer solution.

The mineralization reactions were initiated by inoculation with dry seed crystals in the reaction vessel. The degree of supersaturation maintained at constant levels by the simultaneous addition of ionic species by means of a Metrohm 555 Dosimat coupled in parallel, electronically, to a Metrohm 614 impulsomat titrator. The titrator, in turn, was controlled by a specific ion electrode (Orion Research, Boston, MA) that maintained the Ca^{2+} concentration at its initial pre-set value.

Inhibitor solutions were also introduced as titrants in order to compensate for dilution effects. In addition, samples were periodically withdrawn

and filtered at the reaction temperature through Millipore filters ($0.22 \mu\text{m}$), prior to solution and solid-phase analysis. The data confirmed that the lattice-ion and inhibitor concentrations were constant to within 1%.

3. Results and discussion

The concentrations of free ionic species in the solutions were computed by successive approximations for the ionic strength, I , as described previously [14] using activity coefficients calculated from the extended form of the Debye–Hückel equation proposed by Davies [15]. The rate of precipitation, R , may be expressed in terms of degree of saturation, σ , by Eq. (1):

$$R = dm/dt = R_s \sigma^n \quad (1)$$

in which m is the number of moles precipitated in time t , R a rate constant, n the effective order of reaction and s is proportional to the number of growth sites available on the seed crystals. The degree of saturations are defined in terms of ionic products and solubility products for the calcium sulfate dihydrate salt as in Eq. (2):

$$\sigma = (IP)^{1/2} - K_{\text{SO}}^{1/2} / K_{\text{SO}}^{1/2} \quad (2)$$

where the ionic products, IP , and the solubility product, K_{SO} , are expressed in terms of the appropriate activities of the ionic species $[(\text{Ca}^{2+})(\text{SO}_4^{2-})]^{1/2}$ at time t and at equilibrium respectively.

Crystal growth experimental conditions are summarized in Table 1 in which $[\text{Ca}]_t$ and $[\text{SO}_4]_t$ are the total molar concentration of calcium and sulfate, respectively. Typical time plots of the amount of gypsum per moles precipitate, calculated from the titrants addition, are shown in Fig. 1. The slopes of these lines, reflecting the rates of crystal growth, are summarized in Table 1. Since the extent of the growth reaction

Table 1

Precipitation of calcium sulfate dihydrate at ionic strength 0.5 mol l^{-1} (NaCl), pH = 8.5, $[\text{Ca}]:[\text{So}_4] = 1:1$ and 25°C

| Exp. no. | $[\text{Ca}]/10^{-5} \text{ mol. l}$ | σ | Seed, mg | Rate, $10^{-3} \text{ mol. min}^{-1} \text{ m}^{-2}$ |
|-----------------|--------------------------------------|----------|----------|--|
| 20 _b | 0.88 | 1.05 | 200 | 0.948 |
| 21a | 0.88 | 1.05 | 200 | 0.951 |
| 22 | 1.00 | 1.32 | 50 | 1.471 |
| 23 _b | 1.00 | 1.32 | 100 | 1.490 |
| 24a | 1.00 | 1.32 | 100 | 1.489 |
| 25 | 1.00 | 1.32 | 200 | 1.499 |
| 26 | 1.00 | 1.32 | 300 | 1.501 |
| 27 | 1.00 | 1.32 | 400 | 1.511 |
| 28 _b | 1.20 | 1.79 | 100 | 1.904 |
| 29a | 1.20 | 1.79 | 100 | 1.889 |
| 30 _b | 1.30 | 2.02 | 200 | 2.423 |
| 31a | 1.30 | 2.02 | 200 | 2.433 |
| 32 | 1.30 | 2.02 | 300 | 2.465 |
| 33 | 1.50 | 2.49 | 50 | 3.241 |
| 34 _b | 1.50 | 2.49 | 100 | 3.266 |
| 35a | 1.50 | 2.49 | 100 | 3.308 |

Stirring speed: 300 rpm for experiments (a) and 200 for all others.

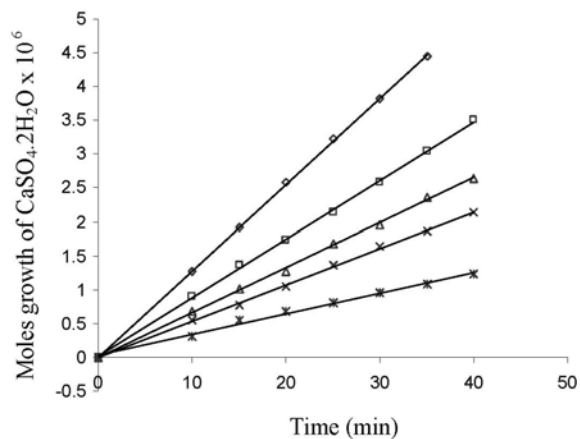


Fig. 1. Plots of moles for the crystal growth of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ against time of different super saturation, $\sigma = 1.05$ (*); $\sigma = 1.32$ (x); $\sigma = 1.79$ (Δ); $\sigma = 2.02$ (\diamond) and $\sigma = 2.29$ (\square).

was small, the change in crystal surface area accompanying the reaction could be ignored. Table 1 shows that the rates of crystal growth of calcium sulfate dihydrate were proportional to the

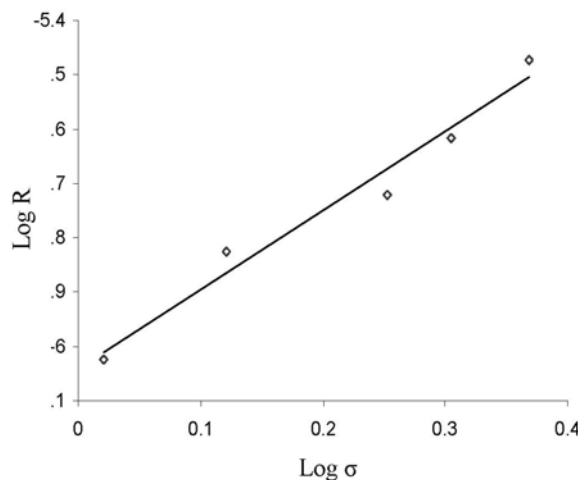


Fig. 2. Plots of $\log R$ against $\log \sigma$.

mass of seed crystals used to initiate the reaction. The effective order of reaction, determined from the slope of typical plots of $-\log R$ against $\log \sigma$, as shown in Fig. 2, confirms a second-order dependence upon relative super saturation ($n \approx 2$)

Table 2

Precipitation of calcium sulfate dihydrate in the presence of some amino acids at $\sigma = 1.32$ and 25°C

| Exp. no. | Additive, $10^{-6} \text{ mol l}^{-1}$ | | Rate, $10^{-6} \text{ mol min}^{-1} \text{ m}^{-2}$ | % inhibition |
|----------|--|----------|---|--------------|
| 23 | 0.0 | — | 1.490 | — |
| 45 | 1.0 | Glycine | 1.435 | 3.691 |
| 46 | 5.0 | Glycine | 1.254 | 15.839 |
| 47 | 8.0 | Glycine | 1.183 | 20.604 |
| 48 | 10.0 | Glycine | 1.104 | 25.906 |
| 49 | 15.0 | Glycine | 0.975 | 34.564 |
| 50 | 20.0 | Glycine | 0.894 | 40.000 |
| 51 | 1.0 | Serine | 1.365 | 8.369 |
| 52 | 5.0 | Serine | 1.062 | 28.725 |
| 53 | 8.0 | Serine | 0.875 | 41.275 |
| 54 | 10.0 | Serine | 0.815 | 45.302 |
| 55 | 15.0 | Serine | 0.727 | 51.208 |
| 56 | 20.0 | Serine | 0.594 | 60.134 |
| 57 | 1.0 | Aspartic | 1.313 | 11.879 |
| 58 | 5.0 | Aspartic | 0.966 | 35.165 |
| 59 | 8.0 | Aspartic | 0.762 | 48.859 |
| 60 | 10.0 | Aspartic | 0.685 | 54.027 |
| 61 | 15.5 | Aspartic | 0.552 | 62.953 |
| 62 | 20.0 | Aspartic | 0.428 | 71.275 |
| 63 | 1.0 | Arginine | 1.065 | 28.523 |
| 64 | 5.0 | Arginine | 0.693 | 53.490 |
| 65 | 8.0 | Arginine | 0.552 | 62.953 |
| 66 | 10.0 | Arginine | 0.456 | 69.396 |
| 67 | 15.0 | Arginine | 0.333 | 77.651 |
| 68 | 20.0 | Arginine | 0.282 | 81.074 |

in Eq. (1). The suggestion of a predominantly surface-controlled process over a range of relative supersaturation may also be supported by the observed independence of the experimental rate of precipitation on changes in fluid dynamics, as shown in Table 1 (compare experiments a and b). A similar mechanism for the crystal growth of calcium sulfate dihydrate has been observed [15–20].

When a solute crystallizes from its supersaturated solution, the presence of a third component can often have a dramatic effect on the crystal growth kinetics and habitually form the crystalline phase; such a third component is effective at relatively low concentrations ($10^{-9} < X$

$\text{mol}^{-1} < 10^{-3}$) and exhibit a marked specificity in their action, factors which have led to the generally held conclusion that they are adsorbed onto growing crystal surfaces [21–23].

Adsorption of impurities onto crystal faces changes the relative surface free energies of the faces and may block sites essential to the incorporation of new solute into the crystal lattice. These effects may result in changes in the growth kinetics.

3.1. Effect of amino acids on the crystal growth

In the present section, the rate of crystal growth of calcium sulfate (gypsum) in sodium

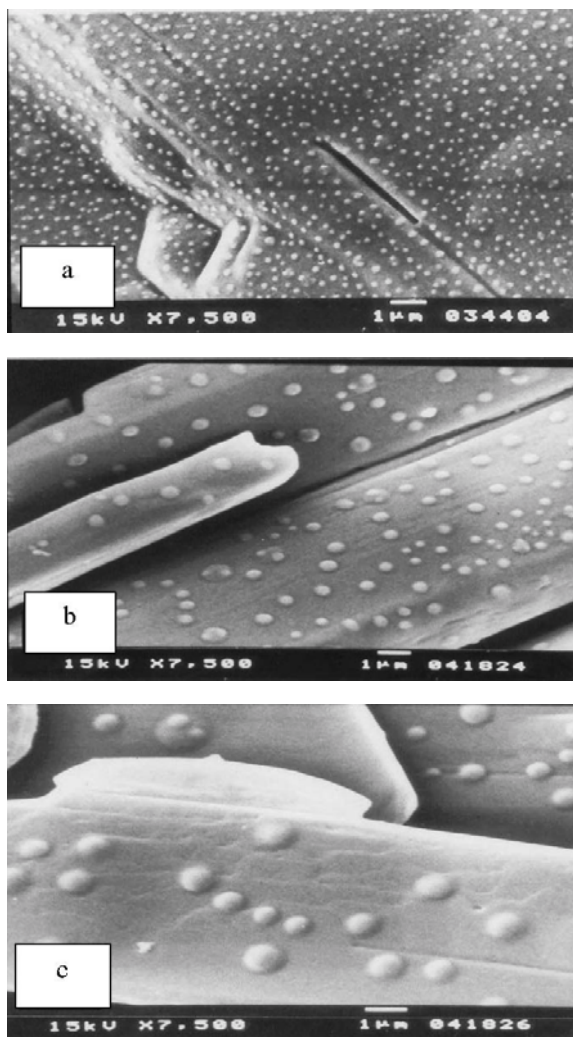


Fig. 3. SEM of gypsum crystal grown without additives (a), in the presence of Arg (b), and in the presence of Arg + PAAC (c).

chloride solutions was studied in the presence of glycine (Gly), serine (ser) aspartic (ASP) and arginine (Arg) acids. Table 2 summarizes the date of precipitation of gypsum in the presence of amino acids at the same supersaturation, $\sigma = 1.32$ for each additive; each experiment was made in duplicate or triplicate. It can be seen that concentrations as low as $20 \times 10^{-6} \text{ mol}^{-1}$ for each additive (experiments 50, 56, 62 and 68) mark-

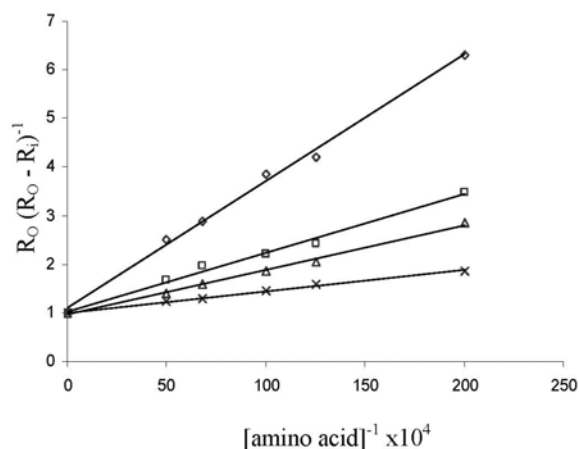


Fig. 4. Plots of $R_o (R_o - R_i)^{-1}$ against $[\text{amino acid}]^{-1} \times 10^4$ Gly (◇), Ser (□), Asp (△) and Arg (×).

edly reduce the precipitation rates by as much as 40.00, 60, 13, 71.28 and 81.07% in the presence of Gly, Ser, ASP, and Arg, respectively. It can be seen that the effectiveness of the inhibition is Arg > Asp > Ser > Gly. As the concentration of additive molecules increases, the active growth sites on the crystal surfaces may be blocked through adsorption and the rate of crystal growth decreases.

Scanning electron microscopy of the precipitates obtained in typical experiments in the absence of additives and in the presence of arginine is shown in Fig. 3(a) and (b), respectively. Fig. 3(a) and (b) shows that the number of active sites may be decreased by adsorbing the arginine molecules on these sites.

Amino acids act as strong chelating agents which their advantages is capability to be adsorbed on inorganic solids. The model proposed suggests that as the amino acids molecule approaches the particle surface, it causes the anions in the stern layer to be released and become attached to the adsorption sites through amino acids/anion-exchange mechanism [24].

The adsorption of the molecules at active sites on the crystals surfaces may be interpreted in terms of the Langmuir adsorption isotherm [23].

Table 3
Some properties of amino acids which used in this study.

| Amino acid | 3-letter code | Structure | Mw | pK ₁ | No. of | | Properties |
|---------------|---------------|--|-----|-----------------|--------------|-------------|--------------------------|
| | | | | | Acidic group | Basic group | |
| Glycine | Gly | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$ | 75 | 2.34 | 1 | 1 | Weak polar |
| Serine | Ser | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CH} \end{array}$ | 105 | 2.21 | 1 | 1 | Polar hydrophilic |
| Aspartic acid | Asp | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array}$ | 133 | 2.03 | 2 | 1 | Polar hydrophilic acidic |
| Arginine | Arg | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{C}=\text{NH} \\ \\ \text{NH}_2 \end{array}$ | 174 | 1.17 | 1 | 2 | Polar Hydrophilic basic |

This requires a linear relationship between the inverse of relative reduction in rate, $R_o/(R_o-R_i)$ and the reciprocal of the inhibitor concentration. R_o and R_i are the rate of precipitation in absence and presence of inhibitor, respectively. The applicability of the Langmuir model is demonstrated by the linearity of plots in Fig 4. The values of the adsorption affinity constants K_L are 22.96×10^4 , 10.54×10^4 , 8.48×10^4 l.mol⁻¹ for arginine, aspartic, serine and glycine, respectively. These

values reflect the high adsorption affinity at the same relative supersaturation ($\sigma = 1.32$) in the order Arg > Asp > Ser > Gly.

Calculations of Ca-AA_s complex formation based on the available literature data [26] showed that it accounts for less than 1% of the initial Ca concentration even at the highest amino acids concentration investigated. Therefore, we assume that the changes in precipitation yields due to the complexation are negligible.

Table 4

Effect of arginine in the presence of some additives on the precipitation of calcium sulfate dehydrate at $\sigma = 1.79$ and 25°C

| Exp. no. | [additive] $\times 10^6 \text{ mol. l}^{-1}$ | Rate $\times 10^6 \text{ mol. min.}^{-1}\text{m}^{-2}$ | % inhibition |
|----------|--|--|--------------|
| 28 | 0 Arg | 1.904 | — |
| 85 | 1 Arg | 1.667 | 12.447 |
| 86 | 5 Arg | 1.142 | 40.021 |
| 87 | 8 Arg | 0.979 | 48.582 |
| 88 | 10 Arg | 0.837 | 56.040 |
| 89 | 20 Arg | 0.567 | 70.221 |
| 90 | 1 Arg + PAAC | 1.624 | 14.916 |
| 91 | 5 Arg+ PAAC | 1.071 | 43.750 |
| 92 | 8 Arg + PAAC | 0.909 | 52.258 |
| 93 | 10 Arg + PAAC | 0.778 | 59.139 |
| 94 | 20 Arg + PAAC | 0.510 | 73.214 |
| 95 | 1 Arg + H_3PO_4 | 1.566 | 17.752 |
| 96 | 5 Arg + H_3PO_4 | 1.031 | 45.851 |
| 97 | 8 Arg + H_3PO_4 | 0.805 | 57.720 |
| 98 | 10 Arg + H_3PO_4 | 0.688 | 63.866 |
| 99 | 20 Arg + H_3PO_4 | 0.430 | 77.416 |
| 100 | 1 Arg + Cd^{2+} | 1.471 | 22.742 |
| 101 | 5 Arg + Cd^{2+} | 0.851 | 55.305 |
| 102 | 8 Arg + Cd^{2+} | 0.688 | 65.288 |
| 103 | 10 Arg + Cd^{2+} | 0.538 | 71.744 |
| 104 | 20 Arg + Cd^{2+} | 0.311 | 83.666 |

The factors that might govern the efficiency of amino acids are: (a) the number of amino and carboxylic groups content, on the structure of amino acids (b) the molecular size, (c) the molecular weight, (d) the pKa value. Table 3 shows that the four factors for the present amino acids fall in the following order: Arg > Asp > Ser > Gly, which is the same order of reactivity in inhibiting the crystal growth rate of gypsum crystals and the adsorption affinity constant K_L values.

The influence of the precipitation driving force upon the degree of inhibition by amino acids is specially interesting. Experiments for the precipitation of gypsum in the presence of arginine (Arg) at different degrees of relative supersaturation ($\sigma = 1.32, 1.7$ and 2.42) were made. Concentrations as low as $20 \times 10^{-6} \text{ mol.l}^{-1}$ from arginine (Arg) reduce the crystal growth rates by at least 78.12, 70.22 and 66.00% compared to that

in pure solution without additives at the same relative supersaturation, respectively. A similar dependence of the degree of inhibition on change in driving force has been observed for the influence of phosphate, sulfate and magnesium ion on the rate of dissolution and crystallization of alkaline earth fluorides in aqueous solutions [5,8, 23,28,29]. As noted for the crystallization of gypsum by Wejinen et al. [30], the effectiveness of the phosphonate [HEDP] as an inhibitor is dependent on the degree of super saturation. In terms of the simple Langmuir equation, the values of the adsorption affinity constant K_L are $2.30, 1.28$ and $1.14 \times 10^5 \text{ L mol}^{-1}$ at relative supersaturation; $\sigma = 1.32, 1.79$ and 2.49 , respectively. These values reflect the high adsorption affinity at low relative supersaturation in the presence of arginine. The marked dependence upon degree of saturation (σ) of the effectiveness

of growth inhibitor has important consequences in assessing the usefulness of these compounds for industrial applications such as the control of scale.

3.2. Mixed additives

In practical situations inhibitors and dispersants are often added as a mixtures. To investigate the possible synergistic effect of such mixtures on growth of gypsum, some additional experiments have been performed at $\sigma = 1.79$ and $\text{pH} = 8.5$.

Table 4 shows the experiments performed in the presence of the same concentrations [$10 \times 10^{-6} \text{ mol l}^{-1}$] of both inhibitors [Arg + PAAC, Arg + H_3PO_4 , Arg + Cd^{2+}]. It can be seen that concentrations of mixed additives reduced the crystal growth rates by at least 59.14, 63.87, and 71.74%, respectively, compared with 56.04% in the presence of Arg only. A similar behavior has been observed for the influence of ethylenediamine tetra(methylene phosphonate), ENTMP, and a polyacrylic acid, K-732 (BF Goodrich) on the crystal growth of calcium fluoride [31]. But we can see that the combined retarding effect of these mixtures was less than the sums of those components at the same saturation. This suggests molecular interference between the additives and essentially electrostatic interaction between the inhibitors and mineralizing surface through the disrupted adsorption layer. Scanning electron microscopy of the crystal surfaces of gypsum in the presence of Arg and mixture from Arg + PAAC are shown in Fig. 3(b) and 3(c), respectively, showing that the number of active growth sites on the crystal surfaces may be blocked through preferential adsorption by the mixture molecules more than in the case of Arg only.

4. Conclusions

Kinetic studies of gypsum precipitation in sodium chloride solutions showed a quadratic

dependence upon the relative supersaturation which suggests surface-controlled growth mechanism.

Crystal growth experiments in the presence of amino acids as inhibitors clearly indicate that the effectiveness of inhibitors was $\text{Arg} > \text{Asp} > \text{Ser} > \text{Gly}$. Results further indicate that this effect was enhanced as the degree of saturation decreased. Additional experiments were performed at the presence of mixed additives. Inhibition effect of these additives was interpreted in terms of a Langmuir adsorption isotherm.

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