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Influence of Some Phosphates on The Rate of Calcium Sulfate Dihydrate Crystallization in sodium Chloride Solution

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Crystallization of calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in sodium chloride solutions at different supersaturation ($\delta = 1.2-2.49$), pH = 3, ionic strength ($I = 0.15 \text{ M}$) and at 25°C was studied. The influence of disodium hydrogen phosphate and sodium tripolyphosphate and disodium dihydrogen phosphate having very low concentrations ($10^{-7} \text{ mol dm}^{-3}$) on the rate of crystallization at different supersaturation was investigated. The rate of crystallization was found to be dependent of the stirring rate suggesting diffusion mechanism. The addition of all additives retarded the rate of crystallization to an extent proportional to their amounts present. Furthermore, the retardation effect was enhanced as the supersaturation decreases. The results also revealed that the increase in both pH (3 -10) and crystallization temperature ($20-80^\circ\text{C}$) brought about an increase in calcium sulfate crystallization rate.

Keyword: Crystallization; Additives; Calcium Sulfate; Solution, Phosphates.

1. Introduction

Calcium sulfate minerals (i.e., gypsum, anhydrite and hemi-hydrate) are common scale-deposit minerals in water treatment plants^[1-4] and oil and gas industry^[5]. Crystallization of calcium sulfate dihydrate (gypsum) is of importance in view of their applications in a number of industrial and environmental precipitation processes. With increasing temperature, the solubility of all calcium sulfate forms decreases. This is the cause of calcium sulfate scale formation on heat transfer surface^[6]. Crystallization can take place on foreign substance or dust particles in the solution and it is very difficult to reproduce the results of such studies^[7]. Earlier, many authors studied the growth of seed crystals of gypsum in super-saturation solutions^[8-12], crystallization of gypsum on other crystal surfaces^[13] and the precipitation on heated metal surface^[14]. The factors that govern this mechanism of precipitation and dissolution of the sparingly

soluble salts are therefore, of considerable interest, especially the influence of anions and cations which may exert a marked effect on the rate of precipitation, either through adsorption or by lattice substitution^[15]. The present work aims at studying the crystallization of gypsum under conditions simulating the cation exchanger regeneration system in case absence and presence some phosphates and polyphosphate additives.

2. Methodology

2.1. Materials

Calcium chloride CaCl_2 and sodium sulfate Na_2SO_4 (BDH, England) were used to prepare seed crystals. Hydrochloric acid HCl (MERCK, Germany) was used to adjust pH. (di-sodium hydrogen phosphate, sodium tri-poly phosphate, di-sodium di-hydrogen pyrophosphate, respectively. Sodium chloride NaCl from El-Nasr Pharmaceutical chemicals (ADWIC, Egypt) was chemical reagent grade. All solutions were

prepared with deionized water of high quality (conductivity $< 0.1 \mu\text{S cm}^{-1}$). A closed thermostatic double-walled vessel of 300 cm³ was used for all the experiments. The experiments were performed in the temperature range of 23-25 °C, and the systems were mechanically agitated with a flat-bladed stirrer at a constant rate (200 rpm).

2.2. Preparation of polycrystalline calcium sulfate dihydrate

Calcium sulfate dihydrate crystals were prepared by precipitation from calcium chloride and sodium sulfate solutions, as described previously by Lui and Nancollas^[16]. The obtained solid was aged at least for one month before being filtered to obtain the dry crystals that were used in crystal growth experiments. The crystals were identified as gypsum by X-ray powder diffraction (Shimadzu XD-3 diffractometer) and IR analysis by scanning electron microscopy. The crystallization of calcium sulfate dihydrate carried out under various conditions was 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.

$$R = dm / dt = R_s \delta^n \dots (2)$$

2.3. Supersaturated Solutions of Calcium Sulfate Dihydrate

Supersaturated solutions of calcium sulfate dihydrate 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 (3) by the controlled addition of hydrochloric acid standard solutions. The pH of solutions was measured using a combined glass electrode 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 crystallization rate followed potentiometric with time using metrohm titrano . The degree of supersaturation maintained at constant levels by the simultaneous addition of ionic species. Inhibitor solutions were also introduced as titrans in order to compensate for dilution effects. In addition, samples were periodically withdrawn and filtered at the reaction temperature through Millipore filters (0.22 μm), prior to solution and solid-phase analysis. The data confirmed that the lattice-ion and inhibitor concentrations were constant to within 1%.

For the calcium sulfate dihydrate crystallization growth experiments, the seed crystals of calcium sulfate dihydrate were prepared by a dropwise addition of 500 cm³ of a 0.6 mol dm⁻³ CaCl₂ solution to 500 cm³ of a 0.6 mol dm⁻³ Na₂SO₄ solution with a continuous magnetic stirring at 70°C over a period of 2 hours. The crystals obtained were filtered through a 0.22 mm membrane filter and washed repeatedly with deionized water until becoming free of NaCl. Then, the crystals were dried in an electric oven at about 105°C overnight.

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^[17] using activity coefficients calculated from the extended form of the Debye–Hückel equation proposed by Davies^[18]. The rate of precipitation, *R*, may be expressed by^[19]

$$R = dm/dt = R_s \delta^n \dots (1)$$

in which *m* is the number of moles precipitated in time *t*, *R* a rate constant, *n* the effective order of

reaction, and s proportional to the number of growth sites available on the seed crystals. The degree of saturations is defined in terms of ionic products and solubility products for the calcium sulfate dihydrate salt by the following expression^[20].

$$\delta = \frac{(IP)^{1/2} - K_{SO}^{1/2}}{K_{SO}^{1/2}} \dots \dots (2)$$

where the ionic products, IP, and the solubility product, K_{SO} , are expressed in terms of the appropriate activities of the ionic species

$$[(Ca^{2+})(SO_4^{2-})]^{1/2}$$

at time t and at equilibrium, respectively.

The degree of supersaturated (δ) of the solutions, which is defined as the ratio of the activity products divided by the thermodynamic solubility product of the mineral (K_{sp}), is where

$$\delta = \left\{ \frac{(Ca^{2+})(SO_4^{2-})}{K_{sp}} \right\}^{1/2} - 1 \dots \dots (3)$$

parentheses denote activities of the respective ions and K_{sp} is the thermodynamic solubility product of the precipitating solid. The activity coefficients of divalent cations and anions were assumed equal and were obtained using the extended Debye-Huckel equation as proposed by Davies^[15]:

$$-\log f_Z = 0.5115 Z^2 \left\{ \frac{I^{1/2}}{(1+I^{1/2})} - 0.3 I \right\} \dots (4)$$

where " f " are the activity coefficients for the Zvalent ions and I is the solution ionic strength. The value of K_{sp} was calculated as a function of temperature by means of the following relationship obtained by Marshall and Shlusher^[21] for calcium sulfate dihydrate in aqueous solutions from 0 to 110°C.

$$\log (K_{sp}) = 390.9619 - 152.6246 \log T - \frac{12,545.62}{T} + 0.0818493 T \dots (5)$$

Crystal growth experimental conditions are summarized in Table 1 in which $[Ca]_t$ and $[SO_4]_t$ 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.

The results cited in Table 1 show that the rate of crystal growth of calcium sulfate dihydrate was proportional to the mass of seed crystals used to initiate the reaction. The suggestion of a predominantly diffusion mechanism over a range of relative supersaturations may also be supported by the observed dependence of the experimental rate of precipitation on changes in fluid dynamics, as shown in Table 1 (compare experiments a, b, c and d), which conclude that the reaction is a mass transfer limited^[22]. A similar mechanism for the crystal growth of calcium sulfate dihydrate has been observed^[22, 23]. The effective order of reaction was determined from the slope of typical plots of $-\log R$ against $\log \delta$, as depicted in Figure 1 which confirms a first-order dependence upon relative supersaturation ($n = 1$) in Eq. (1).

Table 1: Crystallization of calcium sulfate dihydrate crystals, $T_{Ca} : T_{SO4} = 1 : 1$ at $t = 25$ oC, 50 mg seed, 200 rpm, ionic strength = 0.15 mol L⁻¹ (NaCl) and pH = 3

$T_{Ca^{2+}}/10^6 \text{ mol L}^{-1}$	$\delta \times 10$	wt. of seed/mg	$(r/10^4) \text{ mol min}^{-1} \text{ m}^{-2}$
9.482	12	50	1.8
10	13.2	50	2.0
10.775	15	50	2.315
11.637	17	50	2.56
12.93	20	50	2.92
15.04	24.9	50	3.7
(a) 10	13.2	50	2.2
(b) 10	13.2	50	2.4
(c) 10	13.2	50	2.51
(d) 10	13.2	50	2.623

(a): Stirring rate 300 rpm (b): Stirring rate 400 rpm (c): Stirring rate 500 rpm (d): Stirring rate 600 rpm

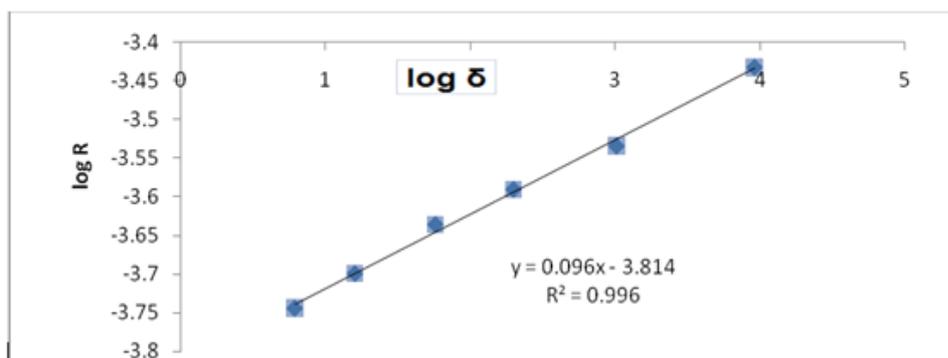


Fig 1: Plots of Log R against Log δ

Additives play an important role in the theory of crystallization and dissolution. Recently, it is found that the presence of metal ions in the reaction medium inhibited the rate of precipitation of calcium sulfate dihydrate. The effects of phosphates and polyphosphate as di-sodium hydrogen phosphate and sodium tri-polyphosphate and di-sodium di-hydrogen pyrophosphate on the rate of crystallization of calcium sulfate dihydrate crystals were studied. Previous studies showed that di-sodium hydrogen phosphate at close similarity conditions and substantiate my results in the percentage of inhibition of calcium sulphate dihydrate (reduce the rate of crystalisation)^[24].

and $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ upon the rate of crystallization of gypsum in sodium chloride solution was studied at 25°C ; stirring speed of 200 rpm, weight of seed crystals of gypsum 50 mg at solution ($\text{pH} = 3$), and a relative supersaturation ($\delta = 1.32$) results obtained are illustrated in Figure (2).

It is clear from Figure (2) that the addition of a very small amount of these compounds retarded the rate of crystallization to an extent proportional to the amount added. The decrease was, however, more pronounced in the case of Na_2PO_4 and stpp and sod.pyrophosphate sequentially. In fact, the presence of 10^{-7} mol decreased the crystallization rate to 61.21, 56.3, 42.5 % respectively.

3.1. Effect of Concentration of the Inhibitors

Concentration: Na_2HPO_4 and stpp ($\text{Na}_5\text{P}_3\text{O}_{10}$)

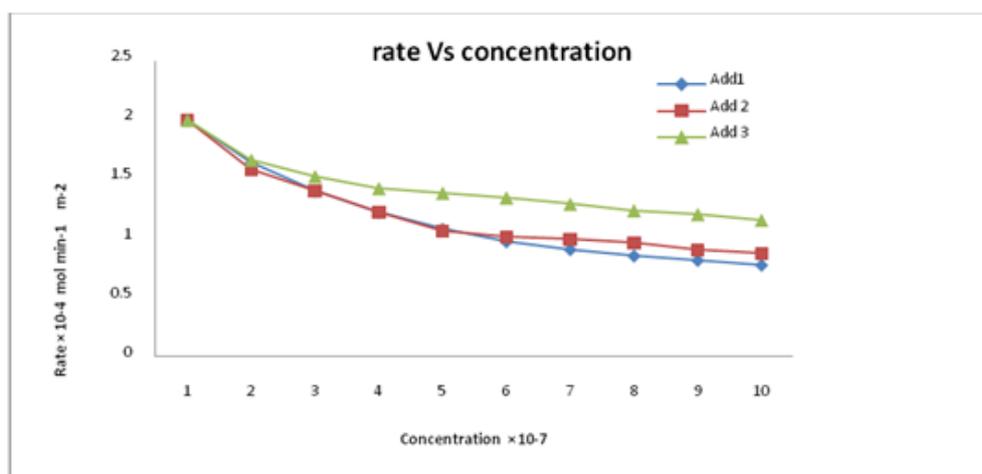


Fig 2: Effect of Add1 and Add2 and Add3 on rates of crystallization of calcium sulfate dihydrate crystals at $\delta = 1.32$, $I = 0.15 \text{ mol dm}^{-3}$, $\text{pH} = 3$ and 50 mg seed.

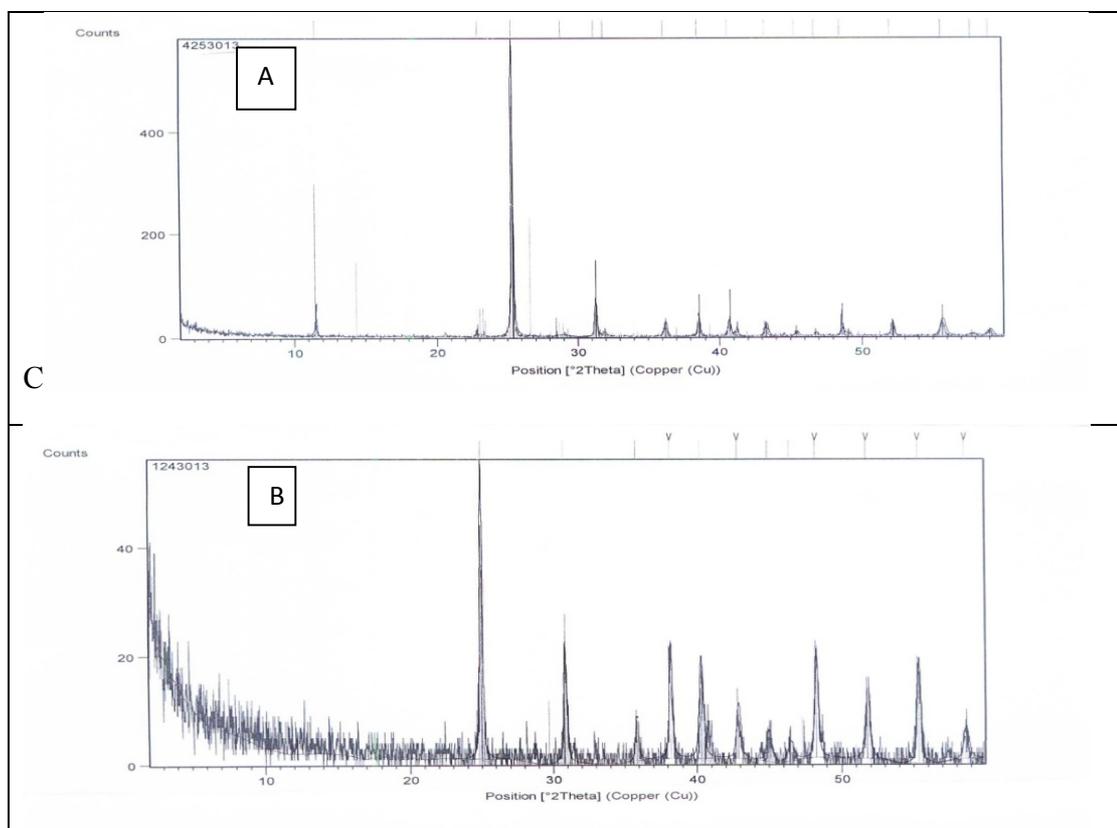
The mechanism of phosphates and poly and pyro phosphates in retardation of the rate of crystallization of calcium sulfate dihydrate has been studied via carrying out the crystallization process at 25°C, pH = 3, I = 0.15 mol dm⁻³, and $\delta = 1.32$ in the presence of 10⁻⁷ mol dm⁻³ of the phosphate compounds. Calculated volumes of CaCl₂, NaCl, phosphate additives, respectively, are added in the same order. After the end of reaction, the solution was filtered and the produced solid was characterized using XRD and SEM techniques.

Figure (3) shows both of the diffractograms of solid left after the formation of calcium sulfate in absence of additives and the diffractogram of calcium sulfate in presence of a known amount of additives 10⁻⁷ mol dm⁻³.

It is seems from Figure (3) show the XRD of CaSO₄.2H₂O and modified by disodium hydrogen phosphate, sodium tripolyphosphate, Disodium pyrophosphate this fig. show that, the cristanility of CaSO₄.2H₂O partially effect when treated with tripoly phosphate and pyrophosphate, however,

the treated of CaSO₄.2H₂O by disodium hydrogen phosphate show that dissappeared some peaks at 2 θ (11.56) and 22.99. the decreases the cristanility of CaSO₄.2H₂O when treated by disodium hydrogen phosphate with increase of particle size. this means that disodium hydrogen phosphate effect on the cristanility and particle siz (4) Scanning electron micrographs of calcium sulfate dihydrate (A) in absence of Additives and (b,c,d) in the presence of 10⁻⁷ M additives 1,2,3 respectively.

Fig(4) show the scanning electron microscopic (SEM) of CaSO₄.2H₂O and treated with different types of phosphates. this fig. show that the CaSO₄.2H₂O more cristaalline when compared with modified additives. the comparison between additives treated with different types of phosphates show that particles are smaller and simillare when treated by disodium hydrogen phosphate. The marphology structure will be confirmed with XRD analysis. this means that the best additive is the CaSO₄.2H₂O with disodium hydrogen phosphate.



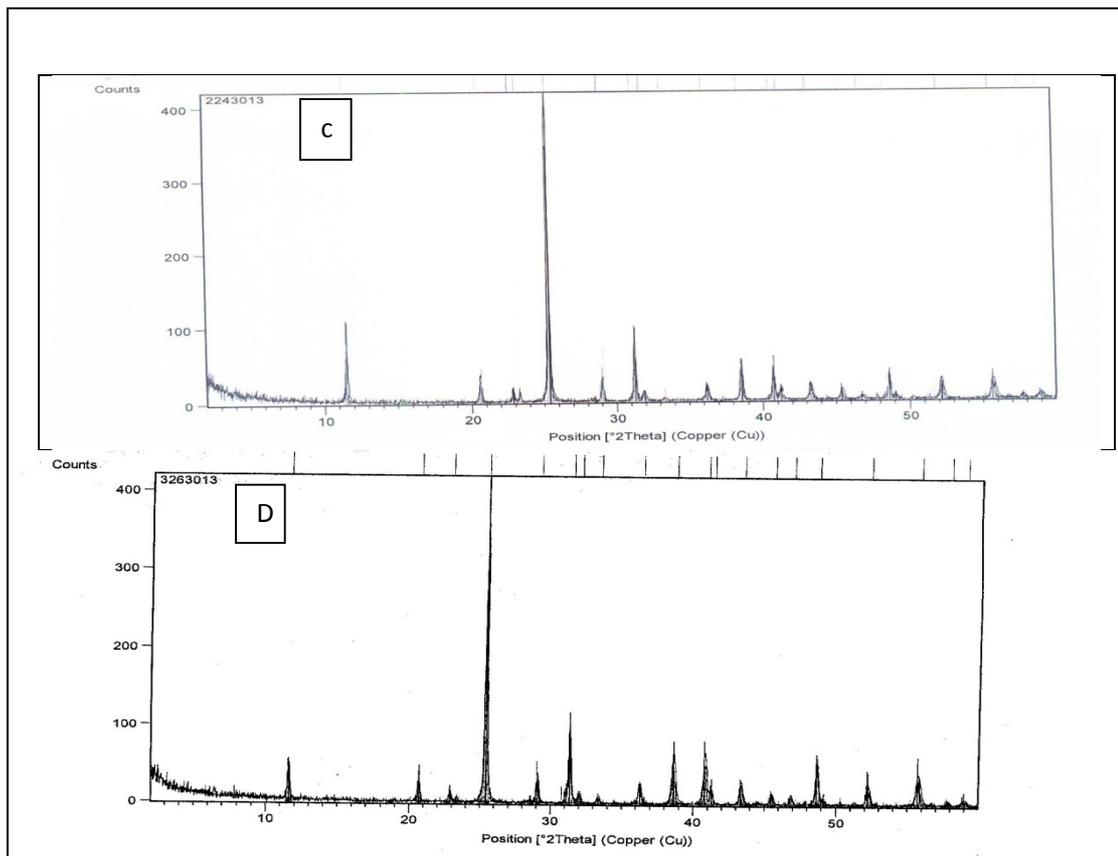
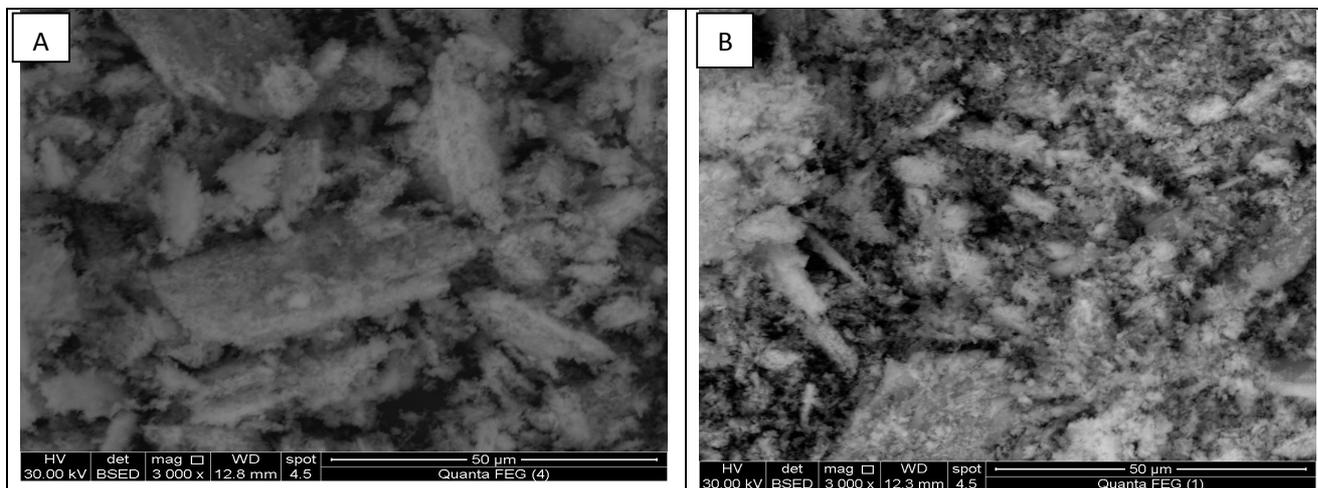


Fig (3): XRD analysis of calcium sulfate dihydrate (A) in absence of all additives (B),(c) ,(d) in the presence of 10^{-7} M of additives 1,2,3 respectively



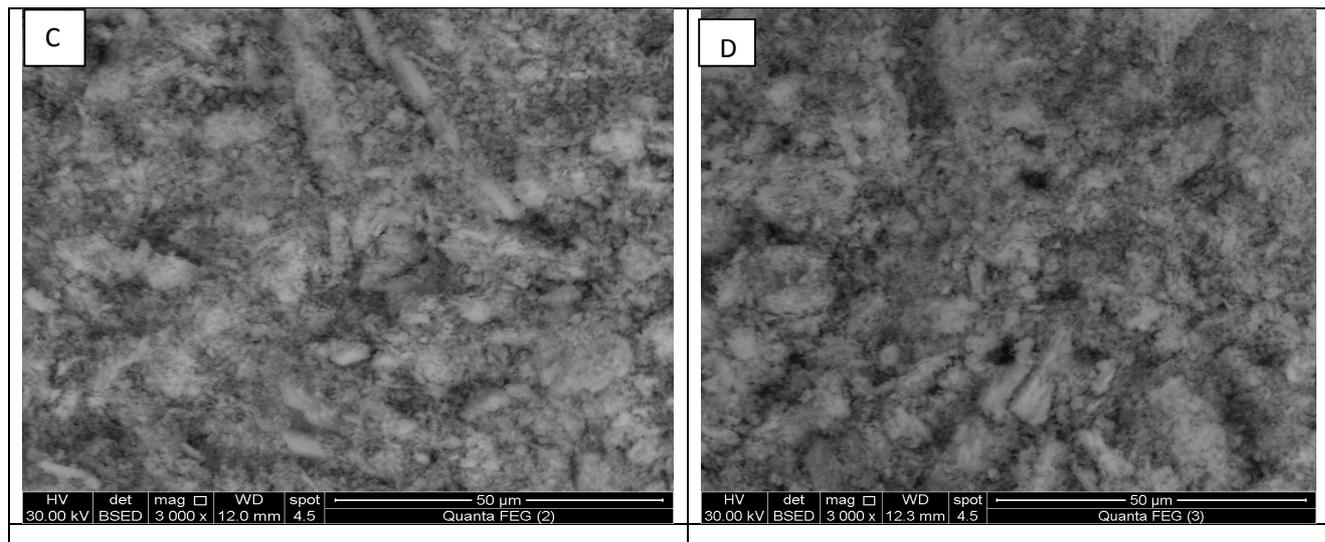


Fig 4: Scanning electron micrographs of calcium sulfate dihydrate (A) in absence of Additives and (b,c,d) in the presence of 10^{-7} M additives 1,2,3 respectively.

3.2. Effect of Supersaturation Degree (δ) on calcium sulfate dihydrate crystallization rate The degree of inhibition maybe interpreted in terms of a simple Langmuir adsorption isotherm^[25]. To investigate the effect of supersaturation degree (δ) on calcium sulfate dihydrate crystallization rates in sodium chloride solution, the crystallization of calcium sulfate in absence and in the presence of additives was investigated at different degrees of supersaturation from 1.2 to

2.49. The other parameters were fixed at an ionic strength solution (I) of 0.15 mol dm^{-3} , reaction temperature of 25°C , stirring speed of 200 rpm, and weight of seed crystals of gypsum of 50 mg at solution (pH = 3). The experimental results are given in Figure (5) as a relation between degree of supersaturation and calcium sulfate dihydrate crystallization rate.

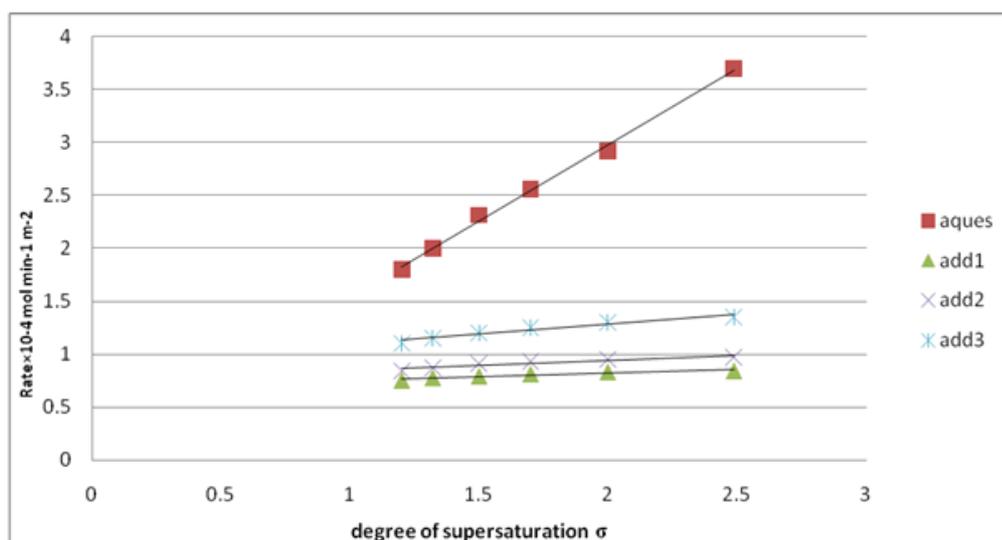


Fig (5): Effect of supersaturation degree (δ) on the rate of crystallization of calcium sulfate dihydrate crystals at pH=3, T= 25°C , I = 0.15 mol dm^{-3} , and 50 mg seed in absence of inhibitors and in presence of additives

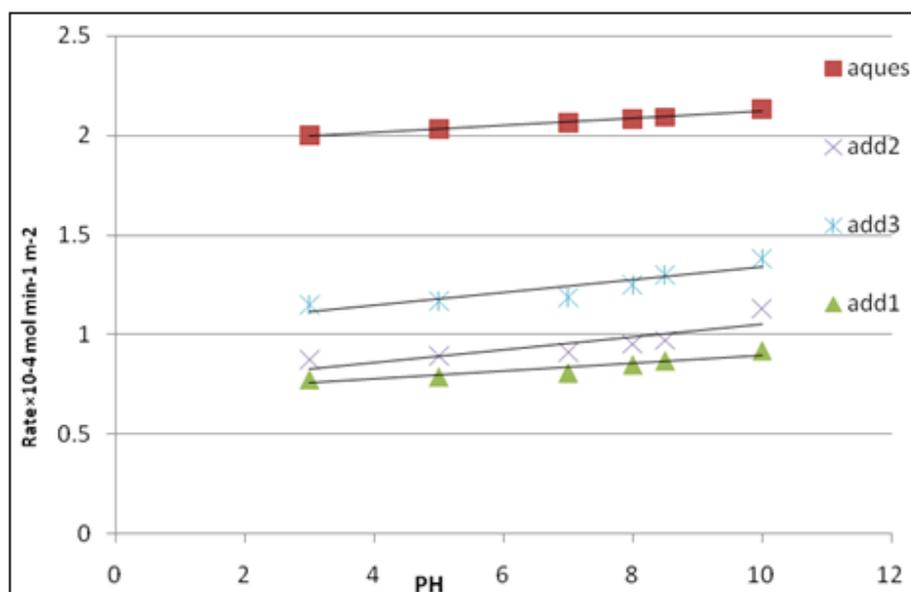


Fig 6: Effect of pH on the rate of crystallization of calcium sulfate dihydrate crystals at $\delta = 1.32$, $T = 25\text{ }^{\circ}\text{C}$, $I = 0.15\text{ mol dm}^{-3}$, and 50 mg seed in absence of inhibitors and in presence of inhibitors

From the figure, it is clear that, as the degree of supersaturation increased from 1.2 to 2.49, the gypsum crystallization rate increased from 1.8 to 3.7 mol min⁻¹ m⁻² in absence of inhibitors and from 2 to 0.776 and from 2 to 0.874 and from 2 to 1.15 mol min⁻¹ m⁻² in presence of three inhibitors respectively. The order in the presence of additives was found to be equal to ($n=1$), which suggests diffusion mechanism.

3.3. Effect of pH on Calcium Sulfate Dihydrate Crystallization Rate

The effects of solution pH on the crystallization growth of calcium sulfate dihydrate in the absence and in the presence of additives were studied at different pH range (3–10). Other experiments conditions were fixed at a reaction temperature of 25°C, stirring speed of 200 rpm, weight of seed crystals of calcium sulfate dihydrate 50 mg at ionic strength ($I = 0.15\text{ M}$), and a relative supersaturation ($\delta = 1.32$). The experimental results are plotted in Figure (6) as a relation between pH and the rates of crystallization of calcium sulfate dihydrate crystals.

Fig (6) Effect of pH on the rate of crystallization of calcium sulfate dihydrate crystals at $\delta = 1.32$, $T = 25\text{ }^{\circ}\text{C}$, $I = 0.15\text{ mol dm}^{-3}$, and 50 mg seed in absence of inhibitors and in presence of inhi

From the above figure, it is clear that with the increase of pH from 3–7, the calcium sulfate dihydrate crystallization rate slightly increased from about 2 to 2.06 mol min⁻¹ m⁻² in absence of inhibitors and from 0.776, 0.87, 1.15 to 0.81, 0.91, 1.19 mol min⁻¹ m⁻² in presence of Additives 1, 2, 3 respectively. This means that pH over a wide range (3–7) does not affect the calcium sulfate dihydrate^[26,27,28]. Further increase in solution pH from 7 to 10 led to increase the calcium sulfate dihydrate rates crystallization from 2.06 to 2.13 mol min⁻¹ m⁻² and from 0.81, 0.91, 1.19 to 0.92, 1.13, 1.38 mol min⁻¹ m⁻² in absence and in presence of Additives^[29,30,31]. This may be due to the increase in degree of deprotonation^[32,33].

3.4. Effect of Ionic Strength (I) on Calcium Sulfate Dihydrate Crystallization Rate

The effect of ionic strength of the crystallization medium on the calcium sulfate dihydrate crystallization rate in sodium chloride solution is studied; several experiments are carried out in absence and in the presence of Additives at different ionic strength from 0.1 to 0.5 M. The other parameters are fixed at reaction temperature of 25°C, stirring speed of 200 rpm, weight of seed crystals of gypsum 50 mg at solution ($\text{pH} = 3$) and a relative supersaturation ($\delta = 1.32$). The

experimental results are given in Figure (7) as a relation between ionic strength and the rates of crystallization Fig (7): Effect of ionic strength (I) on the rate of crystallization of calcium sulfate dihydrate crystals at $\delta = 1.32$, pH=3, T = 25 °c and 50 mg seed in absence of inhibitors and in presence of phosphate inhibitors .

From the figure (7) , it is clear that as the ionic strength increases from 0.1 to 0.5 M, the calcium

sulfate dihydrate crystallization rates increased from about 1.8 to 2.8 mol min⁻¹ m⁻² in absence of inhibitors while it decreased from 0.82,0.9,1.2 to 0.0.63,0.79,0.95 mol min⁻¹ m⁻² in presence of Additives 1,2,3 respectively. This means that, the effect of ionic strength on the rate of crystallizations indicates that the reaction is ionic in its nature.

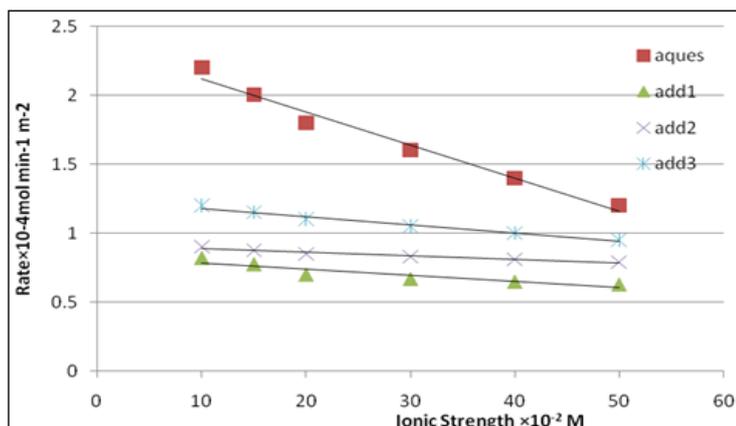


Fig 7: Effect of ionic strength (I) on the rate of crystallization of calcium sulfate dihydrate crystals at $\delta = 1.32$, pH=3, T = 25 °c and 50 mg seed in absence of inhibitors and in presence of phosphate inhibitors

3.5. The Effect of Temperature on Calcium Sulfate Dihydrate Crystallization Rate

The rate of crystallization of calcium sulfate dihydrate is studied in absence of inhibitors and in the presence of additives at temperature range of 20 to 80°C. The experimental results are given in Figure (8) as a relation between temperature and the rates of crystallization of calcium sulfate dihydrate crystals of calcium sulfate dihydrate crystals.

Figure (8) shows clearly that by increasing the temperature from 20 to 80 °C, the rate of crystallization increases from 2 to 2.06 mol min⁻¹ m⁻² in absence of inhibitors while it increases from 0.776,0.87,1.15 to 0.84,0.93,1.21 mol min⁻¹ m⁻² in presence of additives 1.2.3 respectively. The growth rates of calcium sulfate dihydrate crystals markedly increase with the increase in the growth temperature.

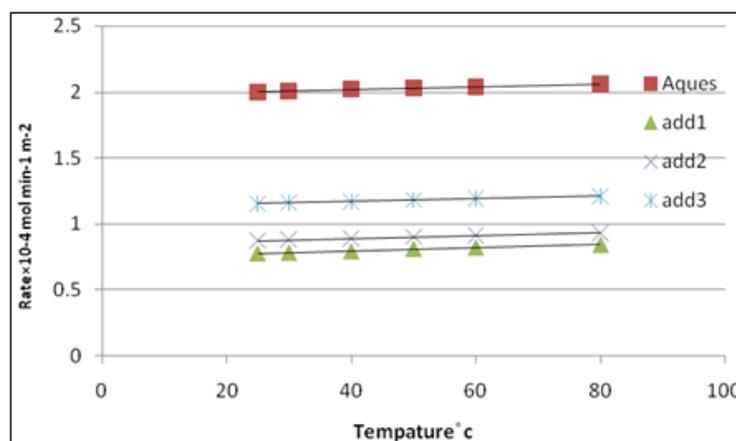


Fig 8: Effect of temperature on the rate of crystallization of calcium sulfate dihydrate crystals at $\delta = 1.32$, pH=3, I = 0.15 mol dm⁻³ and 50 mg seed in absence of inhibitors and in presence of inhibitors.

4. Conclusion

The analysis of the results shows that the presence of disodium hydrogen phosphate, sodium tripolyphosphate and disodium dihydrogen pyrophosphate in the reaction medium inhibited the rate of precipitation of calcium sulfate dihydrate (gypsum). The degree of inhibition depends on the concentration of additives and degree of saturation. Precipitation is inhibited and a precipitation rate is decreased in the following order: disodium hydrogen phosphate > sodium tripolyphosphate > Disodium pyrophosphate. Complete inhibition of precipitation of gypsum was not found in any concentration of these metal ions and degree of saturations. The degree of inhibition of additives (inhibitors) increases in acidic medium, lower ionic strength, higher degree of supersaturation, and lower temperature

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