

## Structural and spectral studies on gypsum crystals under simulated conditions of phosphoric acid production with and without organic and inorganic additives

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In the dihydrate process to produce phosphoric acid, phosphate ore  $[\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6]$  is leached with sulfuric and weak phosphoric acids to produce phosphoric acid and gypsum as a by-product. Crystallization of gypsum occurs as the leaching is taking place. The effect of organic and inorganic additives on the structure and spectrum of gypsum crystals under simulated conditions of phosphoric acid production is studied using x-ray diffraction and infrared spectroscopy. Structure and spectrum of formed gypsum crystals in the absence of additives are slightly different from the standard gypsum crystals (card No. 6-0046), which reflect the effect of preparation medium on the crystal structure of gypsum crystals. Presence of additives such as cetyl trimethyl ammonium bromide and 1,2-dihydroxybenzene-3,5-disulfonic acid,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  increase the crystallinity of gypsum, while presence of additives such as citric acid and sodium dodecyl sulfate decrease the crystallinity of gypsum. Presence of  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  as additives lead to the formation of calcium sulfate hemihydrate beside calcium sulfate dihydrate. Presence of sodium dodecyl sulfate as an additive inhibits the crystallization of gypsum and leads to the formation of anhydrite and calcium sulfate hemihydrate.

### 1 Introduction

Gypsum is produced by dihydrate process in which phosphate concentrate  $[\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6]$  is leached with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and weak phosphoric acid ( $\text{H}_3\text{PO}_4$ ) to produce phosphoric acid and calcium sulfate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) as a by-product. Crystallization of calcium sulfate dihydrate (gypsum) occurs as the leaching is taking place. The reaction takes from 2 to 10 minutes depending on phosphate reactivity and process conditions. However, the crystallization of gypsum extends for long time from 2 to 8 hours [1]. Productivity of phosphoric acid depends mainly on the gypsum filtration. The filtration rate depends on the characteristics of filter cake such as crystal size, size distribution and morphology of the crystals. Therefore, enhancing the formation of large and uniform gypsum crystals is desired in achieving better filtration rate in phosphoric acid manufacture.

The theoretical habit of gypsum crystal are tabular  $\{0,2,0\}$  with  $\{1,2,0\}$ ,  $\{0,1,1\}$  and  $\{-1,1,1\}$  hydrated side forms [2]. Since the water molecules are part of the crystal structure for the  $\{0,1,1\}$  face, they do not have to be removed for continued crystal growth. There are no strong bonds between water molecules and other ions across the  $\{1,1,-1\}$  plane; therefore, the water molecules on the surface have to be dissociated during the growth, thereby reducing its growth rate [2]. The  $\{0,1,1\}$  face grows faster than  $\{-1,1,1\}$ , which becomes a larger terminating face than  $\{0,1,1\}$  since higher growth rate faces will gradually disappear.

Unlike the crystallization of soluble electrolytes in which the growth kinetics is controlled by the linear rate law (diffusion control), the gypsum crystal growth has shown to be a surface controlled process. The surface

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activation energy for gypsum crystal growth is about 45 kJ/mol [2, 3, 4, 5, 6]. In general, the actual process for the crystallization of gypsum using phosphate rock is much more complicated. Six steps involved in the reactions: (1) diffusion of  $H^+$  ions from solution onto the surface of phosphate rock particles; (2) reaction of rock particles with  $H^+$  ions; (3) release of  $Ca^{2+}$  ions from the phosphate structure; (4) diffusion of  $Ca^{2+}$  ions from and  $SO_4^{2-}$  ions to rock particle surface; (5) nucleation of gypsum; and (6) crystal growth of gypsum particles [7].

Liu and Nancollas [8] studied the crystallization kinetics of calcium sulfate dihydrate seed crystals, which were prepared by the slow drop wise addition of calcium chloride solution to sodium sulfate solution at 25°C. The presence of ENTMP [N,N,N,N-ethylene diaminetetra methylene phosphonic acid] and TENTMP [N,N,N,N-triethylene diamine tetra (methylene phosphonic acid)] markedly retarded the rate of crystallization. This is attributed to the adsorption of these additives on available growth sites on the crystal surfaces. Tadros and Mayes [9] showed that addition of NTMP {nitrilotris (methylene phosphonic acid)} retarded the crystallization of calcium sulfate dihydrate and modify the habit of the crystals from the common needle-like form due to inhibition of normal growth on the {1,1,1} faces. The morphology and axial ratio of gypsum crystal forms corresponds to the F cell [10]. The growth occurred mainly on {1,1,0} faces instead of {1,1,1} faces. (He et al.) [11] showed that the nucleation of calcium sulfate in NaCl solutions inhibited by the addition of HDTMP [Hexamethylene-diaminetetra (methylene phosphonic acid)]. Generally the inhibition efficiency of anionic inhibitors increases with increasing lattice cation/anion molar ratio.

Effect of addition of some metal ions on the crystal growth has been investigated. The incorporation of ions, such as,  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Cd^{2+}$ ,  $Sr^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cr^{3+}$  and lanthanides ( $La^{3+}$ ,  $Ce^{3+}$ ,  $Eu^{3+}$ ,  $Er^{3+}$ ) into the gypsum crystal lattice has been studied. Metal ions are known to impose a strong impact on crystallization parameters. The effect of trivalent metal ions on the nucleation and growth kinetics is generally more pronounced than of divalent ions [7].

Tadros and Mayes [9] studied addition of sodium citrate during the crystallization of calcium sulfate dihydrate. They obtained crystals of uniform shape and size. The growth rate of the {010} faces was enhanced appreciably. In addition, they state that maleic acid, succinic acid, tartaric acid, phthalic acid, tricarballic acid, nitrilotri(acetic acid)  $N(CH_2COOH)_3$  have active effect on the crystal modification of calcium sulfate dihydrate but acids like fumaric acid, malonic acid, adipic acid, acetic acid, isophthalic acid, benzoic acid, n-butyric acid, glycolic acid and lactic acid have an inactive effect.

The present paper aims to study the structure and spectrum of gypsum crystals under industrially simulated conditions of phosphoric acid production using x-ray diffraction and infrared spectroscopy.

## 2 Materials and experimental methods

### Materials

- 1 Calcium dihydrogen phosphate  $CaHPO_4$ .
- 2 Sulfuric acid. The acid concentration and density were 96% and 1.84 g/cm<sup>3</sup>, respectively. It was used to prepare sulfuric acid 32.5% concentration and solution containing 27.5%  $P_2O_5$  and 2.5%  $H_2SO_4$ .
- 3 Phosphoric acid. The acid concentration and the density were 85% (61.58%  $P_2O_5$ ) and 1.689 g/cm<sup>3</sup>, respectively. It was used to prepare solution containing 20%  $P_2O_5$  and solution contains 27.5%  $P_2O_5$  and 2.5% free  $H_2SO_4$ .
- 4 Additives materials were used in enhancing or retarding the growth rate of gypsum. They are mainly classified into two principal groups:

#### Organic additives:

Citric acid  $C(OH)(COOH)(CH_2COOH)_2$

1,2-Dihydroxybenzene-3,5-disulfonic acid (DHBDSA)  $(OH)_2C_6H_4(SO_3H)_2$

Cetyltrimethylammonium bromide (CTAB) cationic surfactant,  $C_{19}H_{42}N^+Br$ .

Sodium dodecyl sulfate (SDS) anionic surfactant,  $C_{12}H_{25}O_4SNa$ .

#### Inorganic additives:

Aluminum hydroxide  $Al(OH)_3$

Magnesium oxide  $MgO$

## Apparatus

The reaction is carried out in 800 ml beaker. The solution is heated to 80 °C using water bath. The impeller tip speed is adjusted at 1.44 m/s (550 rpm). Desired amounts of calcium dihydrogen phosphate solution, the required amount of sulfuric acid and 50 ml of deionized water or water/organic or inorganic additive solution are added simultaneously into 500 ml of phosphoric and sulfuric acids solution (27.5% P<sub>2</sub>O<sub>5</sub> & 2.5% H<sub>2</sub>SO<sub>4</sub>).

Philips X-Ray Diffractometer PW 1730 with Ni Filtered Cu-K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) at 40 kV and 30 mA is used to determine the crystallinity of gypsum.

Vibrational spectrum of crystalline powder in KBr is recorded on Fourier Transform and Pye-Unicam SP 300 instrument.

## Procedure

The following solutions were prepared for this experiment:

Solution 1: 27.5% P<sub>2</sub>O<sub>5</sub>/ 2.5% H<sub>2</sub>SO<sub>4</sub>

Solution 2: 20% P<sub>2</sub>O<sub>5</sub>

Solution 3: 32.5% H<sub>2</sub>SO<sub>4</sub>

500 ml of solution 1 was heated to 80°C in an 800 ml beaker using a water bath. 9.4444 g of calcium hydrogen phosphate is dissolved in 100 ml of solution 2. The obtained solution from dissolving, the corresponding sulfuric acid for reaction with calcium hydrogen phosphate (solution 3) and 50 ml of deionized water or water containing additives were added simultaneously to the heated solution. The reaction was maintained at 80°C with constant agitation. The supersaturation ratio of gypsum at given conditions was 1.880 [12].

## 3 Results and Discussion

### Crystallization without additives

X-ray diffraction analysis of the gypsum crystals in absence of additives at supersaturation of 1.880 is given in Fig. 1a. The results reveal that the crystals formed are gypsum, which is slightly different from the standard gypsum that cited by the PDF cards. Some of the peaks that recorded in the PDF cards didn't record in the prepared gypsum crystals. The relative peaks intensities also slightly different from the standard gypsum of PDF cards.

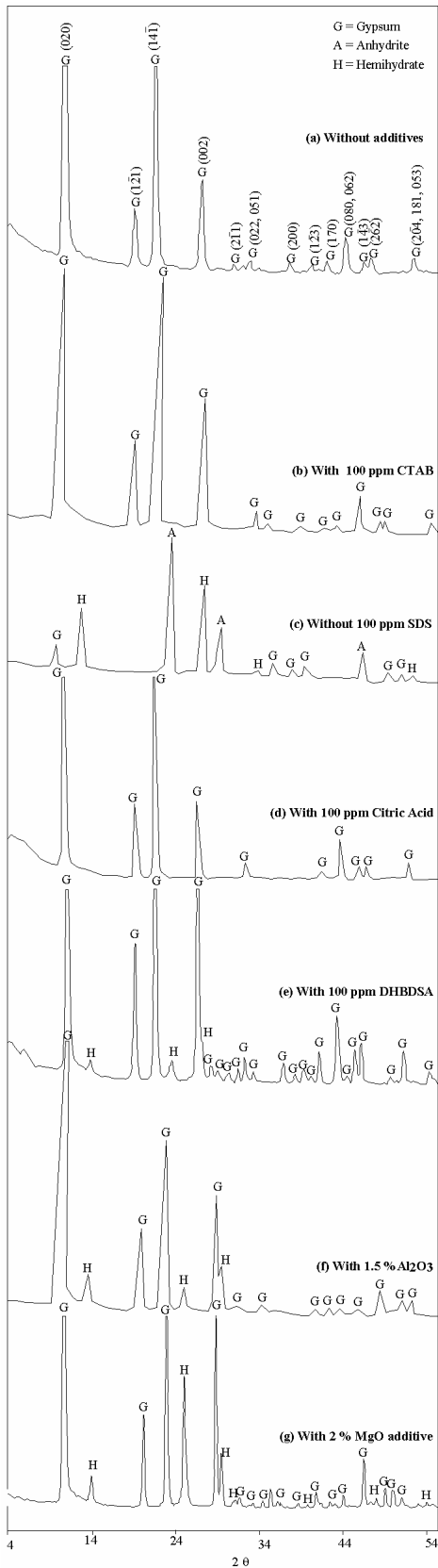
The vibrational spectral characteristics of the gypsum crystals are shown in Figure (2a). The SO<sub>4</sub><sup>-2</sup> ion possesses T<sub>d</sub> symmetry [13, 14] with four active fundamentals in the infrared,  $\nu_1$  at 981 Cm<sup>-1</sup>,  $\nu_2$  at 451 Cm<sup>-1</sup>,  $\nu_3$  at 1104 Cm<sup>-1</sup>, and  $\nu_4$  at 613 Cm<sup>-1</sup>. Twisting and rocking of water molecule were found at 690 and 834 cm<sup>-1</sup>. The absorption bands at 745 and 1074 cm<sup>-1</sup> confirmed the presence of  $\nu_1$  SO<sub>4</sub><sup>-2</sup> and  $\nu_4$  SO<sub>4</sub><sup>-2</sup> respectively. The bands at 1632 cm<sup>-1</sup> and the broad band at 3100 cm<sup>-1</sup> might be due to the presence of  $\nu_2$  H<sub>2</sub>O II and  $\nu_1$  H<sub>2</sub>O III respectively. Infrared pattern of the prepared gypsum is also slightly different from the pattern of standard gypsum cited by Lehr et al. (1967) [15]. Some additional peaks appeared in the prepared gypsum at 3408, 1007 and 834 cm<sup>-1</sup>. These differences reflect the effect of phosphoric acid medium in the crystal structure of gypsum.

### Crystallization with additives

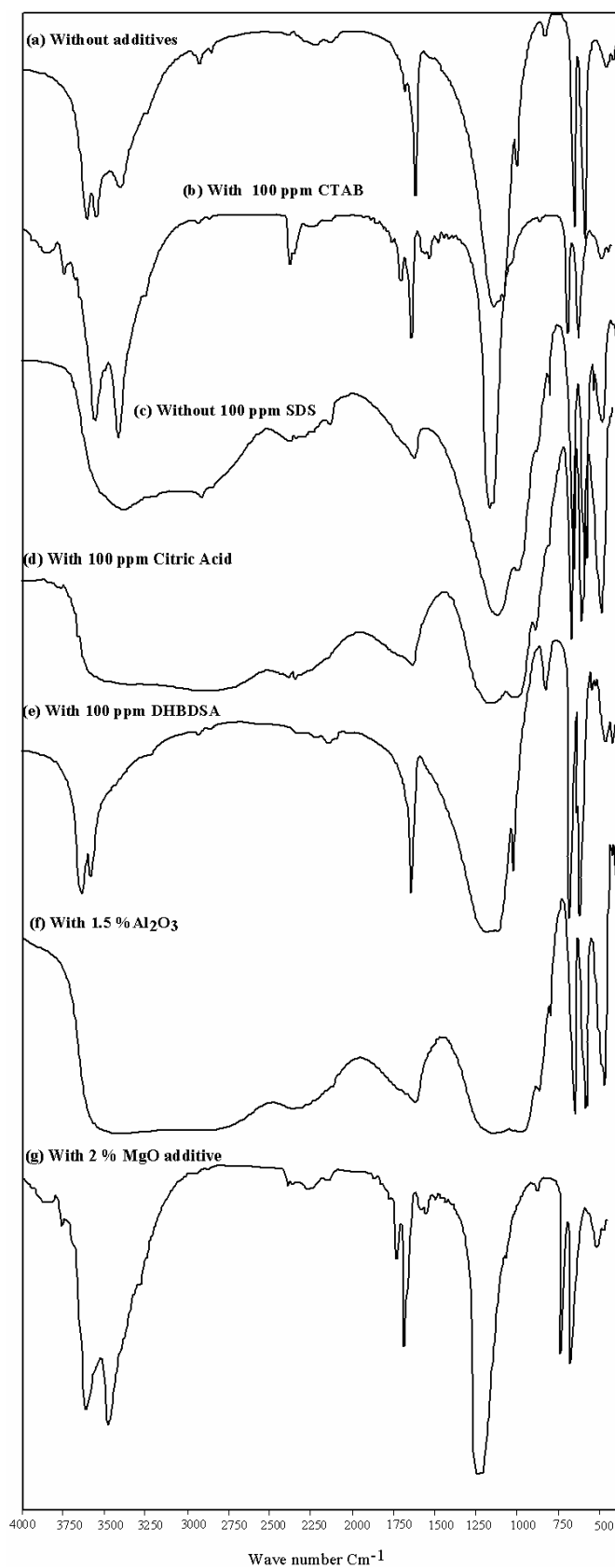
#### Effect of Cetyl Trimethyl Ammonium Bromide Surfactant (CTAB)

X-ray diffraction analysis of the gypsum crystals in the presence of 100 ppm CTAB surfactant at supersaturation of 1.880 compared with the gypsum crystals in absence of additives is given in Fig. 1b. The results reveal that the presence of CTAB increases the relative intensity of gypsum crystals compared to the baseline (without additive). This means that the presence of CTAB increases the crystallization quality of gypsum.

Infrared pattern of gypsum crystals in the presence of CTAB (Fig. 2b) is almost the same as the pattern of standard gypsum cited by (Lehr et al.) [15].



**Fig. 1** XRD analysis of gypsum crystals with and without additives.



**Fig. 2** IR spectrum of gypsum crystals with and without additives.

### Effect of Sodium Dodecyl Sulfate Surfactant (SDS)

X-ray diffraction analysis of gypsum crystals in the presence of 100 ppm SDS at supersaturation of 1.880 is given in Fig. 1c. The results reveal that the crystals contain mixture of dihydrate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , hemihydrate  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  and anhydrite (II)  $\text{CaSO}_4$ . This means that the presence of SDS surfactant leads to formation of other forms of calcium sulfate in a medium suitable for the formation of gypsum. Generally, the relative intensity of formed gypsum crystals is smaller than that formed in absence of additive.

Infrared pattern of gypsum crystal in the presence of SDS additives (Fig. 2c) is completely different from the pattern of standard gypsum cited by (Lehr et al.) [15] and that of the gypsum prepared without additives. Spectra at  $3610$  and  $3556 \text{ cm}^{-1}$  are reduced to give the pattern of anhydrite  $\text{CaSO}_4$  as cited by (Lehr et al.) [15]. Other spectra are broad and weak.

### Effect of Citric Acid

X-ray diffraction analysis of gypsum crystals obtained in the presence of citric acid is given in Fig. 1d. The results reveal that the presence of citric acid decreases the crystallization quality of gypsum compared with the control test (without additive).

Infrared pattern of gypsum crystal in the presence of citric acid additives (Fig. 2d) is completely different from the pattern of standard gypsum cited by (Lehr et al.) [15] and that of the gypsum prepared without additives. Spectra at  $3610$  and  $3556 \text{ cm}^{-1}$  are almost disappeared. Other spectra are broad and weak.

### Effect of 1,2-DihydroxyBenzene 3,5- Disulfonic Acid (DHBDSA)

X-ray diffraction analysis of the gypsum crystals in the presence of DHBDSA compared with the case of the baseline is given in Fig. 1e. The results reveal that the presence of DHBDSA in phosphoric acid medium increases the crystallinity of gypsum as indicated from higher peak intensity of the gypsum compared to that formed without additives. In addition, calcium sulfate hemihydrate is also formed.

Infrared pattern of gypsum crystals in the presence of DHBDSA (Fig. 2e) is almost the same as the pattern of standard gypsum cited by (Lehr et al.) [15]. The sharp peaks at  $3610$  and  $3556 \text{ cm}^{-1}$  are attributed to the formation of hemihydrate  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  that characterized by two peaks in this position.

### Effect of $\text{Al}^{3+}$

X-ray diffraction analysis of gypsum crystals in the presence of 1.5%  $\text{Al}_2\text{O}_3$  at supersaturation of 1.880 compared with the absence of additive is given in Fig. 1f. The results reveal that the crystal form is mainly gypsum with traces of hemihydrate and the relative intensity of peaks increased in case of 1.5 %  $\text{Al}_2\text{O}_3$ , which means the crystallization of gypsum is increased.

Infrared pattern of gypsum in the presence of  $\text{Al}_2\text{O}_3$  additive (Fig. 2f) is completely different from the pattern of standard gypsum cited by (Lehr et al.) [15] and that of the gypsum prepared without additives. Spectra at  $3610$  and  $3556 \text{ cm}^{-1}$  are almost disappeared in the case of  $\text{Al}_2\text{O}_3$ . Other spectra are broad and weak.

### Effect of $\text{Mg}^{2+}$

X-ray diffraction analysis of gypsum crystals obtained in the presence of 2%  $\text{MgO}$  at supersaturation of 1.880 compared with the baseline is given in Fig. 1g. The results reveal that the presence of  $\text{MgO}$  forms a mixture of gypsum and hemihydrate. This means that the presence of  $\text{MgO}$  forms hemihydrate in high percentage under conditions suitable for the formation of gypsum. Therefore, the expected % fines (hemihydrate crystals) are relatively high.

Infrared pattern of gypsum crystal in the presence of  $\text{Mg}^{2+}$  impurity (Fig. 2g) is almost the same as the pattern of standard gypsum cited by (Lehr et al.) [15]. The sharp peaks at  $3610$  and  $3556 \text{ cm}^{-1}$  are attributed to the formation of hemihydrate  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  that characterized by two peaks in this position.

## 4 Conclusions

From x-ray diffraction and infrared spectroscopic studies, it can be concluded that preparation medium affects the structure and spectrum of gypsum crystals that prepared under industrially simulated conditions of phosphoric acid production. Presence of additives such as cetyltrimethylammonium bromide and 1,2-dihydroxybenzene-3,5-disulfonic acid,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  increase the crystallinity of gypsum crystals, while presence of additives such as citric acid and sodium dodecyl sulfate decrease the crystallinity of gypsum. Presence of  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  as additives leads to the formation of calcium sulfate hemihydrate beside gypsum. Presence of SDS as an additive inhibits the crystallization of gypsum crystals and leads to the formation of anhydrite (II) and calcium sulfate hemihydrate.

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