

EFFECT OF SODIUM, IRON IONS AND TIME OF (STIRRING)
ON THE CRYSTAL-LATTICE AND MORPHOLOGY
OF THE GYPSUM CRYSTALS.

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ABSTRACT

The influence of the presence of Na^+ and Fe^{++} ions on the crystal-lattice and - morphology of gypsum crystals has been investigated. Generally, the degree of crystallinity is affected by the replacement of Ca^{++} by metal ions. The replacement and the partial deformation of crystal is more in case of incorporated Na^+ than that of Fe^{++} ions. The minimum allowed concentration of Na^+ as impurities in the gypsum must not exceeds 4% to obtain ideal gypsum crystals. Also the effect of different stirring time was examined. The change in stirring time results in irregular crystal faces of gypsum crystals.

INTRODUCTION

The sequence of precipitation of salts from seawater during evaporation was originally worked out by Usiglo (1849). The growth of calcium sulphate crystals has important applications in areas such as desalination technology, geochemistry and petroleum technology (e.g.. Spriegler, 1962; Stumm and Morgan, 1970; Vitter and Philips, 1970). During crystallization processes of gypsum in industrial environments usually all kinds of impurities are present which influence on the crystallization processes in many aspects, not only the nucleation and kinetics of crystal growth, but also the crystal shape and morphology are subjected to drastic changes (Nancollas et al., 1978). According to Weijnen et al. (1983); in processes where gypsum is formed as by-product, the ores being processed are important source for metal ions, particularly, heavy metal ions like Cd^{2+} , Pb^{2+} and Cu^{2+} are often incorporated into the gypsum lattice; Weijnen et al. (1983).

The present study aims to follow up the incorporation of both Na^+ and Fe^{++} ions into the gypsum crystals. Time of stirring as controlling factor for the variation of crystal lattice and morphology of the gypsum crystals has been also investigated.

MATERIALS AND METHODS

Analytical reagent grade chemicals, triply distilled water and graded glass were used. Solutions of calcium chloride, sodium sulphate, sodium chloride and ferrous chloride were prepared using reagent grade (J.I. Backer Co.), chemical solutions were filtered ($0.22 \mu\text{m}$, millipore filters) before used. Metal ion concentrations were determined by passing aliquots through a cation exchange resin (Dowex 50) in the hydrogen form and titrating the diluted acid against standardized sodium hydroxide.

Dehydrate calcium sulphate crystals were precipitated by drop-wise addition of 500 ml 0.2 M calcium chloride solution to 500 ml of 0.2 M sodium sulphate solution at 70°C . The crystals were washed repeatedly with triply distilled water. The solid material was subjected to X-ray powder diffraction studies and Scanning Electron Microscopy.

To determine the effect of stirring time on crystal-lattice and morphology, different time periods of stirring e.g. 1/2 h, 1 h, 2 h, 4 h, 8 h, 16 h, 24 h, 48 h have been suggested.

To examine the effect of metal ion incorporation on both crystal-lattice and - morphology, different concentrations of Na^+ and Fe^{++} were added during synthesise of gypsum crystals. The incorporated Na^+ was measured using "Corning 400 flame photometer" while incorporated Fe^{++} was determined using atomic absorption spectroscopy (Perkin Elmer 2380 A.A.S.). The solid phases were examined by X-ray diffraction (Philips 1840) and scanned using Scanning Electron Microscope SEM (Jeal SEM-25S II).

RESULTS AND DISCUSSIONS

Time of stirring as controlling factor for the variations in crystal-lattice and morphology:

The variations in both crystal-lattice and morphology have been followed up by X-ray diffraction analysis and Scanning Electron Microscope, considering time of stirring as controlling factor for such variations. Figure (1) reveals that the gypsum crystals show their ideal form after 1 hour with d-spacing for (020), 7.5553\AA . The continuous stirring results in shifting of the d-spacing that reflects continuous deformation of the crystals. Figure (2) illustrates the uniformity of the crystal after 1 hour of stirring, while Figure (3)

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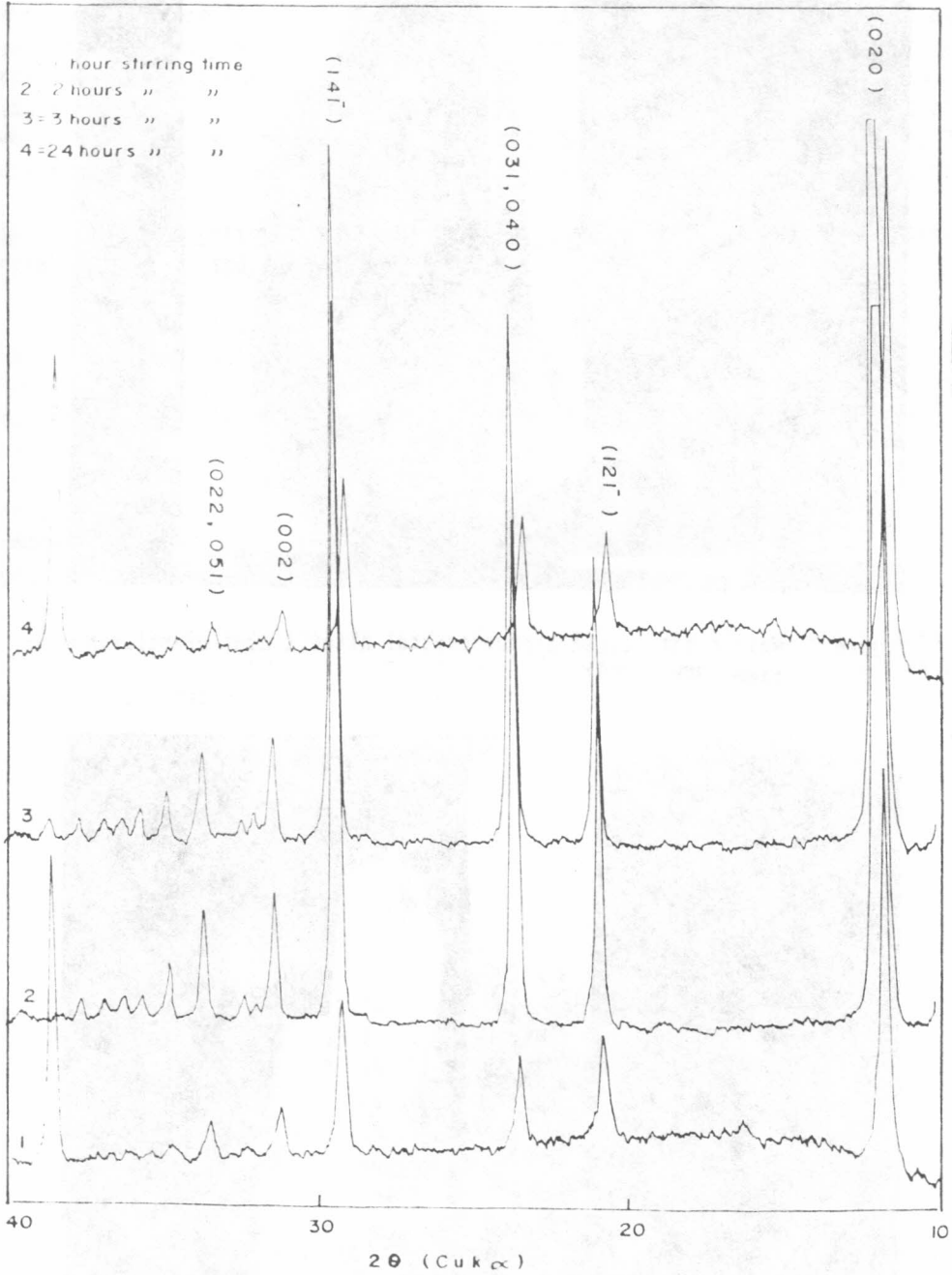


Figure 1. Effect of stirring time on the crystal lattice of gypsum.

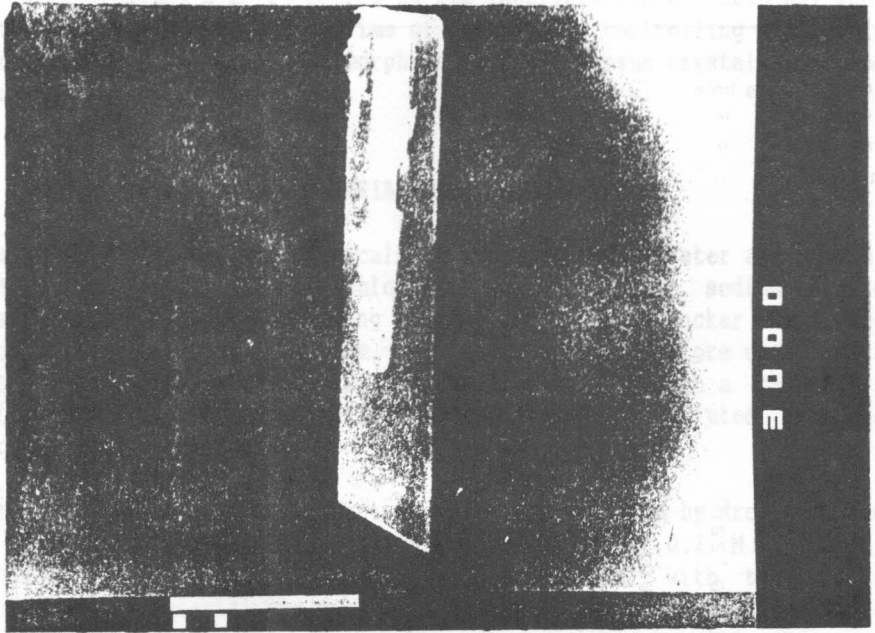


Figure 2. Well crystallized gypsum crystal after 1 hour of stirring time (SEM X3000).

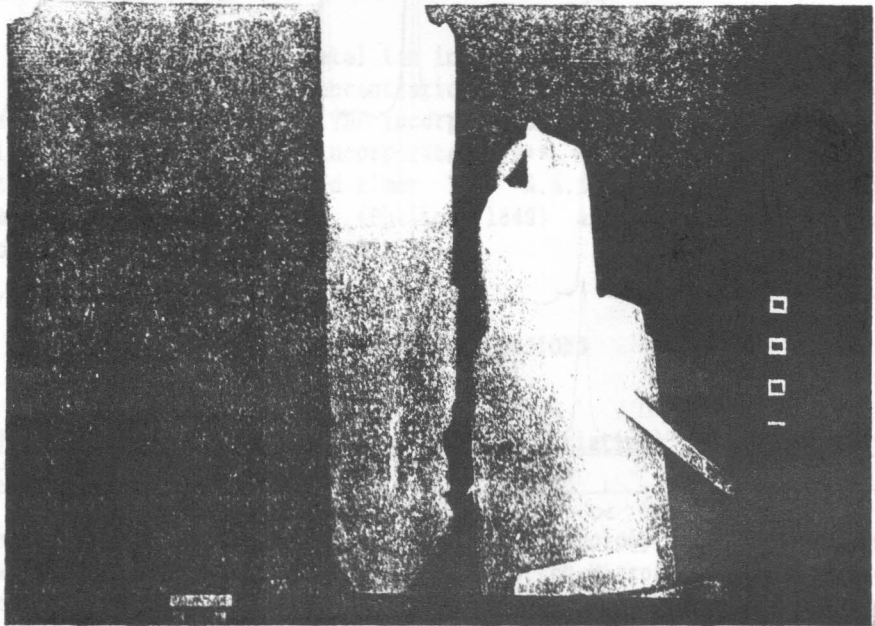


Figure 3. Deformed gypsum crystal after 48 hours of stirring time (SEM X1000).

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illustrates the changes which occur in the crystal morphology after 48h of stirring. Figure (2) shows also the precipitation model by which the seeding of gypsum proceeds, whereas one crystal acts as nucleus for the following precipitated crystals. Figure (4) illustrates that the shift in diffraction angle attains its maximum value after 8 hours of continuous stirring after which a general tendency of decrease toward the ideal form of the gypsum. This can be interpreted on basis of the crystal homogeneity after certain stirring time.

Na⁺ ion incorporation in the crystal-lattice of gypsum and its effect on crystal-lattice and - morphology:

The present study deals with the incorporation of Na⁺ ions into the crystal lattice of synthesized gypsum and the possibility of synthesizing a series of intermediate solid phases between Thenardite Na₂ SO₄ and gypsum CaSO₄.2H₂O. Natural Thenardite forms under certain conditions of high temperature, high salinity, strong ionic exchange (Smykatz 1974), i.e. beginning with gypsum it is very difficult to attain complete replacement of Na⁺ ions in the sites of Ca⁺⁺ ions under normal conditions of laboratory. The ions of alkali metals are loosely hydrated, thus the full replacement of Na⁺ ions to replace Ca⁺⁺ ions completely in the crystal of gypsum is limited Luder et al. (1965).

In the present investigation it could be seen that one can obtain a series of solid phases of gypsum containing Na⁺ with different concentrations ranging from 4.2 to 19.04% Table (1).

Table (1): Effect of Na⁺ ion incorporated into gypsum crystals.

Sample No.	Conc. of NaCl add (M)	Percent of Na ⁺ incorporated in the gypsum crystal %	Na/Ca Molar	20 d-spacing	20 d-spacing
1	0.01	4.20	0.0438	11.7	7.5571
2	0.05	8.50	0.0924		--
3	0.10	15.81	0.1880	11.85	--
4	0.15	17.98	0.2190	11.7	7.4305
5	0.20	19.04	0.2350	11.8	7.4555
6	0.40	11.75	0.1300	11.7	7.4932
7	0.50	8.50	0.0920	11.66	7.4305

Figure (5) illustrates the shift in d-spacing as result of Na⁺ incorporation into the gypsum crystal lattice. It has been found that the allowed minimum concentration of Na⁺ as impurities in the synthesis of gypsum must not exceed 4% to obtain ideal gypsum. Figure (6) reveals the shift in the diffraction angle as result of Na⁺ ion incorporation into crystal lattice of gypsum. Figure (7) shows the relation between NaCl added (M) and Na/Ca molar ratio, whereas this ratio attains its maximum (0.235) when NaCl added is 0.2 M, after which

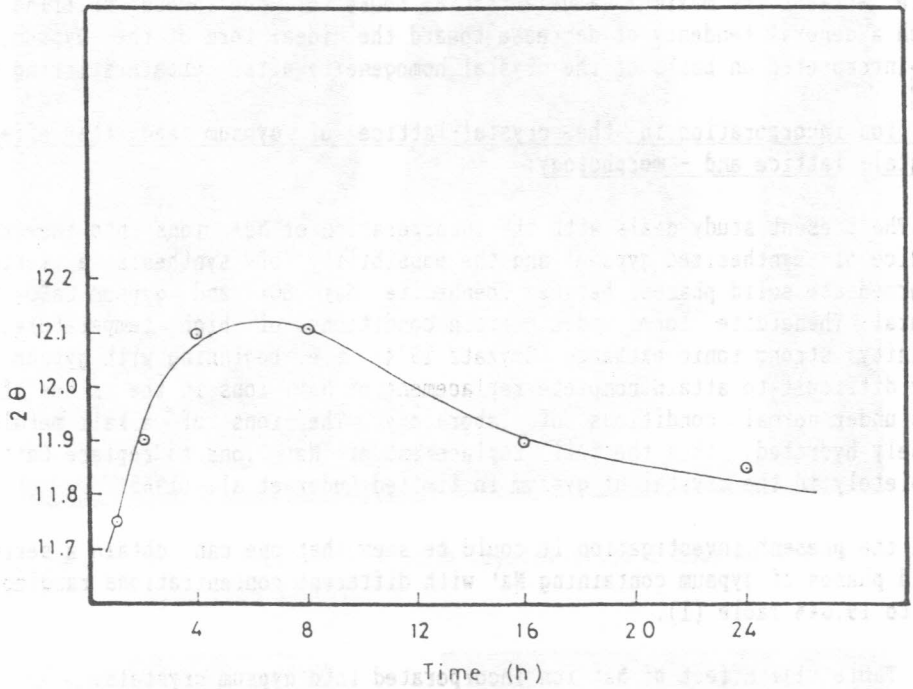


Figure 4. Effect of stirring time on the diffraction angle of (020) in gypsum crystals.

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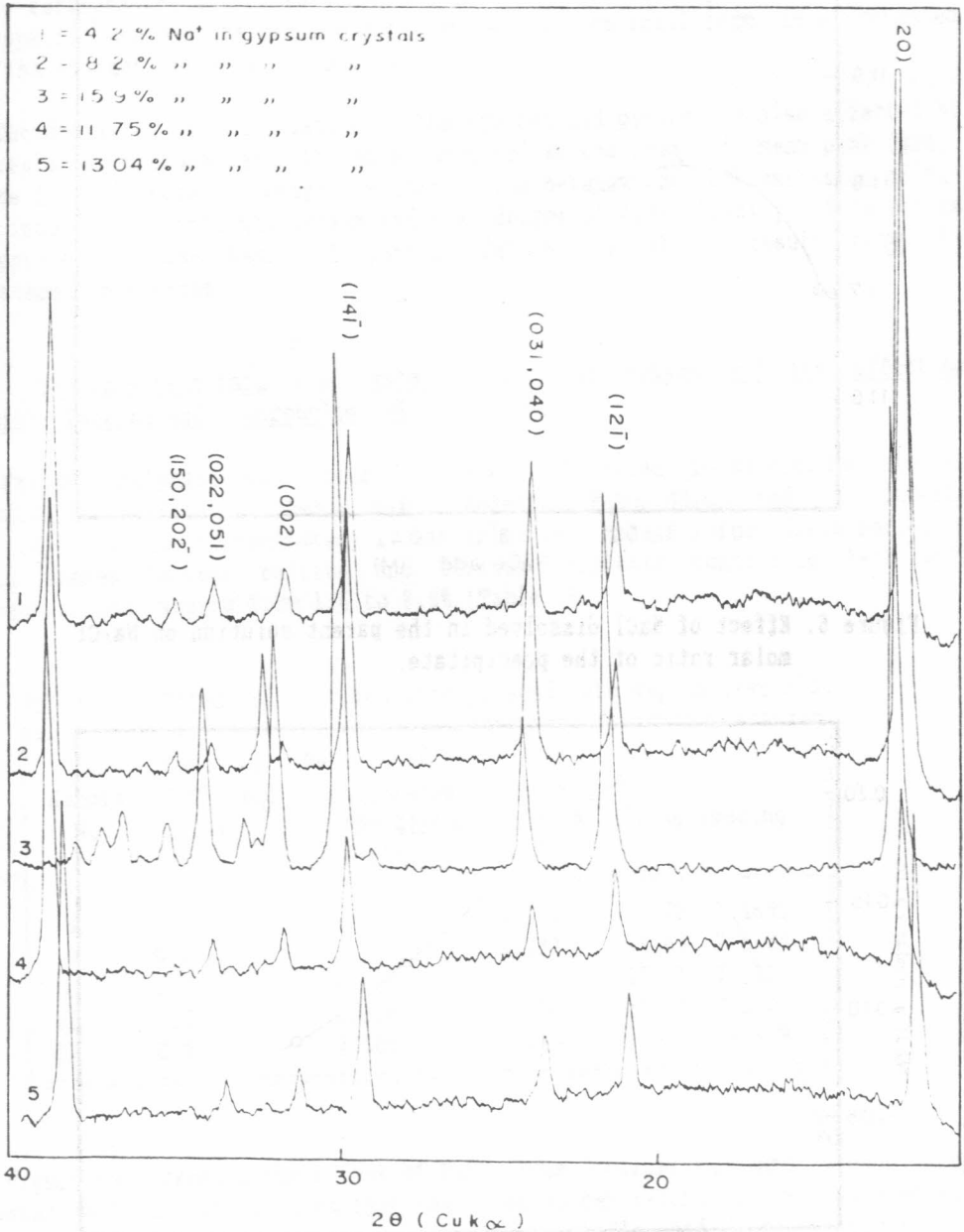


Figure 5. Effect of Na⁺ ion incorporation on the crystal lattice of gypsum.

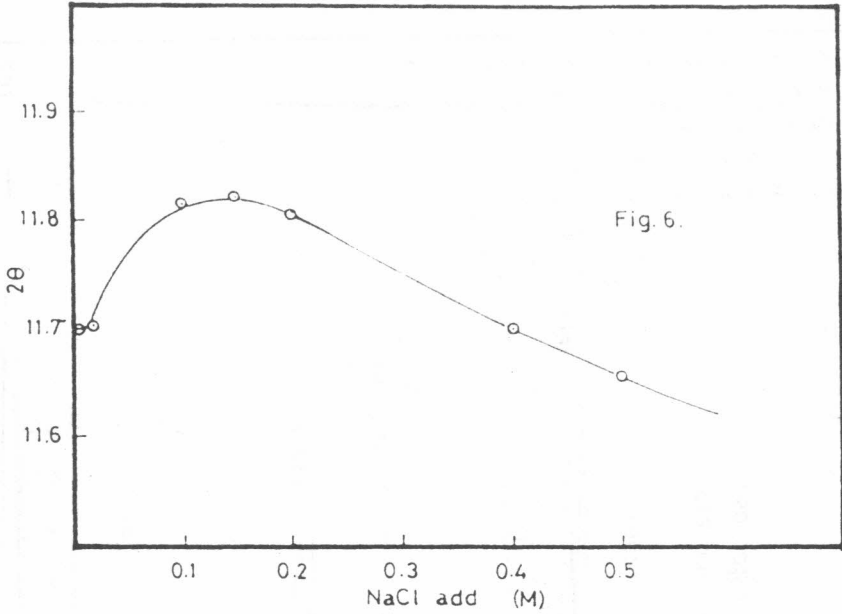


Figure 6. Effect of NaCl dissolved in the parent solution on Na/Cl molar ratio of the precipitate.

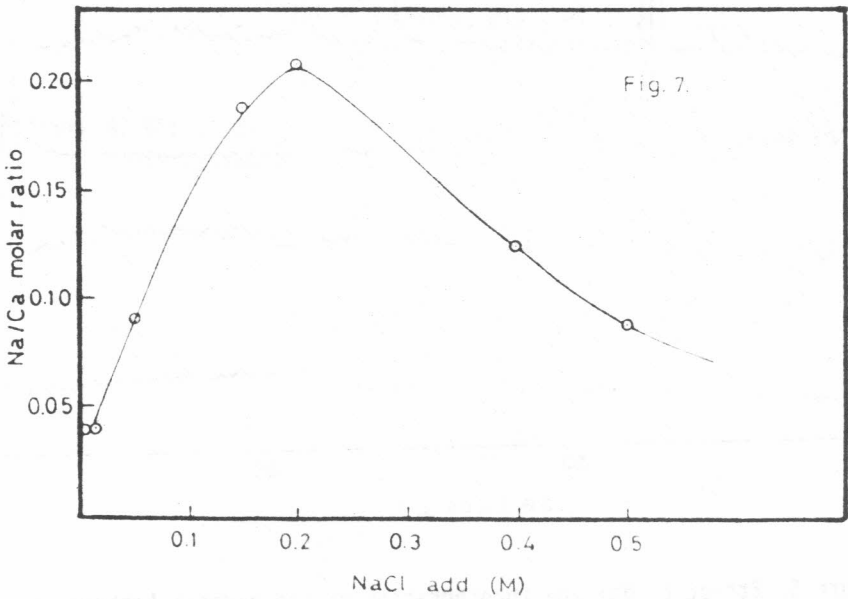


Figure 7. Effect of Na⁺ ion incorporation on the diffraction angle (2θ) of (020) in gypsum crystals.

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Na/Ca ratio decreases suggesting that the ability of the found crystals to accept new incorporated Na⁺ ions decreases. The comparison between Figures 6 and 7 reflects the strong relation between the ionic exchange and the variation of d-spacing whereas the maximum shift in 2θ from the ideal form is accompanied with the highest value of Na/Ca molar ratio.

The degree of crystallization of the synthesized gypsum is also affected by the replacement processes. It can be measured as the area of mean peak (020). Figure (8) illustrates a negative correlation between the concentration of Na⁺ ions incorporated into the gypsum and the degree of crystallinity. This can be interpreted on the basis of partial deformation which result from the replacement processes.

Fe²⁺ incorporation into the crystal lattice of gypsum and its effect on crystal-lattice and - morphology of the gypsum:

Ferrous sulphate may occur in several hydrated forms e.g. Melanterite FeSO₄.7H₂O, Siderotil FeSO₄.5H₂O, Rozenite FeSO₄.4H₂O and Szomolnokite FeSO₄.H₂O. In the present study it was able to obtain intermediate series of solid phases between calcium and ferrous sulphates containing Fe²⁺ with concentrations ranging from 1.6 to 8.9% (Table 2).

Table (2): Effect of Fe⁺⁺ ion incorporated into gypsum crystals.

Sample No.	Conc. of FeCl ₂ add (M)	Percent of Na ⁺ incorporated in the gypsum crystal	Fe/Ca Molar %	2e	d-spacing
8	0.1	1.664	0.170	11.70	7.4895
9	0.2	3.120	0.032	11.85	7.5189
10	0.3	8.920	0.097	11.75	7.5829
11	0.4	6.300	0.070	11.65	7.5102
12	0.5	4.500	0.050	- - -	- - -

Figure (9) reveals the effect of Fe⁺⁺ ions incorporated into gypsum on its crystal lattice. It is noted that the lower concentration of incorporated Fe⁺⁺ the crystal lattice of gypsum is not markedly affected. Figure (10) illustrates the shift in diffraction angle 2θ of (020) as a result of Fe⁺⁺ incorporation into gypsum crystals. Figure (11) reveals that the conversion point at which Fe/Ca molar ratio attains its maximum value corresponds about 0.3 M of added FeCl₂. However the comparison of both Na⁺ and Fe⁺⁺ incorporation reveals the susceptibility of gypsum crystals to take up Na⁺ is higher than Fe⁺⁺.

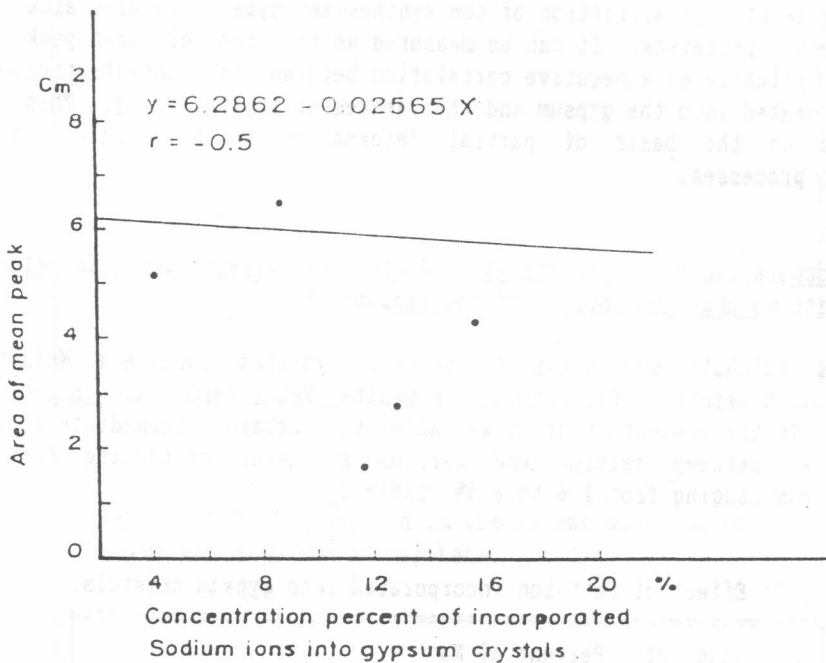


Figure 8. The degree of crystallinity versus Na⁺ ion incorporated into the gypsum crystals.

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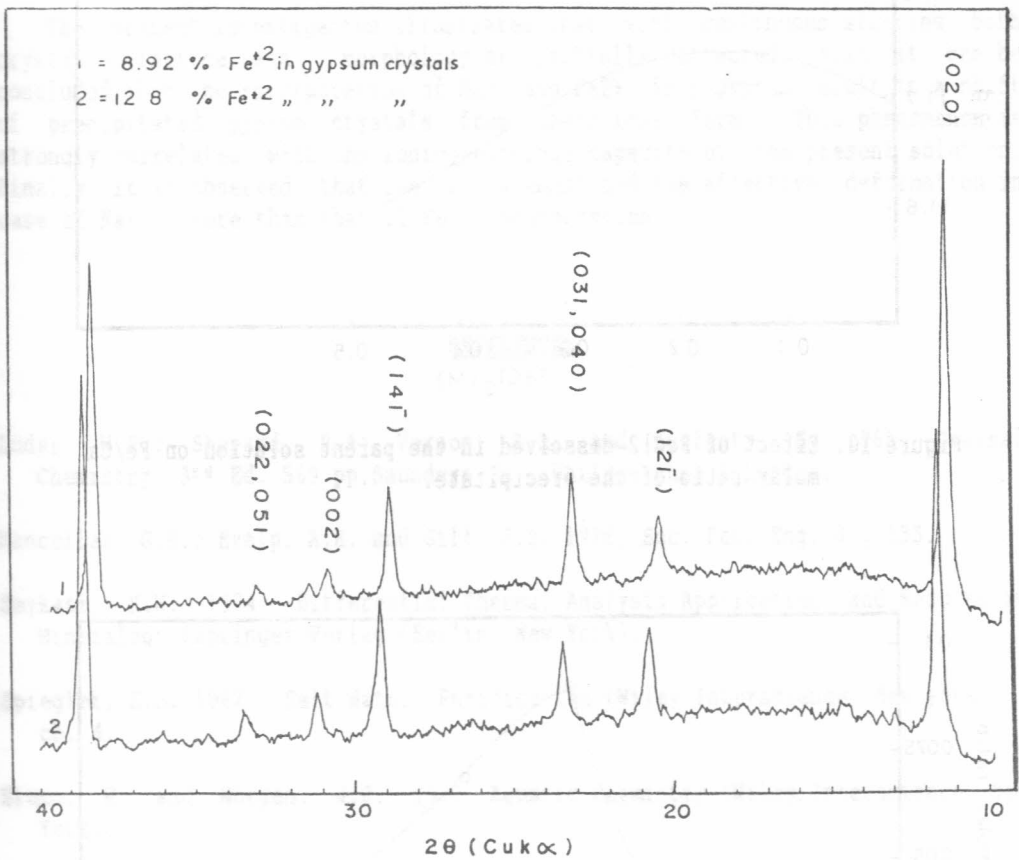


Figure 9. Effect of Fe^{2+} ions incorporated on the crystal lattice of gypsum.

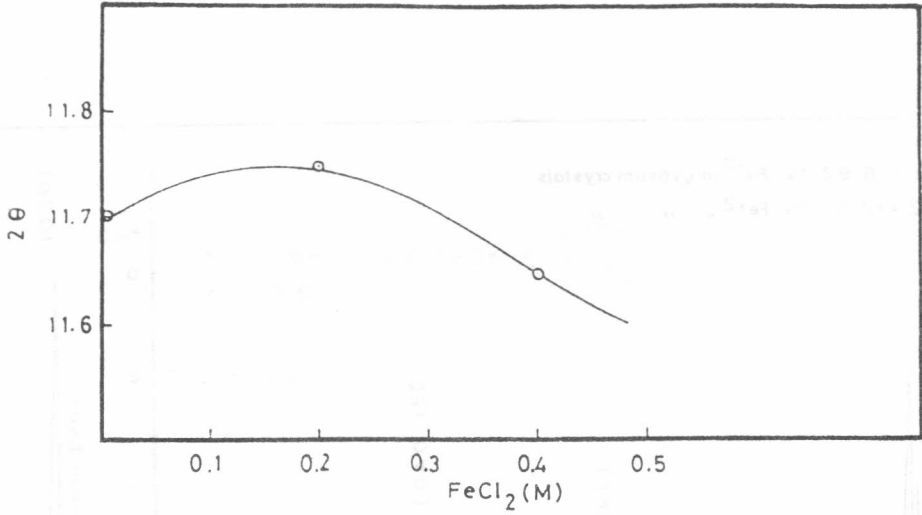


Figure 10. Effect of FeCl₂ dissolved in the parent solution on Fe/Ca molar ratio of the precipitate.

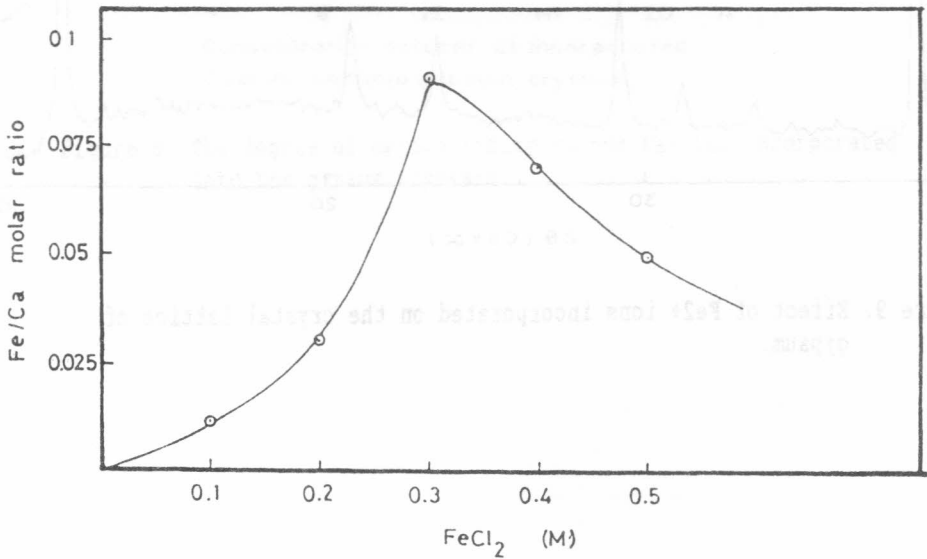


Figure 11. Effect of Fe²⁺ incorporated ions on the diffraction angle of (020) in the gypsum crystals.

CONCLUSION

The present investigation illustrates that with continuous stirring, both crystal - lattice and - morphology are partially affected. Also it can be concluded that the incorporation of Na^+ and Fe^{2+} into gypsum result in a shift of precipitated gypsum crystals from their ideal form. This phenomenon is strongly correlated with the ionic exchange capacity of the present solution. Finally it is observed that the replacement and the effective deformation in case of Na^+ is more than that of Fe^{2+} incorporation.

REFERENCES

- Luder, W.F.; Shepard, R.A; Vernon, A.A. and Zuffanti, S. 1965. General Chemistry. 3rd Ed. 569 pp, Saunders Co., Philadelphia & London.
- Nancollas, G.H.; Evalp, A.E. and Gill, J.S. 1978. Soc. Pet. Eng. J., 133.
- Smykatz, K.W. 1974. Differential Thermal Analysis Application and Results in Mineralogy (Springer Verlag (Berlin, New York).
- Spiegler, K.S. 1962. Salt Water Purification (Wiley Interscience, New York), ch. 4.
- Stumm, W. and Morgan, J.J. 1970. Aquatic Chemistry (Wiley Interscience, New York).
- Usiglo, J. 1849. Annalen der Chemie (27) 92.
- Vetter, O.J.G. and Phillips, R.C.J. 1970. Petro Technology 1299.
- Weijnen, M.P.C.; Marchee, W.G.J. and van Rosmalen, G.M. 1983. Desalination 47: 81.