Tranformations of Gypsum to Calcium Sulfate Hemihydrate and Hemihydrate to Gypsum in NaCl Solutions

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Synopsis. The transformations of gypsum to calcium sulfate hemihydrate and hemihydrate to gypsum were carried out in NaCl solutions containing a small amount of strontium ions in order to elucidate their mechanisms. The values of the apparent partition coefficient of strontium between solution and solids were followed during the transformations and the gypsum and hemihydrate crystals were observed by SEM. The results showed that the transformations progressed by a dissolution-reprecipitation process.

Calcium sulfate minerals, gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$), occur widely as sedimentary deposits in nature.[1] Calcium sulfate hemihydrate, $CaSO_4 \cdot 1/2H_2O$ (in mineral form, bassanite), which is an intermediate product in the transformation of gypsum to anhydrite, occurs exclusively in evaporitic environments, such as sabkha or arid zones.[2—4] The hemihydrates prepared by the dehydration of gypsum in an oven are generally metastable.[5] The hemihydrates formed in concentrated NaCl solutions contain sodium up to 5% by weight and are more stable than those of Na-free.[6,7] The kinetics of gypsum dehydration[8] and the hydration of hemihydrate[5] have been studied. Crystallographic studies of the hemihydrates have been made.[7,9] A dissolution-reprecipitation process was suggested as being the mechanism for the transformation of gypsum to anhydrite.[10,11] The mechanism for the transformation of gypsum to hemihydrate and hemihydrate to gypsum in NaCl solutions has not yet been clarified.

The calcium sulfates incorporate strontium ions; some experimental studies concerning this incorporation have been made.[12—14] The incorporation behavior of strontium ions in calcium sulfates can be conveniently described by an apparent partition coefficient, $D_{Sr} = (Sr/Ca)_m/(Sr/Ca)_s$, where $(Sr/Ca)_m$ and $(Sr/Ca)_s$ denote the weight ratios of Sr/Ca in the calcium sulfates (m) and solution (s), respectively. Some investigators have used the D_{Sr} values for the elucidation of the mechanism of the phase transformation, e.g. gypsum to anhydrite[9] and aragonite to calcite.[15] The purpose of this study was to establish the mechanism of transformations of gypsum to hemihydrate and hemihydrate to gypsum in NaCl solutions by observing the variation in the D_{Sr} values during the transformations. The transformations were also inspected by observing powder X-ray diffractgrams (XRD) and photos of scanning electron microscopy (SEM).

Experimental

The most important parameters controlling the relative stability of calcium sulfates are the temperature and salinity.[16] The experiments were conducted in two systems: the transformation of gypsum to hemihydrate (G-H) and

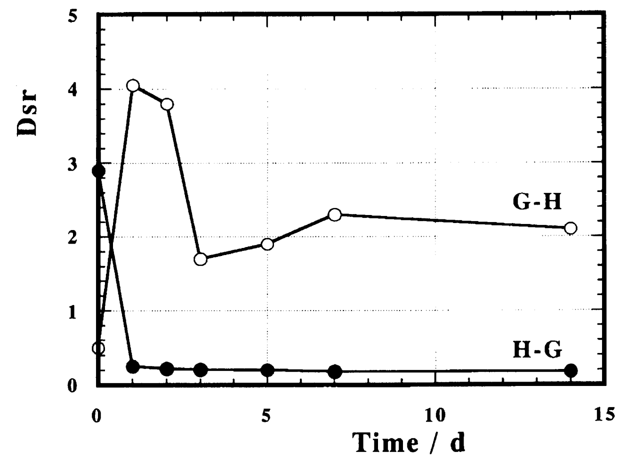

Fig. 1. Relationship between D_{Sr} values and the duration time. ○: Transformation of gypsum to hemihydrate (G-H). ●: Transformation of hemihydrate to gypsum (H-G).

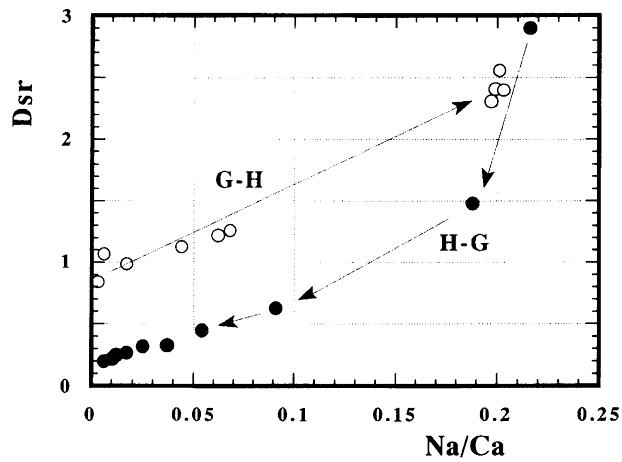

Fig. 2. Changes in D_{Sr} values with Na/Ca ratios in the solids at intervals of three hours. The arrows indicate the progressing pathway of the transformations (the circles are plotted every three hours during the period of 30 h). ○: Transformation of gypsum to hemihydrate (G-H). ●: Transformation of hemihydrate to gypsum (H-G).

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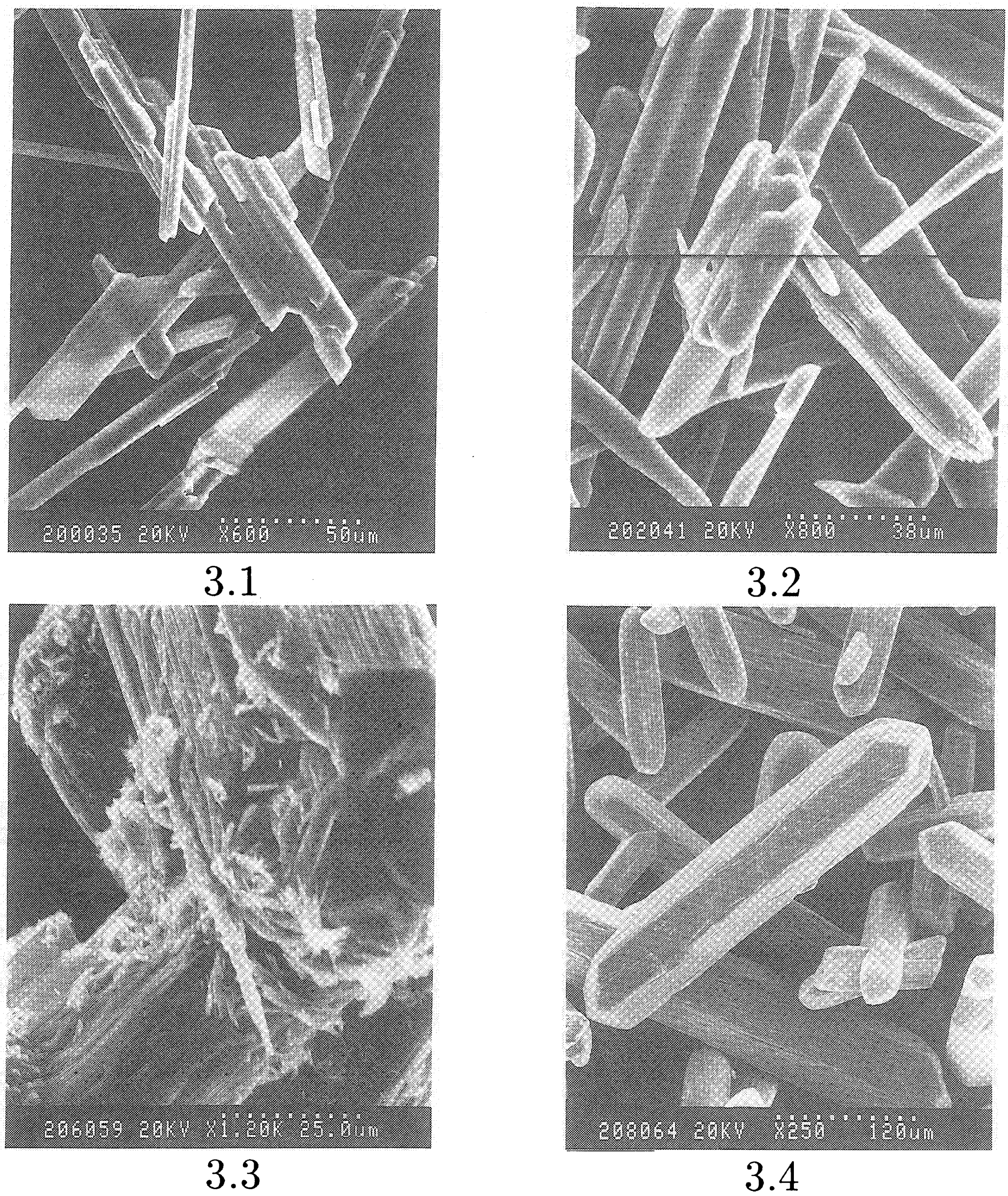

Fig. 3. SEM photos for the transformation of gypsum to hemihydrate at some stages. 3.1: 0 h, 3.2: 6 h, 3.3: 18 h, 3.4: 24 h.

hemihydrate to gypsum (H-G). The G-H system was carried out at 85 °C using a natural sample of gypsum, alabaster, already containing strontium ions, in 75% NaCl saturated solution containing a small amount of strontium ions. The H-G system was conducted at 23—30 °C using hemihydrates which were synthesized in the NaCl solutions containing a small amount of strontium at 85 °C.[17] We used 81% evaporatively-concentrated seawater in the G-H system as well.

The experimental procedure of the G-H system, for example, was as follows: 20 cm^3 of NaCl solution containing a small amount of strontium was added to 200 mg of powdered gypsum in a polypropylene bottle. The NaCl solution was saturated with respect to hemihydrate at 85 °C prior to the run. The bottle was then vigorously shaken and permitted to stand at 85 °C for 14 d until equilibrium was reached. The solution and the solid were analyzed for calcium, sodium and strontium, which were determined by atomic absorption spectro-photometry. A part of calcium was determined by the chelate-titration method using EDTA.

Results and Discussion

D_{Sr} Values as a Function of Run Time. An example of the relation between D_{Sr} values and the duration time in the G-H and H-G systems is shown in Fig. 1. In each system, the D_{Sr} values at the end of run were equal to the equilibrium values that had been estimated for gypsum and hemihydrate, around 0.2 and 2, respectively.[17] Although the D_{Sr} values in the H-G systems fell steeply near to 0.2 within one day, the values

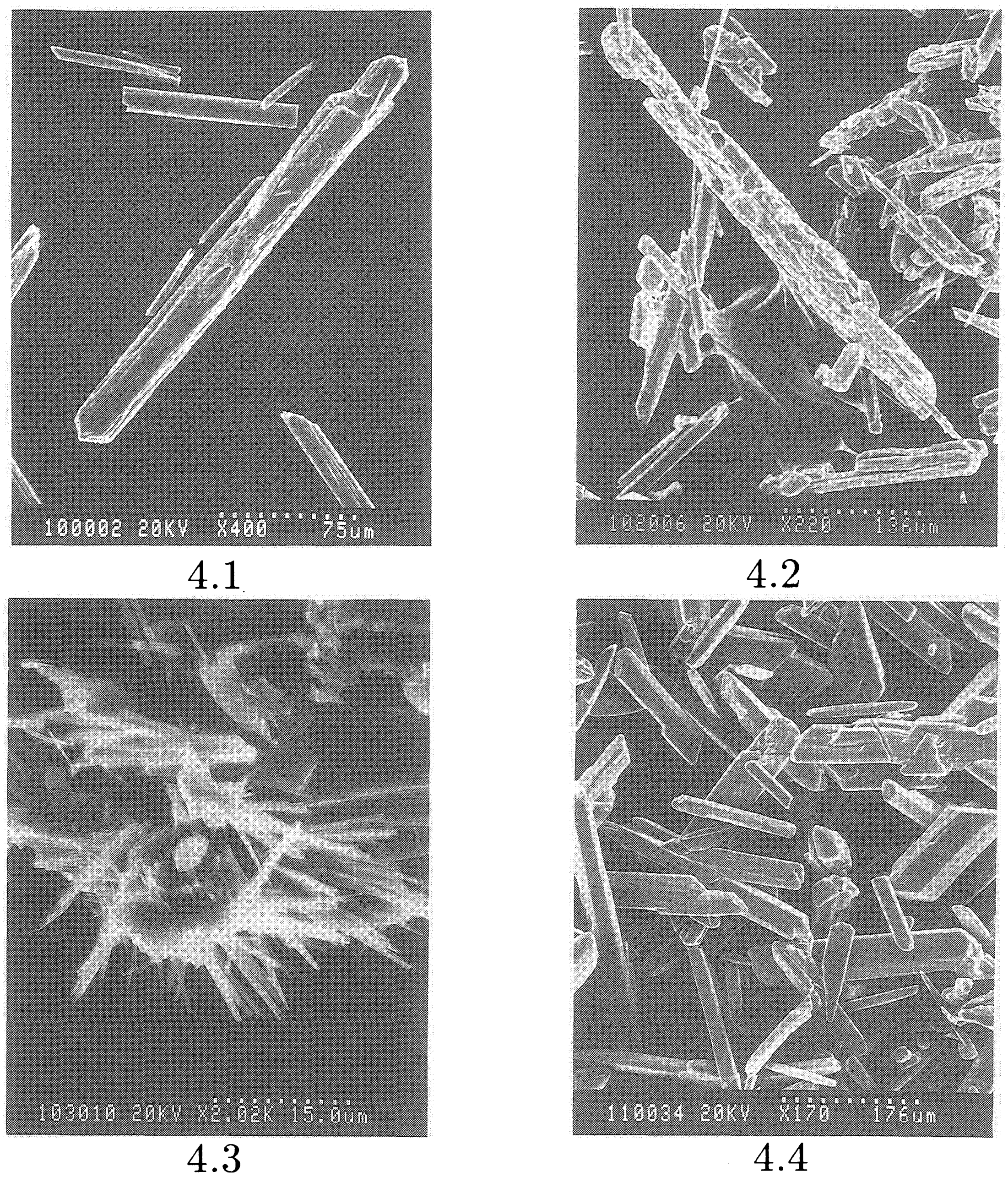

Fig. 4. SEM photos for the transformation of hemihydrate to gypsum at some stages. 4.1: 0 h, 4.2: 6 h, 4.3: 9 h, 4.4: 30 h.

for the G-H system varied in a complex manner: the D_{Sr} values rose from 0.5 to 4 first, and then fell to less than 2 (Fig. 1). The up-and-down variation in the values may be attributed to the peculiar structure of an intermediate metastable-hemihydrate formed during the early stage of the G-H system. The metastable-hemihydrate can accommodate larger amounts of strontium ions in its lattice, relative to stable hemihydrates.[9] After five days the transformation of gypsum to hemihydrate was nearly completed and the D_{Sr} values for the system were almost constant, as shown in Fig. 1. These facts suggest that the transformation rate in hemihydrate to gypsum is larger than that in gypsum to hemihydrate under these conditions. Gypsum was also completely transformed into hemihydrate after five days in 81% evaporatively-concentrated seawater at 85 °C. The concentrated seawater corresponds to a solution saturated with respect to gypsum[8] and favors the transformation of gypsum to hemihydrate. This supports the fact that bassanite is found in arid zones near to the coast such as the Arabian Gulf.[2]

Changes in D_{Sr} Values with Na/Ca Ratios. As mentioned above, hemihydrates prepared in NaCl solutions contain sodium-replacing calcium. The changes in the D_{Sr} values with Na/Ca weight ratios in the solids were traced every three hours during a period of about 30 h. The result is given in Fig. 2. This figure shows a steep fall in the D_{Sr} values for three hours in the begining of the transformation of hemihydrate to gypsum. Following the rapid decrease in the D_{Sr} values, the Na/Ca ratios in the solid became lower. This suggests that the strontium ions predominantly escaped from the crystal, and that the sodium ions successively separated from the structure. On the other hand, the transformation of gypsum to hemihydrate indicates that the strontium ions were gradually incorporated in the framework of hemihydrate along with the sodium ions.

Mechanism of the Transformations. The phase transformations were followed by XRD at intervals of three hours. New peaks of XRD for hemihydrate in the G-H system appeared after six hours. The peaks for gypsum almost disappeared after 27 h from the beginning. New peaks for gypsum in the H-G system appeared after three hours. The prominent peaks for hemihydrate were almost changed to those for gypsum after about 18 h. These results suggest that the transformations are gradual and that the G-H transformation proceeds faster than the H-G transformation under these conditions.

The crystals formed in the transformations were also observed by SEM. Figures 3 and 4 show the SEM photos of selected steps in the transformations. In the G-H system gypsum dissolved in an early stage and gradually changed into fine new crystals (Figs. 3.2—3.4). In the H-G system a part of the hemihydrate crystals was dissolved during the initial stage (Fig. 4.2), and was consequently dismembered; needle-shaped gypsum was then formed on the surface of hemihydrate (Fig. 4.3). The gypsum on the surface grew and the conversion was completed along with the passage of time.

If the phase transformation progresses in the solid state, the original concentrations of incorporated ions, strontium and sodium, in solids and solutions may be preserved. However, if the transformation of gypsum to hemihydrate takes place by a process of dissolution-reprecipitation, strontium and sodium ions will be redistributed between the newly-formed hemihydrate and the solution. In this case the dissolution of gypsum and the precipitation of hemihydrate would occur concurrently. The variations in the values of D_{Sr} and Na/Ca ratios described above and the SEM photos strongly suggest that the transformation progress due to the dissolution-reprecipitation process is the same as the process for the transformation of gypsum to anhydrite suggested by Ostroff[10] and Kushnir.[11]

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References

1) W. A. Deer, R. A. Howie, and J. Zussman, "Rock-Forming Minerals," Longman, London (1972), Vol. 5, p. 202.
2) W. Smykatz-Kloss, G. Istrate, H. Hotzl, H. Kossl, and S. Wohnlich, *Chem. Erde*, **44**, 67 (1985).
3) A. Gunatilaka, A. Al-Temeemi, A. Saleh, and N. Nassar, *J. Univ. Kuwait (Sci)*, **12**, 157 (1985).
4) E. G. Akpokodje, *Chem. Geol.*, **47**, 361 (1984/1985).
5) M. J. Ridge and J. Beretka, *Rev. Pure Appl. Chem.*, **19**, 17 (1969).
6) D. A. Powell, *Aust. J. Chem.*, **15**, 868 (1962).
7) G. A. Lager, Th. Armbruster, F. J. Rotella, J. D. Jorgensen, and D. G. Hinks, *Am. Mineral.*, **69**, 910 (1984).
8) Abdel A. A. Khalil, *Thermochim. Acta*, **55**, 201 (1982).
9) S. Chatterji and J. W. Jeffery, *Nature*, **4905**, 463 (1963).
10) A. G. Ostroff, *Geochim. Cosmochim. Acta*, **28**, 1363 (1964).
11) J. Kushnir, *Geochim. Cosmochim. Acta*, **46**, 433 (1982).
12) J. Kushnir, *Geochim. Cosmochim. Acta*, **44**, 1471 (1980).
13) B. C. Purhayastha and A. Chatterjee, *J. Indian Chem. Soc.*, **43**, 687 (1966).
14) M. Ichikuni and S. Musha, *Chem. Geol.*, **21**, 359 (1978).
15) A. Katz, E. Sass, A. Starinsky, and H. D. Holland, *Geochim. Cosmochim. Acta*, **36**, 481 (1972).
16) R. A. Berner, "Principles of Chemical Sedimentology," McGraw-Hill, Inc., New York (1972), p. 79.
17) T. Miyoshi, M. Imahashi, Y. Yoshino, and K. Katsuki, *Chikyu-kagaku (Geochemistry)*, **21**, 55 (1987).
18) P. Sonnenfeld, "Brines and Evaporites," Academic Press, Inc., Orlando (1984), p. 102.