Some Observations on the Process of Dehydration and Rehydration of Gypsum by Means of Proton Magnetic Resonance

By Tatsuo SAITO

(Received February 15, 1961)

In the previous paper[1], the proton resonance spectra of thermally dehydrated products of alumina trihydrate in vacuo and their rehydrated specimens were measured and the relations between the phase transformation and the movements of bound water were investigated.

In the present paper, the process of thermal dehydration of natural gypsum in vacuo and their rehydration by saturated water vapor were investigated by the variation of line shapes of proton resonance spectra.

On the study of the process of dehydration and rehydration of gypsum extensive literatures have appeared. Several authors[2-8] deduced that the hemihydrate obtained from the partial dehydration of gypsum has a zeolitic type of structure such that water molecules can enter and leave it without destroying the lattice. Other authors[9] deduced that the calcium sulfate hemihydrate has a definite chemical composition and that the process of dehydration is not zeolitic in character. On the other hand, Mitsuki[10] and Razouk[8] explained that the dehydration of gypsum in vacuo leads directly to the formation of a soluble anhydrite.

The present author found by the observations of the proton resonance spectra that the soluble anhydrite produced by the thermal dehydration of gypsum occludes some quantity of movable water in the space of its crystal lattice and that the hemihydrate obtained by the rehydration of dehydrated gypsum has a definite crystal water and some quantity of movable water.

Experimental

Experimental Apparatus.—The NMR measurements were performed at room temperature using the modulation technique described by Bloembergen, Purcell and Pound[11]. The detecting apparatus[12] has the ordinary constitution, which is composed of an r–f oscillator, an r–f amplifier, a detector, an audio frequency amplifier, a lock-in amplifier and a recorder. The pole face diameter of the permanent magnet is 140 mm. and the air gap length is 40 mm. The magnet has the field intensity of 4140 gauss, with a uniformity of 2×10^{-5} over the whole sample volume. Continuous variation of the static magnetic field linear with time was achieved by an automatic current scanning apparatus[13].

Specimens.—The starting material used in this experiment was fibrous gypsum (Produces in Iwasawa, Iwate Prefecture) containing the stoichiometric amount of water according to the formula, $CaSO_4 \cdot 2H_2O$. The X-ray diffraction diagram of this material is shown in Fig. 1.

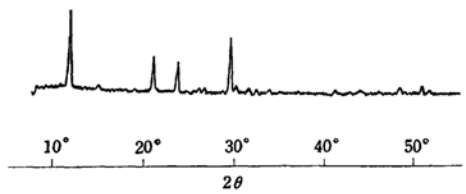
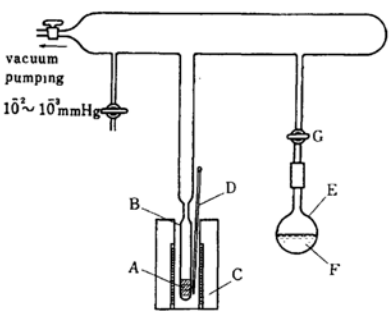


Fig. 1. X-ray diagram of the starting material, gypsum.



A: sample cake (dia. 8 mm.) B: resonance sample tube C: electric furnace D: thermometer E: flask (100 cc.) F: distilled water in evacuated flask G: cock.

Fig. 2. Apparatus used for the preparation of the specimens.

1) T. Saito, This Bulletin, **34**, 757 (1961).
2) G. Linck and H. Jung, *Z. anorg. allgem. Chem.*, **137**, 407 (1924).
3) C. S. Gibson and S. Holt, *J. Chem. Soc.*, **1933**, 638.
4) W. A. Caspari, *Proc. Roy. Soc.*, **A, 155**, 41 (1936).
5) C. W. Bunn, *J. Sci. Instru.*, **18**, 70 (1941).
6) S. J. Gregg and E. G. J. Willing, *J. Chem. Soc.*, **1951**, 2916.
7) R. Kiriyama and H. Ibamoto, This Bulletin, **26**, 109 (1953).
8) R. I. Razouk, A. S. Salem and R. S. Mikhail, *J. Phys. Chem.*, **64**, 1350 (1960).
9) H. B. Weiser, W. O. Milligan and W. C. Ekholm, *J. Am. Chem. Soc.*, **58**, 1261 (1936); H. B. Weiser and W. O. Milligan, ibid., **59**, 1456 (1937).
10) C. Mitsuki, *J. Ceram. Assoc. Japan*, **60**, 92 (1952).
11) N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).
12) S. Yano, *J. Phys. Soc. Japan*, **14**, 952 (1959).
13) T. Sidei, S. Yano and S. Sasaki, *J. Appl. Phys. Japan*, **27**, 513 (1958).

Each dehydration-specimen or rehydration-specimen was prepared in the vacuum system illustrated in Fig. 2. To prepare each specimen by thermal dehydration in vacuo, about 2 g. of powdered gypsum was pressed in the form of small cakes A and put into the resonance sample tube B which was connected to the high vacuum system. This sample tube B was heated from outside by an electric furnace C for 3 hr. in a high vacuum and was then sealed off. The dehydration temperatures were 70, 80, 90, 95, 100, 105, 110, 115, 125, 150 and 200°C. For the preparation of rehydration-specimens, each sample after the treatment of the thermal dehydration in vacuo was immediately exposed for 15 hr. to saturated water vapor which was introduced through the cock G from the flask E at room temperature. Then, each sample tube containing this rehydrated specimen was pumped out to a high vacuum for 12 hrs. at room temperature and was then sealed off. In this experiment, the temperature of the dehydration in vacuo was 80, 95, 110, 125, 135, 150, 165, 180, 220, 250 and 300°C.

X-Ray powder diffraction was made with a "Geigerflex" recording X-ray spectrometer using filtered CuK_α radiation.

Results and Discussion

Thermal Dehydration in vacuo.—The experimental derivative curves of the proton resonance obtained from the dehydrated products are shown in Figs. 3 and 4. The photographs of a and b in Fig. 4 show the recorded spectra of the typical derivative curves.

As is seen in Fig. 3, the derivative curve of the starting material shows a typical line shape of two spin system[14] with broad width of about 14 gauss. While in the line shape of the specimen dehydrated at 70°C a single peak appeared overlapping the line of the starting material at its center, for the specimen dehydrated at 90°C only the center peak was observed. This characteristic single sharp peak was also observed for the specimen dehydrated at 150°C, while for the specimen dehydrated at 200°C no proton resonance signal was observed. It is known that this single sharp peak of proton resonance originates from the water molecules which are in the thermal motion.

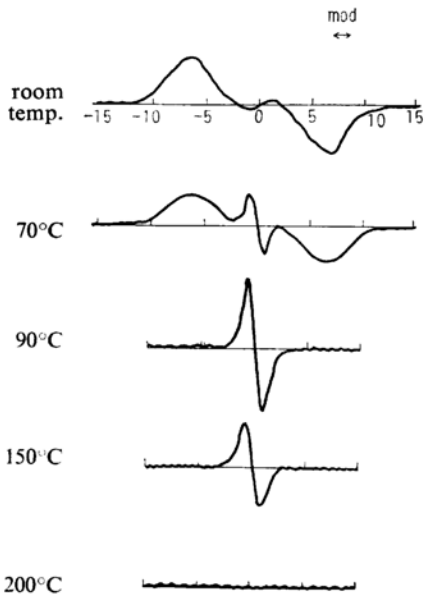
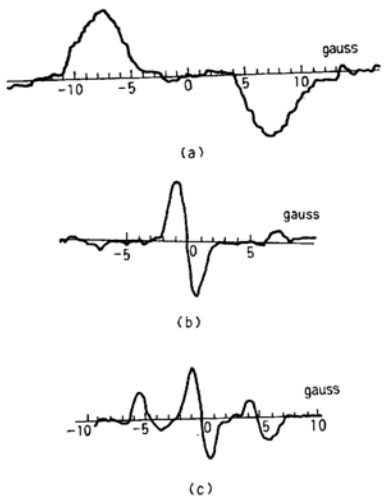


Fig. 3. Experimental derivative curves of proton resonance in the dehydration-specimens.



(a) starting material, gypsum.
(b) dehydrated gypsum at 95°C.
(c) rehydrated product of (b)

Fig. 4. Recorded derivatives of proton resonance in the dehydration or rehydration-specimens.

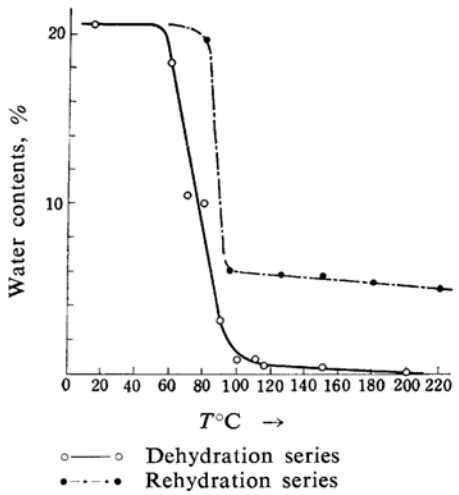


Fig. 5. Variation of water contents in the dehydration or rehydration-specimens the dehydration temperature.

14) G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948).

To compare the above results with the change of chemical composition, the water content of each dehydration-specimen was measured and the values of percentage of weight loss at 800°C were plotted in Fig. 5 as the function of the dehydration temperature.

As is seen in Fig. 5, the water content decreases suddenly at about 70°C from the value corresponding to dihydrate to the value of 1~2% corresponding to soluble anhydrite, while the remaining water can not be completely removed even at 150°C and in this process of dehydration the steps corresponding to the formation of hemihydrate were not observed. This is in agreement with the results obtained by other authors[8,10].

In the X-ray diffraction studies, the crystallographical phase transformation was observed for the dehydration at about 70°C as shown in Fig. 6.

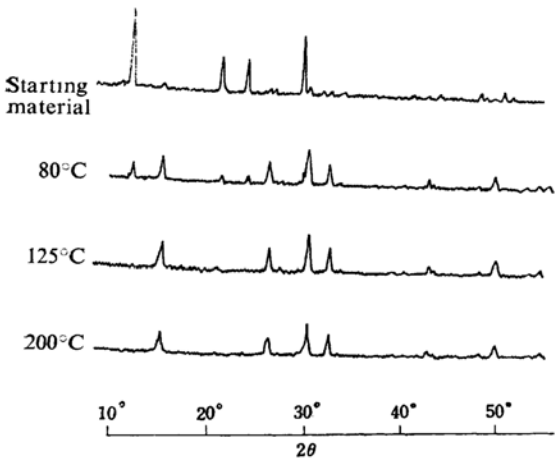


Fig. 6. X-ray diffraction diagrams of the dehydration-specimens.

From these experimental results, it is assumed that the decomposition of this gypsum occurs at 60~70°C, that some quantity of water released during the dehydration remains in the space of the crystal lattice which is introduced by the dehydration and that this movable water is gradually removed with rises of temperature, having no influence upon the crystal lattice.

On the other hand, the crystal structure of gypsum[15] may be described as a complex layer structure in which the layers are bound together by bonds from water molecules, each of which is joined to a Ca^{2+}, 0 atom of a SO_4^{2-} ion of one layer and an 0 atom of SO_4^{2-} ion of an adjacent layer.

It might be concluded from the experiments described above that these O–H–O bonds are so weak that the crystal structure of gypsum can be broken down even at low temperature and that the evolution of the binding water may occur at the same time, while some quantity of this water may remain in the space of the lattice which is introduced by the decomposition at low temperature.

Rehydration of the Dehydration-Specimens in vacuo.—The NMR measurements were carried out on the specimens prepared by the rehydration of gypsum thermally dehydrated in vacuo. The typical experimental derivative curves obtained from these measurements are shown in Fig. 7.

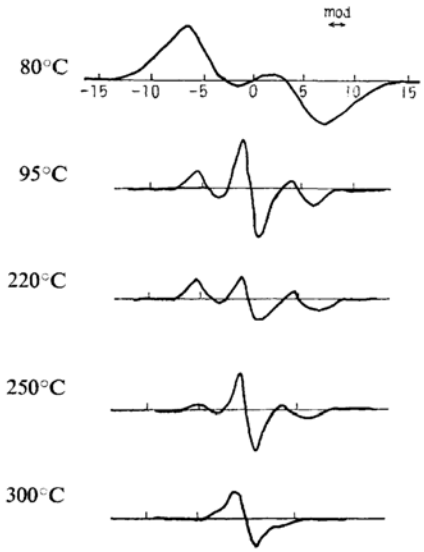


Fig. 7. Experimental derivative curves of proton resonance in the rehydration-specimens.

As is seen in Fig. 7, the rehydrated specimens of gypsum dehydrated at the temperature from 95 to 250°C show the same line shapes. The photograph of c in Fig. 4 shows the recorded spectrum of this typical derivative curve, while the rehydrated specimen of gypsum dehydrated at 80°C shows the same line shape as that of the starting material. From the measurements of the water content of these rehydrated specimens, it was found that the line shapes observed for the rehydrated specimens of gypsum dehydrated from 95 to 250°C correspond to the phase of hemihydrate, $CaSO_4 \cdot 1/2\,H_2O$. The values of the water content of these specimens were also plotted in Fig. 5 as the function of the dehydration temperature.

While these rehydration-specimens corresponding to hemihydrate were crystallographically quite similar to the dehydrated gypsum corresponding to soluble anhydrite from the result of the X-ray study, the line

15) A. F. Wells, "Structural Inorganic Chemistry", Oxford University Press, London (1950), p. 440.

shapes observed for these rehydration-specimens are different from that for the dehydrated gypsum and are presumably understood as the signal of three spin type with an intensive center peak. The line width of this line shape (the separation between peaks in side band) was about 11～12 gauss.

The product obtained from this hemihydrate by the thermal treatment at 100°C for 3 hr. in vacuo showed only the single center peak corresponding to the movable water. This movable water may also be explained as the zeolitic water existing in the space of the crystal lattice which was introduced by the dehydration of hemihydrate.

On the other hand, the rate of rehydration of gypsum dehydrated at 125°C by saturated water vapor was examined by NMR measurements and it was found that all the specimens obtained from the rehydration for one to 48 hr. showed the same line shapes as that corresponding to hemihydrate. This result means that hemihydrate is considerably stable against saturated water vapor and that the rate of hydration of soluble anhydrite is very high. This result is in agreement with the result obtained by other authors[8].

However, gypsum dehydrated at 80°C is easily rehydrated by saturated water vapor directly to dihydrate. This fact means that the product dehydrated at 80°C has the pseudolattice of gypsum and transforms easily to the phase of dihydrate by the addition of water molecules.

Summary

1) On the thermal dehydration in vacuo, the characteristic single sharp peak of proton resonance was observed for the specimens dehydrated at the temperature from 70 to 150°C.

It is assumed that this single sharp peak is attributed to the zeolitic water probably existing in the space of the crystal lattice of soluble anhydrite and that this zeolitic water can be interpreted as being a part of the water molecules which originate from dihydrate during the thermal decomposition.

2) Calcium sulfate hemihydrate was formed by the rehydration of gypsum dehydrated in vacuo. This hemihydrate showed the proton resonance spectrum corresponding to the signal of three spin type with an intensive center peak. This intensive center peak can be interpreted as an indication of the movable water existing in the space of the crystal lattice of hemihydrate.

3) This hemihydrate was considerably stable under the atmosphere of saturated water vapor. This was ascertained by the NMR measurements.

The author wishes to express his sincere thanks to Dr. Y. Kotera of this Institute for his kind advice.

The author also wishes to express his hearty thanks to Professor Tokutaro Hagiwara of Hiroshima University for his kind direction and also to Professor Tunahiko Sidei and Dr. Syukuro Yano of Kyoto University for their continual guidance and encouragement throughout this study.

Government Chemical Industrial Research Institute, Tokyo
Shibuya-ku, Tokyo