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REACTIONS OF MAGNESIUM CARBONATES BY DIRECT X-RAY
DIFFRACTION UNDER HYDROTHERMAL CONDITIONSSHIN-ICHI IWAI, YOSHIZI SOTOME, HIDEKI AOKI,
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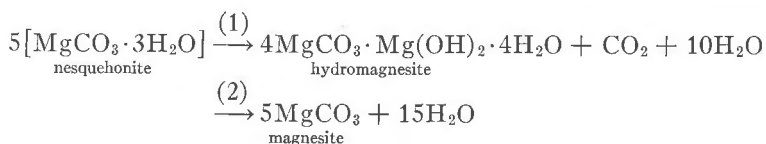
ABSTRACT

Wet emulsions sealed in a capillary tube in a high-temperature Weissenberg camera gave X-ray powder diffraction patterns at temperatures to 220°C and pressures to 35 kg/cm². Kinetics of the decomposition of nesquehonite to hydromagnesite and then to magnesite were followed by this method. The decomposition of nesquehonite to magnesite appears to be first-order around 200°C, with an activation energy of 33 kcal/mole.

A method of X-ray analysis with which reactions of substances under hydrothermal conditions can be continuously observed has been developed. An application of this technique to a study of hydrothermal changes of nesquehonite (MgCO₃·3H₂O) to magnesite will be reported in this note.

A capillary tube 0.3–0.4 mm in inner diameter, 0.5–0.6 mm in outer diameter, and 10–15 mm in length was made of hard glass. An emulsion of 2 mole/l MgCO₃·3H₂O, which had been synthesized with MgCl₂ and Na₂CO₃ solutions, was packed into the tube by capillary action. After the edges of the tube had been sealed by an oxygen-fuel gas flame the tube, was set in a high temperature Weissenberg camera. Powder photographs were taken at successive steps at elevated temperatures, 190°C–220°C, with exposure times of 10 minutes, using 50 kV–80 mA Cu-Kα radiation (rotor unit RU-3, Rigaku Denki Co., Japan).

It was observed from the powder photographs that nesquehonite started to transform into hydromagnesite (4MgCO₃·Mg(OH)₂·4H₂O) within 10 minutes at 190°C–220°C; and that hydromagnesite began to change into magnesite at 190°C in 3 hours, at 200°C in 70 minutes, at 210°C in 50 minutes, and at 220°C in 20 minutes. The chemical reactions are considered to be follows:



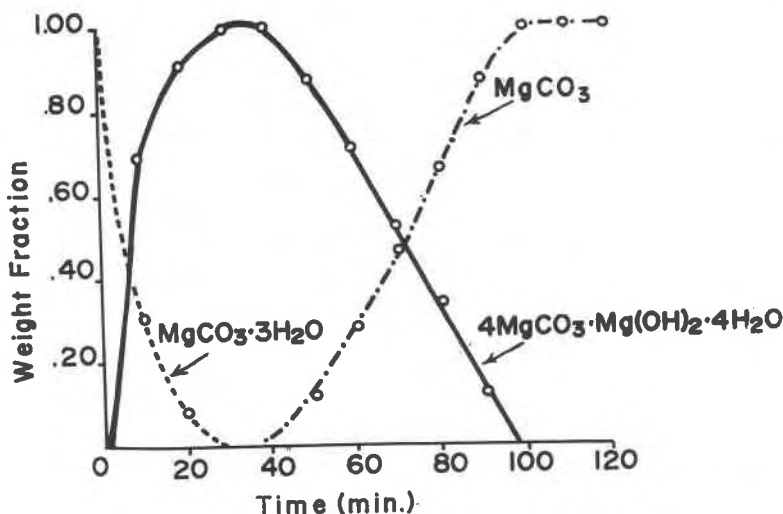


FIG. 1. Reaction of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ under hydrothermal conditions at 210°C .

The total pressure in the capillary increases with the liberation of CO_2 in the first reaction step and then decreases as CO_2 reacts in the second step. For instance, at 200°C , water vapor pressure is 17.4 kg/cm^2 , the partial pressure of CO_2 was calculated to be 17.6 kg/cm^2 at its maximum (considering the volume of the capillary and the packing fraction of the emulsion), and the total pressure was 35 kg/cm^2 .

Figure 1 shows the changes of the weight fraction of nesquehonite, hydromagnesite, and magnesite with time under hydrothermal conditions at 210°C , estimated with the aid of the calibration curve of weight fraction versus intensity. The intensities were corrected visually by standard intensity scales.

It was concluded from the kinetic analysis that the reaction from hydromagnesite to magnesite was of first order. The magnitude of the rate constants was determined to be $k_{200^\circ\text{C}} = 2.53 \times 10^{-4} (\text{sec}^{-1})$, $k_{210^\circ\text{C}} = 3.91 \times 10^{-4} (\text{sec}^{-1})$, and $k_{220^\circ\text{C}} = 9.20 \times 10^{-4} (\text{sec}^{-1})$. The analysis of Arrhenius type gave 33 kcal/mole as the apparent activation energy of this reaction. This method of continuous observation of hydrothermal reactions can be applied to many other materials, and not only qualitative but also quantitative information can be obtained.