

Chemical Reactions in the System MgO–MgCl₂–H₂O Followed by Time-Resolved Synchrotron X-Ray Powder Diffraction

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The chemical reactions in the system MgO–MgCl₂–H₂O were investigated by on-line synchrotron X-ray powder diffraction at temperatures up to 100°C. The crystalline reaction products formed were Mg(OH)₂ and MgCl₂ · 5Mg(OH)₂ · 8H₂O. The reaction rates in these heterogeneous systems are strongly dependent upon the concentrations of the magnesium chloride solutions, the molar ratio MgCl₂/MgO, and the temperature. © 1995 Academic Press, Inc.

INTRODUCTION

Sorel's cement is obtained in a reaction of magnesium oxide with solutions of magnesium chloride (1). In these reactions magnesium hydroxide or magnesium chloride hydroxide hydrates are formed depending upon the concentrations of the magnesium chloride solutions and the temperature. Low concentrations result in the formation of magnesium hydroxide. With increasing concentrations of magnesium chloride, magnesium chloride hydroxide hydrates with increasing content of chloride are obtained. Bianco (2) investigated such reactions under hydrothermal conditions up to 175°C and identified the compounds listed in Table 1.

Crystallization processes in heterogeneous systems may be followed using time-resolved X-ray and neutron powder diffraction. A preliminary time-resolved X-ray diffraction investigation of the system MgO–MgCl₂–H₂O showed that the reaction products were magnesium hydroxide and a magnesium chloride hydroxide hydrate,

depending upon the concentrations of the solutions of magnesium chloride used in the investigation (4). Time-resolved X-ray powder diffraction using synchrotron radiation has been used in further studies of the systems MgO–MgCl₂–H₂O and MgO–H₂O, and the results are reported below. The crystalline reaction products found were Mg(OH)₂ and MgCl₂ · 5Mg(OH)₂ · 8H₂O.

EXPERIMENTAL

The chemicals used in the investigation were MgO made from basic magnesium carbonate (Merck p. a.), and MgCl₂ (Alpha Inorganic). In the preparation of a batch of MgO the basic magnesium carbonate was kept in a crucible of Al₂O₃ at 700°C for 12 hr, and MgO so obtained was stored in an airtight plastic bottle. A preliminary investigation of the system MgO–MgCl₂–H₂O was made at 25°C and under hydrothermal conditions at 125°C to determine conditions for the formation of Mg(OH)₂ and the magnesium chloride hydroxide hydrates, and the reaction products were identified from X-ray powder patterns.

In the on-line diffraction experiments the samples used were wet pastes made from 50 or 100 mg MgO and 0.20, 0.40, or 0.80 ml of the magnesium chloride solutions. This gave molar ratios MgCl₂/MgO in the range from 0.22 to 1.53. The paste was housed in a 0.3-mm diameter quartz capillary tube. The wet paste was introduced into the capillary tube using a syringe with the capillary, open at both ends, placed on the syringe instead of a needle. The open ends of the capillary tube were closed with cyanoacrylate glue. The sample was placed on the diffractometer and heated with a flow of hot, compressed air.

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TABLE I
Composition of Magnesium Chloride Hydroxide Hydrates

| Compound | Short notation | JCPDS card no. | Ref. of structure |
|--|-------------------|----------------|-------------------|
| MgCl ₂ · 5Mg(OH) ₂ · 8H ₂ O | Cl _{5,8} | 12-122, 7-420 | (3) |
| MgCl ₂ · 3Mg(OH) ₂ · 8H ₂ O | Cl _{3,8} | 7-412, 36-388 | |
| MgCl ₂ · 9Mg(OH) ₂ · 5H ₂ O | Cl _{9,5} | 12-123, 7-409 | |
| MgCl ₂ · 2Mg(OH) ₂ · 4H ₂ O | Cl _{2,4} | 12-116 | |
| MgCl ₂ · 2Mg(OH) ₂ · 2H ₂ O | Cl _{2,2} | 12-133 | |

Note. Notation after Bianco (2).

A small heater for the flow of air was placed in a glass tube and the power of the heater was adjusted by a variable transformer. A thermocouple was placed just outside the tube in the flow of air and close to the capillary to measure the temperature.

Synchrotron X-ray powder patterns were measured of the capillaries on a Huber diffractometer at the beam line X7B at NSLS, Brookhaven National Laboratory at 2.5, 5.0, 10.0 min intervals. A type CPS 120 curved INEL position-sensitive detector covering 120° in 2θ was mounted on the θ-arm of the diffractometer. The channel to angle relationship of the detector was found from the position of the primary beam measured in a 2° 2θ step scan with the detector. Positions thus obtained were used to calculate a detector step vs 2θ function by cubic interpolation (5). The diffraction patterns were then recalculated to equal step patterns using a cubic spline function. This gave Δ2θ = 0.02922° for the detector. The wavelength λ = 1.1895 Å was found in a profile refinement of a powder pattern of silicon (a = 5.4305 Å).

In real time X-ray powder diffraction a rather large number of patterns are recorded for each sample. The patterns are plotted in a display so that the evolution in time of the powder patterns can be observed (see below). Relative quantities of reactant or product can be measured by integration of selected Bragg reflections of the crystalline solids. The end products of the reactions were identified from the last X-ray powder pattern in each series of measurements. The DIFFRAC AT program (Siemens D5000 software) was used for plotting the powder patterns, and the program FIT was used to determine integrated intensities by profile fitting (Siemens D5000 software).

RESULTS AND DISCUSSIONS

Identification of Reaction Products

The investigation by Bianco (2) of the system MgO–MgCl₂–H₂O in the temperature range 0–175°C indicated

that the reaction products were Mg(OH)₂ and five magnesium chloride hydroxide hydrates depending upon temperature and the concentration of the magnesium chloride solutions used in the synthesis. However, preliminary investigations at 25°C indicated that the composition of the reaction product was also dependent upon the molar ratio MgCl₂/MgO used in the synthesis so that products with increasing chloride content would be formed when the molar ratio was increased. A series of syntheses was made which shows that the reaction products Mg(OH)₂, Cl_{5,8}, Cl_{3,8}, and Cl_{2,4} were formed at room temperature.

The system MgO–MgCl₂–H₂O was also investigated hydrothermally at 125°C. Reaction mixtures of MgO and MgCl₂ solutions were heated in Pyrex glass containers in pressure vessels of steel, and the reaction products were identified from their X-ray powder patterns. The reaction products formed were Mg(OH)₂, Cl_{5,8}, Cl_{3,8}, and Cl_{9,5}.

In the time-resolved synchrotron X-ray experiments 50 mg MgO and 0.2 ml to 0.8 ml magnesium chloride solution or water were used so the only parameters were the temperatures and the MgCl₂/MgO ratios.

Reactions of MgO with Water

Figure 1 displays part of the synchrotron X-ray powder patterns of the MgO–H₂O mixture at 30°C recorded at 5 min intervals. After an induction period of 45 min, the formation of Mg(OH)₂ starts. The quantities of crystalline MgO and Mg(OH)₂ in the reaction mixture were determined by integration of the 200 reflection for MgO, and the 110 reflection for Mg(OH)₂, respectively. After 160 min half the original quantity of MgO has been converted to Mg(OH)₂. At 70°C it takes approximately 5 min, and at 100°C approximately 3 min, to convert half of the original quantity of MgO to Mg(OH)₂, and at these temperatures it was not possible to follow in detail the rate of reaction.

Reactions of MgO with up to 3 M MgCl₂ Solutions at 30°C

The reaction product of MgO and these solutions at 30°C was Mg(OH)₂. In contact with the MgCl₂ solutions it takes approximately 80 min before half of the original quantity of MgO is reacted to Mg(OH)₂. This is approximately twice as fast as in the reaction between MgO and pure water at 30°C. It was also observed previously that the reaction of MgO at 20°C to produce Mg(OH)₂ was faster in a 1.50 M MgCl₂ solution than in pure water (4).

Reactions of MgO with up to 3 M Solutions of MgCl₂ at 70 and 100°C

In all these experiments the reaction products were Mg(OH)₂, and its formation was so fast that no conclusion should be drawn concerning concentration dependence of the reaction rate. At 70°C half the quantity of Mg(OH)₂

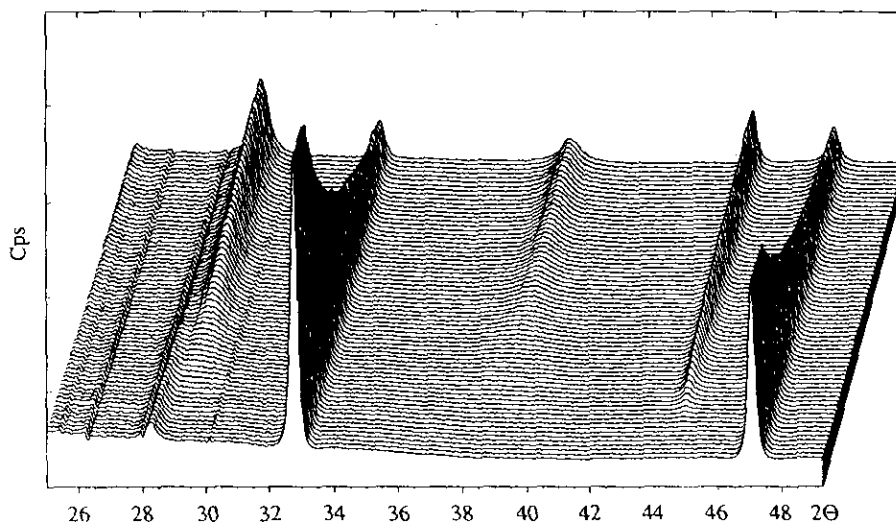


FIG. 1. X-Ray powder diffraction diagrams of a MgO-H₂O mixture at 30°C recorded at 5-min intervals.

is formed in approximately 5 min, and at 100°C in approximately 3 min.

An understanding of the nature of the reaction may be gained in a study of the time dependence of $\alpha(t)$, the degree of reaction which is equal to the degree of formation of Mg(OH)₂ at time t . The reaction between water and a grain of MgO takes place in an interface, and when this reaction interface moves at a constant rate, the reaction kinetics are said to be linear. Parabolic reaction kinetics involves a rate controlled by mass transport through a layer on the reacting particle. When α is the degree of hydration, a plot of $\log \alpha/(1 - \alpha)$ vs $\log t$ for the reaction of MgO with water to Mg(OH)₂ at 30°C shows a linear relation (Fig. 2). The reaction can be assumed to move at a constant rate at the reacting interface.

The formation of Mg(OH)₂ from MgO in the MgCl₂ solutions at different temperatures result in a temperature-

dependent particle size. Figure 3 displays the FWHM for the 110 Mg(OH)₂ reflection obtained in synthesis at 30, 70, and 100°C, respectively, in the 1.376 M MgCl₂ solution. The average values of the final FWHM are approximately 0.30, 0.26, and 0.20 at these three temperatures. The largest particles of Mg(OH)₂ are thus obtained at 100°C. Figure 3 shows a weak tendency of particle growth corresponding to reduction in FWHM during the time-resolved experiments.

Reaction of MgO with a 4 M Solution of MgCl₂ at 25, 30, and 45°C

In these three experiments the reaction products were Cl_{5,8}. Figure 4 depicts the synchrotron X-ray powder patterns of the mixtures of MgO with the MgCl₂ solution recorded at 5-min intervals at 30°C. Reflections from the reaction product start to appear in the pattern after 80

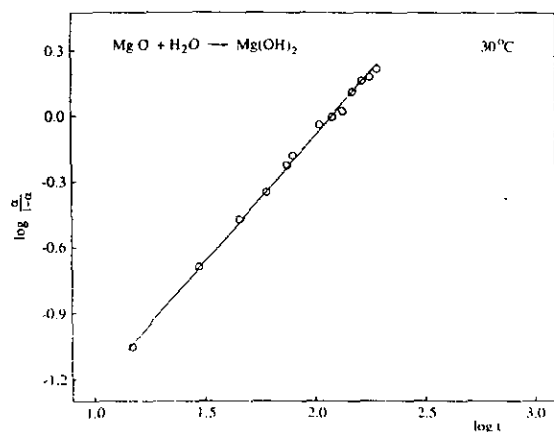


FIG. 2. Plot of $\log \alpha/(1 - \alpha)$ vs $\log t$; 15 min between data points.

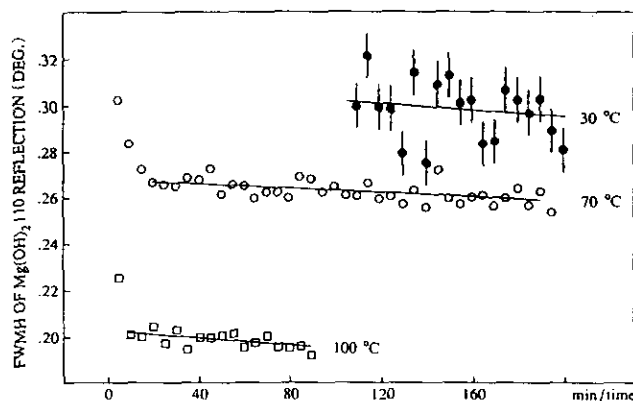


FIG. 3. FWHM of the Mg(OH)₂ 110 reflection from the reaction of MgO with a 1.376 M MgCl₂ solution at 30, 70, and 100°C.

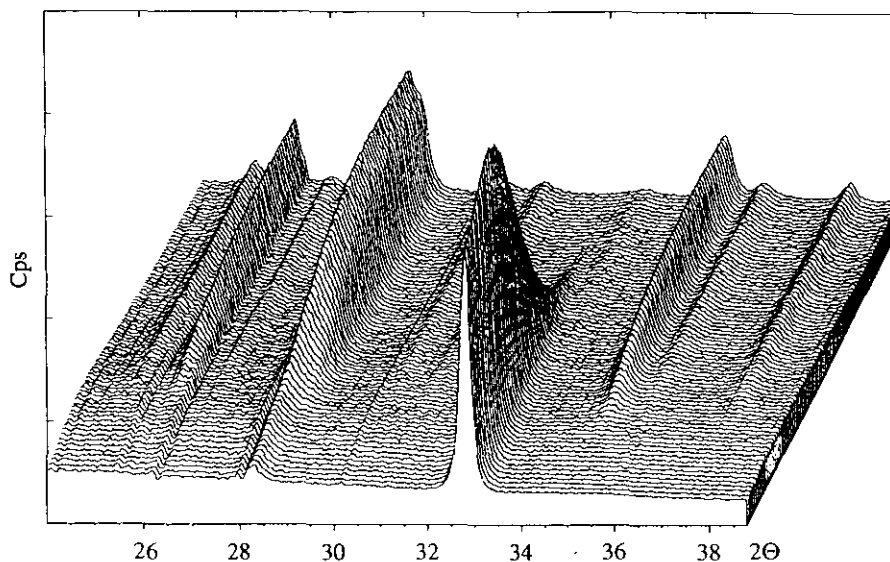


FIG. 4. X-ray powder diffraction diagrams of a mixture of MgO and a 4 M MgCl₂ solution at 30°C recorded at 5-min intervals. The reaction product is Cl_{5,8}.

min. The quantity of the crystalline reaction product Cl_{5,8} was determined by integration of its reflection at $2\theta = 9.07^\circ$. Figure 5 displays the quantities of Cl_{5,8} and MgO vs time for the experiments at the three temperatures. Half the original quantity of MgO is consumed after 60, 163, and 216 min at the temperatures 45, 30, and 25°C, respectively. For the reaction at 30°C this corresponds to the same rate as that for the formation of Mg(OH)₂ in the MgO-H₂O system at 30°C.

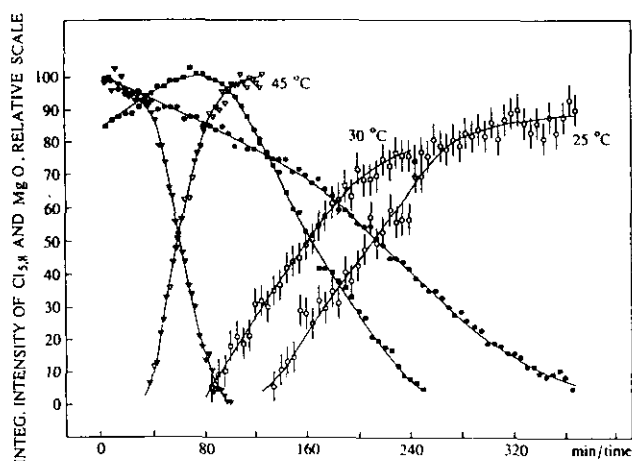


FIG. 5. Integrated intensity of MgO (filled symbols) and Cl_{5,8} (open symbols) vs time for the reactions between MgO and a 4 M MgCl₂ solution at 25°C with the molar ratio MgCl₂/MgO 0.765 (○, ●), at 30°C with the molar ratio MgCl₂/MgO 1.530 (□, ■), and at 45°C with the molar ratio MgCl₂/MgO 0.765 (▽, ▼).

The reaction rate for the formation of Cl_{5,8} is assumed to depend on the quantity of MgO and the quantity and concentration of the MgCl₂ solution. When the solution is in excess, an approximate expression for the rate of consumption of MgO, which is equal to the rate of formation of Cl_{5,8} is $dA/A = k dt$. At the time $t_{0,5}$, half the quantity of MgO has been consumed. The Arrhenius expression $A = A_0 \exp(-E_a/RT)$ can then be transformed to $\ln t_{0,5} = E_a/100R \cdot 100/T + \text{constant}$. From an Arrhenius plot of $\ln t_{0,5}$ vs $100/T$ an activation energy $E_a = 50.7$ kJ/mol is derived.

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REFERENCES

1. P. Pascal, "Nouveau Traité de Chimie Minérale," Vol. 4, p. 177. Masson et Cie, Paris, 1958.
2. Y. Bianco, *Ann. Chim. 13th Serie*, **3**, 370 (1953).
3. P. M. De Wolff, and L. Walter-Levy, *Acta Crystallogr.* **6**, 40 (1953).
4. A. N. Christensen, *Mater. Res. Soc. Symp. Proc.* **205**, 259 (1992).
5. K. Staahl, and J. C. Hanson, *J. Appl. Crystallogr.* **27**, 543 (1994).