Time-Resolved Synchrotron X-Ray Powder Diffraction Study on Samples from the System MgO–MgCl$_2$–H$_2$O

A. Nørlund Christensen,[†,a] P. Norby[b] and J. C. Hanson[b]

[a]Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark and [b]Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, USA

Christensen, A. N., Norby, P. and Hanson, J. C., 1995. Time-Resolved Synchrotron X-Ray Powder Diffraction Study on Samples from the System MgO–MgCl$_2$–H$_2$O. – Acta Chem. Scand. 49: 331–334 © Acta Chemica Scandinavica 1995.

Time-resolved synchrotron X-ray powder diffraction was used to study chemical reactions in the system MgO–MgCl$_2$–H$_2$O at temperatures up to 100°C. The crystalline reaction products formed were Mg(OH)$_2$, MgCl$_2$·5Mg(OH)$_2$·8H$_2$O, MgCl$_2$·9Mg(OH)$_2$·5H$_2$O and MgCl$_2$·2Mg(OH)$_2$·4H$_2$O. The reaction rates are strongly dependent upon the temperature and slightly dependent on the concentration of the magnesium chloride solutions.

In a recent investigation, chemical reactions in the system MgO–MgCl$_2$–H$_2$O were studied by on-line synchrotron X-ray powder diffraction at temperatures up to 100°C.[1] The crystalline reaction products formed were Mg(OH)$_2$ and MgCl$_2$·5Mg(OH)$_2$·8H$_2$O, when the concentrations of the magnesium chloride solutions were in the range from 0 to 4 M. In this work, the system is further investigated with magnesium chloride solutions in the range from 3.8 to 4.9 M.

The solid magnesium chloride hydroxide hydrates formed in the system MgO–MgCl$_2$–H$_2$O are components in Sorel's cement.[2] The system was investigated at hydrothermal conditions at temperatures up to 175°C by Bianco,[3] and the crystalline magnesium chloride hydroxide hydrates identified by Bianco are listed in Table 1. The short notation for the compounds will be used below.

Table 1. Composition of magnesium chloride hydroxide hydrates, notation as in Ref. 3.

Compound	Short notation[a]	JCPDS card No.
MgCl$_2$ · 5Mg(OH)$_2$ · 8H$_2$O	Cl$_{5,8}$	12–122, 7–420
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

[a] As only the composition was known by Bianco,[3] it was given as MgCl$_2$ · pMg(OH)$_2$ · qH$_2$O, and the short notation as Cl$_{p,q}$.

The heterogeneous system MgO–MgCl$_2$–H$_2$O, where the reactant, the crystalline MgO, is consumed, and where crystalline reaction products are formed in time, is ideal for time-resolved diffraction experiments. The reactions are rather slow at room temperature and relatively fast at 100°C.

Experimental

The chemicals used in the investigation were basic magnesium carbonate (Merck p.a.) and magnesium chloride hexahydrate, MgCl$_2$·6H$_2$O (Merck p.a.). The basic magnesium carbonate was identified from its X-ray powder patterns as magnesium carbonate hydroxide hydrate, Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O, hydromagnesite (JCPDS index card No. 25-513). Differential thermal analysis and thermogravimetric analysis were made of the basic magnesium carbonate on a Stanton Redcroft TG-DTA simultaneous thermal analyser STA 1000/1500. A sharp endothermic peak at 537°C corresponds to the formation of MgO, and a total weight loss of 57% was in good agreement with the chemical formula for hydromagnesite. In the preparation of a batch of MgO the basic magnesium carbonate was kept in a crucible of Al$_2$O$_3$ at 700°C for 12 h, and MgO so obtained was stored in an air-tight plastic bottle.

A preliminary investigation of the system MgO–MgCl$_2$–H$_2$O was made at hydrothermal conditions at 125°C to determine conditions for formation of Mg(OH)$_2$ and the magnesium chloride hydroxide hydrates. The reaction products were identified from their X-ray powder patterns, and Fig. 1 displays the results obtained at
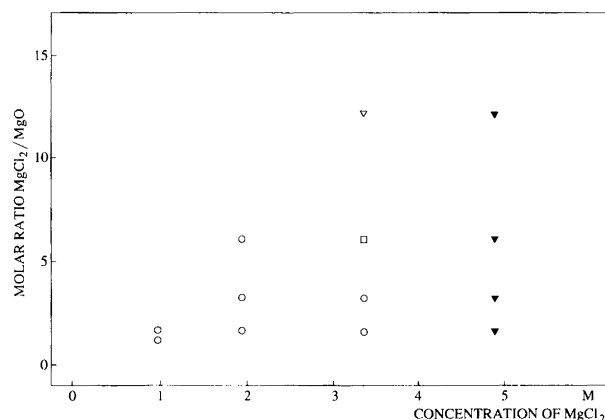
Fig. 1. Investigation of the system MgO–MgCl$_2$–H$_2$O at 125 °C: Mg(OH)$_2$(O), Cl$_{5,8}$ (□), Cl$_{3,8}$ (▽) and Cl$_{9,5}$ (▼). The composition of the reaction product depends upon the concentration of the MgCl$_2$ solutions and the molar ratio MgCl$_2$/MgO.

125°C. In the on-line diffraction experiments the samples used were wet pastes made from 50 mg MgO and 20 drops of the magnesium chloride solutions. The paste was housed in a 0.3 mm diameter quartz capillary. The samples were prepared as described previously[1] and were placed on the diffractometer and heated with a flow of hot, compressed air.

Synchrotron X-ray powder patterns were measured at 1.0, 2.5, 5.0 or 10.0 min intervals of the capillaries on a Huber diffractometer at the beam line X7B at NSLS, Brookhaven National Laboratory. A type CPS 120 curved INEL position-sensitive detector covering 120° in 2θ was mounted on the θ-arm of the diffractometer. The detector was calibrated as described previously,[1] and the wavelength used, λ = 1.2097 Å, was determined in a profile refinement of a powder pattern of a silicon standard with a = 5.4305 Å.

In a real-time X-ray powder diffraction a rather large number of patterns are recorded for each sample. The patterns are plotted in a display which shows the evolution in time of the powder patterns (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 X-ray powder patterns of the last patterns in each series of measurements. The DIFFRAC AT program 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 discussion

In the preliminary hydrothermal investigation of the system MgO–MgCl$_2$–H$_2$O at 125°C, the reaction products formed were Mg(OH)$_2$, Cl$_{5,8}$, Cl$_{3,8}$ and Cl$_{9,5}$ (Fig. 1). For the formation of Mg(OH)$_2$ this is in agreement with the results found in Ref. 1.

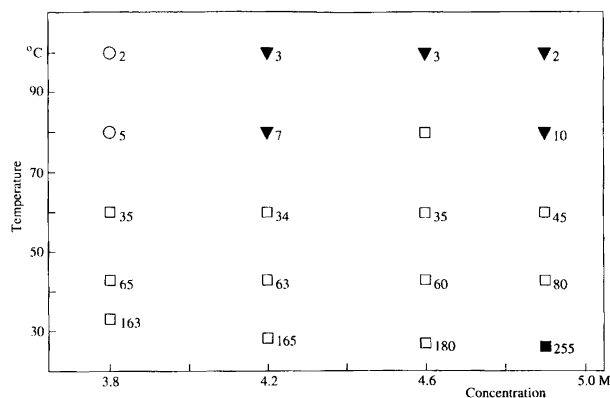*Fig. 2.* Reaction products in the time-resolved diffraction investigation of the system MgO–MgCl$_2$–H$_2$O: Mg(OH)$_2$ (O), Cl$_{5,8}$ (□), Cl$_{9,5}$ (▼) and Cl$_{2,4}$ (■). The numbers adjacent to the symbols indicate the time in min necessary to produce half the final quantity of the respective reaction products.

In all the time-resolved synchrotron X-ray experiments 50 mg MgO and 20 drops of the magnesium chloride solutions were used, so the only parameters were the temperatures and the concentration of the solutions. The reaction products found in these experiments are shown in Fig. 2 and are the compounds Mg(OH)$_2$, Cl$_{5,8}$, Cl$_{9,5}$ and Cl$_{2,4}$, indicated by the four different symbols. Four solutions of MgCl$_2$ were applied with the concentrations 3.8, 4.2, 4.6 and 4.9 M. With the 3.8 M solution, Mg(OH)$_2$ was obtained at 80 and 100°C, and with the 4.2, 4.6 and 4.9 M solutions Cl$_{9,5}$ was obtained at 80 and 100°C. Only in one case, with the 4.9 M solution at 26°C, the magnesium chloride hydroxide hydrate Cl$_{2,4}$ was obtained, and for the four solutions Cl$_{5,8}$ was formed at temperatures up to 60°C.

The rate of reactions in the heterogeneous systems can be visualized when the powder patterns of a series are plotted slightly shifted and in the same sequence as they have been recorded. In that way, it is possible to observe the decrease of Bragg reflections from the reactant (MgO) and the increase of the intensities of the Bragg reflections
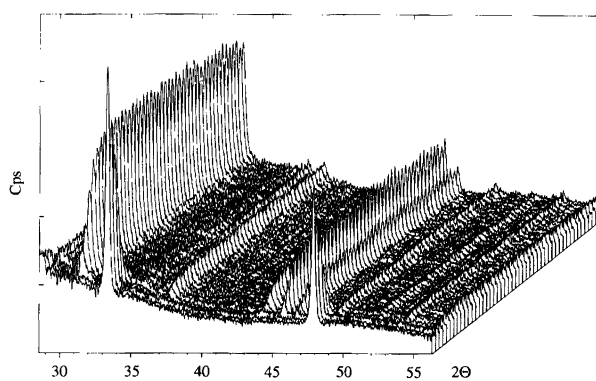

Fig. 3. X-Ray powder diffraction diagrams of a mixture of MgO and the 4.9 M MgCl$_2$ solution at 80°C recorded at 2.5 min intervals. The reaction product is Cl$_{9,5}$.
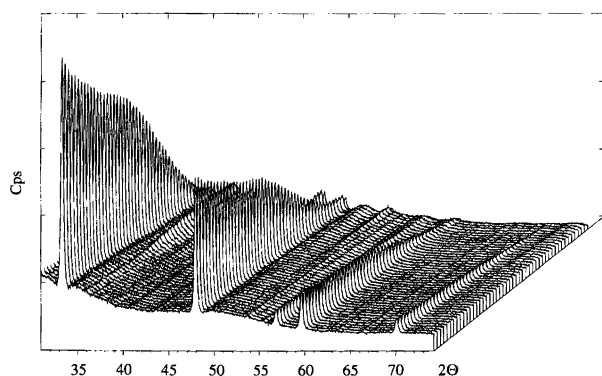
Fig. 4. X-Ray powder diffraction diagrams of a mixture of MgO and the 4.9 MgCl$_2$ solution at 26 °C recorded at 10 min intervals. The reaction product is Cl$_{2,4}$.

Fig. 6. Integrated intensities of Bragg reflections of MgO (filled symbols) and Cl$_{5,8}$ (open symbols) vs. time for the reaction between MgO and the 4.2 M MgCl$_2$ solution at 28, 45 and 60°C, respectively.

of the reaction products (the magnesium chloride hydroxide hydrates). Figure 3 shows such a display of a sample of MgO and the 4.9 M solution of MgCl$_2$ at 80°C where the powder patterns are recorded at 2.5 min intervals. It is obvious that the consumption of MgO as well as the production of Cl$_{9,5}$ is relatively fast. Figure 4 displays the powder patterns from the reaction between MgO and the 4.9 M solution at 26°C. The powder patterns are in this case recorded at 10 min intervals, and the consumption of MgO as well as the production of the product, Cl$_{2,4}$, is slow.

A measure of the quantities of reactant and products is obtained from integration of selected Bragg reflections. Figures 5–8 display the results of such integrations for the reactions between MgO and the 3.8, 4.2, 4.6 and 4.9 M MgCl$_2$ solutions, respectively, at the temperatures 60 and 45°C, and room temperature (33–26°C). The curves in Figs. 5–8 are drawn to guide the eye. In 11 of the 12 experiments the reaction product is Cl$_{5,8}$, and only in the experiment with the 4.9 M solution at 26°C is the reaction product Cl$_{2,4}$ (Fig. 2). The rate of consumption of MgO is temperature dependent, but apparently only
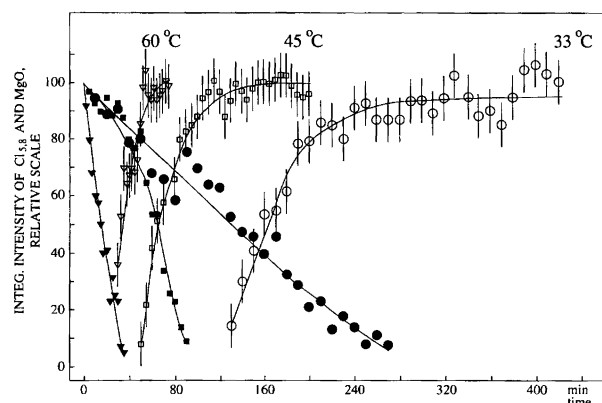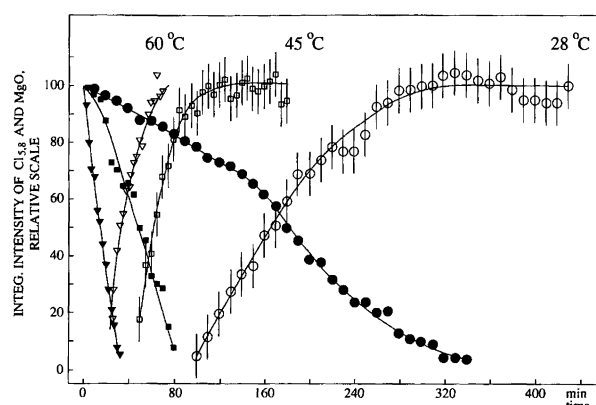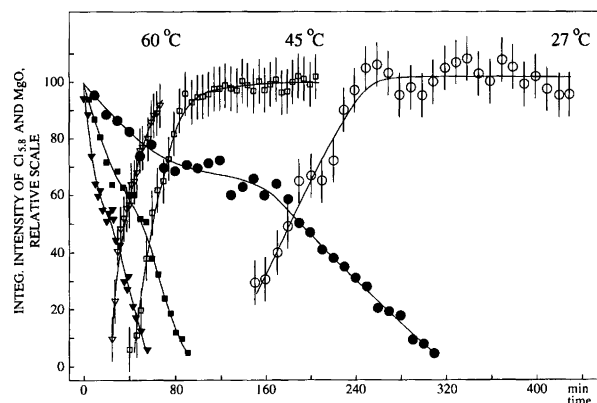

Fig. 7. Integrated intensities of Bragg reflections of MgO (filled symbols) and Cl$_{5,8}$ (open symbols) vs. time for the reaction between MgO and the 4.6 M MgCl$_2$ solution at 27, 45 and 60°C, respectively.

Fig. 5. Integrated intensities of Bragg reflections of MgO (filled symbols) and Cl$_{5,8}$ (open symbols) vs. time for the reaction between MgO and the 3.8 M MgCl$_2$ solution at 33, 45 and 60°C, respectively.
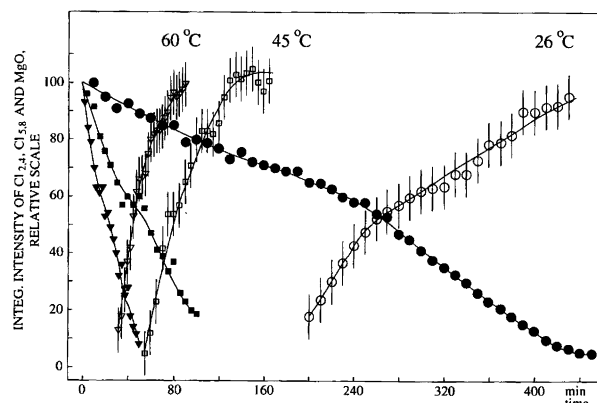

Fig. 8. Integrated intensities of Bragg reflection of MgO (filled symbols) and Cl$_{5,8}$ and Cl$_{2,4}$ (open symbols) vs. time for the reaction between MgO and the 4.9 M MgCl$_2$ solution at 26, 45 and 60°C, respectively.

333

Table 2. Rate constants k(in min^{-1}) and t_0 (in min) from the exponential fit of the degree of crystallization using the expression $I = 100\{1-exp[-k(t-t_0)]\}$. The values listed for each experiment are k, t_0.

| T/°C | Concentration of $MgCl_2$ solution/M | | | |
	3.8	4.2	4.6	4.9
100	0.28, 1	0.70, 2	0.75, 2	0.87, 1
80	0.13, 0	0.63, 4	0.067, 29[a]	0.15, 5
60	0.070, 23	0.060, 21	0.049, 31	0.052, 31
45	0.038, 46	0.054, 42	0.041, 41	0.032, 53
26–33	0.017, 119	0.013, 103	0.021, 141	0.0086, 178

[a] This value is most likely in error. The temperature of the sample may have been lower than 80°C.

slightly dependent on the $MgCl_2$ concentrations (Figs. 5–7). Only in the case with the 4.9 M $MgCl_2$ solution is the consumption of MgO significantly slower (Fig. 8). This may be an effect of increasing viscosity of the solutions. The curves showing the consumption of MgO indicate that the consumption does not proceed with constant rate; this is best observed in Figs. 6–8 for the room-temperature experiments. It is also observed that the consumption of MgO is significant before the Bragg reflections of the reaction products are observed. This may indicate that the formation of the reaction products goes through an amorphous state for MgO. Figures 5–8 show the formation of the reaction product $Cl_{5,8}$ to be strongly temperature dependent. The time (in min) used to produce half the quantity of the reaction products can be estimated from Figs. 5–8, and these numbers are indicated adjacent to the respective symbols for the experiments in Fig. 2, which also have the corresponding values for the experiments performed at 80 and 100°C.

The integrated intensity of a selected Bragg reflection of the reaction product is representative for the degree of crystallization of the product. These data for the crystallization curves from the 20 experiments (Fig. 2) were fitted using the exponential expression $I = 100\{1 - exp[-k(t - t_0)]\}$. I is the amount of crystalline reaction product, k is the rate constant (in min^{-1}), and t_0 is the time (in min) at which the crystallization starts. The data gave acceptable fits to this expression. In Table 2 are listed the values obtained for k and t_0. The

results for the experiments with the 4.6 M $MgCl_2$ solution at 80°C are most likely in error. The temperature of the sample may have been lower than 80°C, which also explains why the reaction product obtained was $Cl_{5,8}$ and not $Cl_{9,5}$.

References

1. Christensen, A. N., Norby, P. and Hanson, J. C. *J. Solid State Chem. 114* (1995) 556.
2. Pascal, P. *Nouveau Traité de Chimie Minérale*, Masson et Cie, Paris 1958, *Vol. 4*, p. 177.
3. Bianco, Y. *Ann. Chim. 13th Ser. 3* (1953) 370.