

Hydrothermal Crystal Growth Rate of Goethite and Haematite from Amorphous Iron(III) Hydroxide Investigated by X-Ray Diffraction and Neutron Diffraction

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The rate of crystallization of amorphous iron(III) hydroxide to α -Fe₂O₃ and α -FeOOD was investigated at hydrothermal conditions by measurements of neutron powder diffraction diagrams simultaneously with the hydrothermal crystallization treatment of the specimens. Amorphous iron(III) hydroxide precipitated to pH = 10.0 is converted very fast to a mixture of α -Fe₂O₃ and α -FeOOD when treated hydrothermally at temperatures from 104 to 121 °C. The crystallization is complete after one hour, and the observed rate is practically independent of temperature applied. The hydrothermal crystallization of iron(III) hydroxide precipitated to pH = 4.5 is slower, and the product is pure α -Fe₂O₃. Treated at 109 °C the crystallization is complete within four hours, treated at 180 °C the crystallization is complete within one hour. The acidity of the hydrothermal solution is increased during the hydrothermal treatment due to complete hydrolysis.

The hydrothermal preparation of goethite, α -FeOOH, and haematite, α -Fe₂O₃, from amorphous iron(III) hydroxide has been investigated previously.^{1,2} Freshly precipitated iron(III) hydroxide was made from solutions of iron(III) nitrate and ammonia and was treated hydrothermally in sealed pyrex ampoules kept in a thermostated oven at 180 °C for 48 h.¹ The precipitations of iron(III) hydroxide were interrupted at different pH-values. Pure haematite was the crystalline hydrothermal product when pH of the mother liquid before the hydrothermal treatment was less than 5. In these cases the precipitation of iron(III) hydroxides was not quantitative and a more complete precipitation

and crystallization was obtained by the hydrothermal treatment, resulting in a decrease in pH of the mother liquid.^{1,2} At 180 °C this decrease in pH was complete within 1 h of hydrothermal treatment.² Mixtures of haematite and goethite were the crystalline hydrothermal products when pH of the mother liquids before the hydrothermal treatments were in the range 8–11 pH units. Increasing pH values resulted in increasing quantities of goethite in the crystalline products.

The rates of hydrothermal crystallization of α -FeOOH and α -Fe₂O₃ have been further investigated using the techniques described previously^{1,2} and X-ray powder diffraction of the obtained crystalline compounds. In addition, on-line neutron powder diffraction of the hydrothermal crystallization process has been applied, a technique that to our knowledge has not been used previously.

EXPERIMENTAL

Hydrolysis of solutions of iron(III) nitrate at 180 °C. Solutions of iron(III) nitrate with the concentrations 1, 0.1, 0.01 and 0.001 M were made from Fe(NO₃)₃·9H₂O. pH of the solutions was measured with a Radiometer PHM64 Research pH-Meter. The solutions were sealed in thick-walled pyrex ampoules and kept at 180 ± 1.5 °C in a thermostated oven for up to 4 hours. After the hydrothermal treatment the pH of the solutions was measured again. The solid products formed by the hydrolysis were washed with water, dried in air at 25 °C and identified from their X-ray powder patterns obtained with a Guinier camera using CuK α ₁ radiation. The results of the investigation are displayed in Fig. 1.

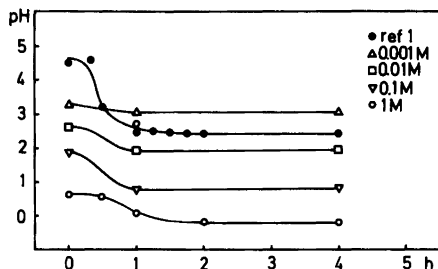


Fig. 1. Hydrolysis of iron(III) nitrate solutions at 180 °C. For comparison are shown results from Ref. 1 indicating the pH of the mother liquids from precipitation of iron(III) nitrate solutions with ammonia followed by hydrothermal treatments of the amorphous precipitates.

Preliminary determination of rate of crystallization of amorphous iron(III) hydroxide at hydrothermal conditions. All precipitates of iron(III) hydroxides were made from solutions of iron(III) nitrate and sodium hydroxide by adding dropwise the base to the iron(III) nitrate solution. The precipitation was interrupted when the pH-values 4.5 or 10 were reached, indicated by Aclit (Merck) indicator strips. The freshly precipitated iron(III) hydroxide was washed with water, sealed in thick-walled pyrex ampoules, and heated in a thermostated oven at the experimental conditions listed in Table 1. After the hydrothermal treatments the solid products were washed with water and dried in air at 25 °C. X-Ray powder patterns were recorded of the products by using a Philips powder diffractometer and CoK α radiation. Only the crystalline compounds α -Fe₂O₃ and α -FeOOH were found in the products. In the cases where the products were mixtures of the two compounds, the relative quantities were estimated from the intensities of the α -Fe₂O₃ 104 reflection and the α -FeOOH 110 reflection. The degree of crystallinity was normalized to 100 for patterns using the same two reflections for products where the

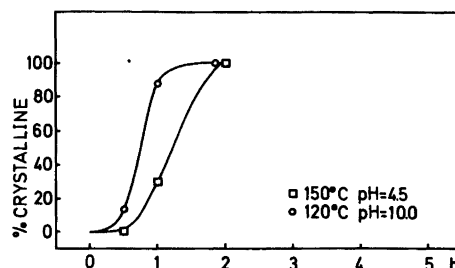


Fig. 2. Hydrothermal crystallization of amorphous iron(III) hydroxide precipitated to pH = 4.5 and pH = 10.0 of the mother liquids.

reflections had reached their maximum values. The results are listed in Table 1 and displayed in Fig. 2.

Determination of rate of crystallization of amorphous iron(III) hydroxide at hydrothermal conditions by on-line neutron diffraction. Precipitates of iron(III) hydroxide for the neutron diffraction experiments were made from solutions of iron(III) nitrate in D₂O and solutions of sodium hydroxide made from sodium metal and D₂O. The freshly precipitated iron(III) hydroxide was washed with D₂O on a paper filter. The precipitate was squeezed between two double layers of filter paper to reduce the water content. This procedure was repeated until the product had a consistency of a paste. By using a syringe with a needle of 3 mm inside diameter the paste was placed in ampoules of quartz and sealed. The ampoules were stored at room temperature for 1–3 weeks before the diffraction experiments. Two sizes of quartz ampoules were used with inside diameter 11 and 17 mm, respectively. The heights of the ampoules were 60 mm. The ampoules contained paste corresponding to approximately 0.6 and 1.2 g α -Fe₂O₃, respectively.

The neutron diffraction powder patterns of the ampoules were measured using a multiple detector at the powder diffractometer D1B of the Laue-Langevin Institute. The ampoules were placed in a

Table 1. Results of X-ray scattering measurements.

Exp. No.	Temp. °C	Time treated h	Composition from X-ray powder pattern	pH of mother liquid before
1	150	0.5	α -Fe ₂ O ₃	4.5
2	150	1	α -Fe ₂ O ₃	4.5
3	150	2	α -Fe ₂ O ₃	4.5
4	120	0.5	50 % α -Fe ₂ O ₃ , 50 % α -FeOOH	10.0
5	120	1	40 % α -Fe ₂ O ₃ , 60 % α -FeOOH	10.0
6	120	2	40 % α -Fe ₂ O ₃ , 60 % α -FeOOH	10.0

thermostated oven with a temperature stability of $\pm 1.5^\circ\text{C}$. The oven was built from a 25 mm diameter aluminium tube which was replaced by a vanadium tube of the same dimensions in the position of the neutron beam. It had a 50 watt heating element to heat a flow of air. In all experiments a constant air flow of 20 l min^{-1} was used. Each hydrothermal experiment was started by a fast heating of the ampoule in a 700 W laboratory tube furnace to the desired temperature. The ampoule was then transferred to the oven, set to the same temperature, at the spectrometer table. The neutron diffraction powder patterns of the ampoules were recorded repeatedly and were extracted at 15 min intervals. After the hydrothermal diffraction experiments the contents of the quartz ampoules were investigated further. The pH values of the pastes were measured using Acilit indicator strips and the crystalline products were washed with water and dried in air. The X-ray diffraction powder patterns were then recorded of these specimens using a powder diffractometer and $\text{CoK}\alpha$ radiation.

RESULTS AND DISCUSSIONS

The hydrolysis of the 1 and 0.1 M iron(III) nitrate solutions at 180°C is a relatively fast process as precipitates of crystalline $\alpha\text{-Fe}_2\text{O}_3$ are formed within 1 h. The acidity of the solutions was increased as the iron(III) ions were liberating protons from water in the formation of $\alpha\text{-Fe}_3\text{O}_3$. The acidity of the 1 M solution attained its maximum value after 2 h and that of 0.1 M after 1 h, respectively, corresponding to a quantitative precipitation of the iron content. In the 0.01 M and the 0.001 M iron(III) nitrate solutions no

precipitates were formed. However, these solutions showed also an increase in the acidity corresponding to a partial hydrolysis. The colours of these two solutions became darker, indicating formation of polynuclear hydrolysis complexes.

The preliminary determination of the rate of crystallization of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ from freshly precipitated iron(III) hydroxide (Table 1 and Fig. 2) shows also that the formation of crystalline $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ at the experimental conditions investigated are relatively fast processes. Crystalline $\alpha\text{-FeOOH}$ in a mother liquid with $\text{pH} = 10$ is formed faster than $\alpha\text{-Fe}_2\text{O}_3$ in a mother liquid of $\text{pH} = 4.5$, even when the temperature is lower in the hydrothermal experiment resulting in the formation of $\alpha\text{-FeOOH}$. In acid solutions the crystalline product is $\alpha\text{-Fe}_2\text{O}_3$. In basic solutions the crystalline product is a mixture of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ and is in some cases pure $\alpha\text{-FeOOH}$. The relative quantities of the two compounds vary from experiment to experiment in an unsystematic way.

The neutron diffraction powder patterns measured simultaneously with the hydrothermal crystallization process show Bragg reflections and can be used to determine the time needed to transform amorphous iron(III) hydroxide to crystalline $\alpha\text{-Fe}_2\text{O}_3$ or $\alpha\text{-FeOOH}$. Fig. 3a (experiment 5, Table 2) shows the diffraction pattern of the quartz ampoule with amorphous iron(III) hydroxide after $\frac{1}{2}$ h of hydrothermal treatment at 109°C . The pattern shows mainly scattering contributions from the quartz and from D_2O , and has no characteristic Bragg peaks. Fig. 3b (same specimen) shows the diffraction pattern after 1.25 h,

Table 2. Result of neutron scattering measurements. For expts. 3 and 4 the measurements were repeated at higher temperature without any observable change in the material.

Exp. No.	Size of ampoule ^a	Temp. $^\circ\text{C}$	Max. after h	Composition from X-ray powder pattern	pH of mother liquid	
					before	after
1	B	104	3/4	95 % $\alpha\text{-Fe}_2\text{O}_3$, 5 % $\alpha\text{-FeOOH}$	10.0	12.5
2	B	114	3/4	50 % $\alpha\text{-Fe}_2\text{O}_3$, 50 % $\alpha\text{-FeOOH}$	10.0	12.5
3	A	121	3/4		10.0	11.0
4	A	150		90 % $\alpha\text{-Fe}_2\text{O}_3$, 10 % $\alpha\text{-FeOOH}$		
		105	—		4.5	5.5
5	A	135		$\alpha\text{-Fe}_2\text{O}_3$		
		109	4	$\alpha\text{-Fe}_2\text{O}_3$	4.5	1.0
6	B	131	—	$\alpha\text{-Fe}_2\text{O}_3$	4.5	5.5
7	A	151	2	$\alpha\text{-Fe}_2\text{O}_3$	4.5	1.5
8	B	180	1/4	$\alpha\text{-Fe}_2\text{O}_3$	4.5	1.0

^aA: large ampoule. B: small ampoule.

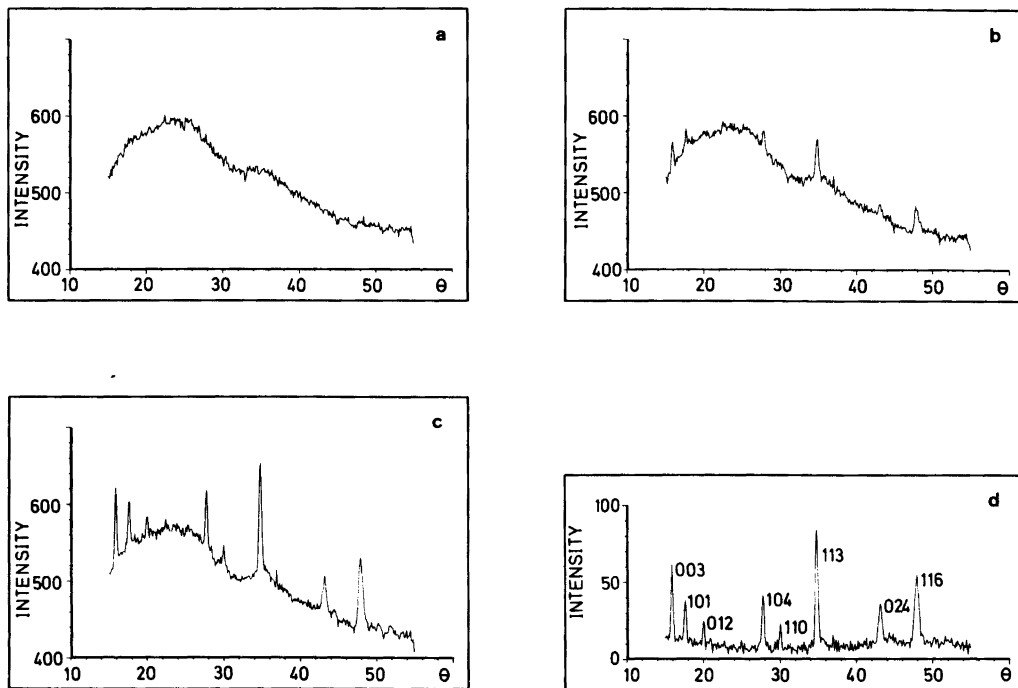


Fig. 3. Neutron diffraction pattern of a quartz ampoule with amorphous iron(III) hydroxide paste in D_2O (experiment No. 5, Table 2). *a*: After 1/2 h of hydrothermal treatment at 109 °C. (The scattering contribution is from the quartz and from D_2O). *b*: After 1 1/4 h of hydrothermal treatment. The pattern clearly shows Bragg reflections from $\alpha\text{-Fe}_2\text{O}_3$. *c*: After 5 h of hydrothermal treatment. The Bragg reflections from $\alpha\text{-Fe}_2\text{O}_3$ have now reached their maximum intensity. *d*: Difference diagram between the diffraction patterns *c* and *a*. The indices for the $\alpha\text{-Fe}_2\text{O}_3$ reflections are indicated (hexagonal setting). Wave length of neutrons is 2.52 Å.

and Fig. 3c the diffraction pattern after 5 h of hydrothermal treatment. Fig. 3d is a difference diagram between the two patterns shown in Figs. 3c and a. The intensities of the reflections of the $\alpha\text{-Fe}_2\text{O}_3$ diffraction diagram were calculated by fitting the peaks to a Gaussian function.⁴ The sum of all the intensities of the peaks in the diffraction pattern was assumed to be proportional to the degree of crystallinity of the solid iron(III) compounds of the specimen. In the diffraction experiments the amount of iron(III) compounds in the neutron beam was kept constant justifying the above-mentioned assumption. The degree of crystallinity was normalized to 100 for patterns where the intensities of the Bragg reflections of $\alpha\text{-Fe}_2\text{O}_3$ had reached their maximum values. These calculations were made for each recorded diffraction pattern, and the results are listed in Table 2 and displayed in Figs. 4 and 5.

For amorphous iron(III) hydroxide in a mother liquid with pH = 10 the transformation to crystalline

products at hydrothermal conditions in the temperature range investigated (104–121 °C) is very fast. Within 3/4 h the reflections of the diffraction patterns have reached their maximum intensities, and a further increase in temperature does not have

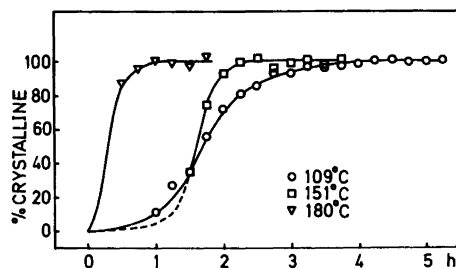


Fig. 4. Hydrothermal crystallization of amorphous iron(III) hydroxide precipitated to pH = 4.5 of the mother liquid. At 109 °C the crystallization is complete after 4 h, at 180 °C after 1 h.

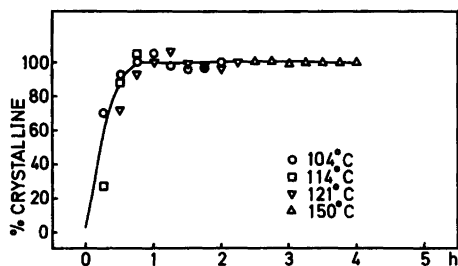


Fig. 5. Hydrothermal crystallization of amorphous iron(III) hydroxide precipitated to pH = 10.0 of the mother liquid. The crystallization is complete after 1 h almost independently of the temperature used in the hydrothermal experiment. The triangles indicate one experiment (No. 3 in Table 2) where the temperature was increased from 121 to 150 °C after 2.25 h.

any effects. As the duration of the crystallization is comparable to the time resolution it is quite difficult to estimate the velocity, but it seems to be practically independent of temperature. The crystalline products obtained are mixtures of α -Fe₂O₃ and α -FeOOH. No conclusion concerning the relative quantities of the two compounds can be drawn from the experiments listed in Table 2.

The hydrothermal crystallizations of amorphous iron(III) hydroxide in contact with mother liquids of pH = 4.5 are slower than found for the basic solutions. The rate of formation of crystalline products is strongly dependent upon the temperature used for the hydrothermal crystallization and possibly also upon the pH of the mother liquid. In Table 2 the pH-values before the hydrothermal reactions are listed as 4.5 for all five experiments. However, these values are estimated with an error of ± 0.5 pH units. For the two experiments (No. 4 at 105 °C and No. 6 at 131 °C) where no significant scattering contributions from α -Fe₂O₃ could be observed in the neutron diffraction powder patterns, the pH-values could have been close to 5. After the hydrothermal experiments the solutions had the pH-values 5.5. It is well known that amorphous iron(III) hydroxide is aged slowly in contact with neutral or slightly acidic solutions.³ In these two experiments the pH of the solution may have been too high. X-Ray powder patterns of the solid products from the two experiments show, however, that approximately 10–15% of the products are crystalline α -Fe₂O₃ with the highest content in the product from experiment No. 6 (Table 2).

The investigations show that the hydrothermal crystallization processes for hydrolysis of iron(III) nitrate solutions to α -Fe₂O₃ and for formation of α -Fe₂O₃ and α -FeOOH from freshly precipitated amorphous iron(III) hydroxide are relatively fast processes. Except for two neutron measurements where only a limited reaction occurred (4 and 6) the results of both X-ray and neutron experiments show that the rate of crystallization increases with increasing pH and temperature. This is in agreement with the observed strong tendency of aqueous iron(III) complexes to hydrolysis in solutions. The Fe(H₂O)₆³⁺ complex is indeed so strong an acid that it is only found in solutions with pH near zero.⁵ The net result of the hydrothermal hydrolysis of iron(III) nitrate solutions is an O²⁻ transfer from water to iron in the Fe(H₂O)₆³⁺ complex: $2\text{Fe}(\text{H}_2\text{O})_6^{3+} + 3\text{H}_2\text{O} \rightarrow \alpha\text{-Fe}_2\text{O}_3 + 6\text{H}_3\text{O}^+$. In precipitation of iron(III) nitrate solutions with bases the hydrolysis goes over a series of polynuclear complexes of the form $[\text{Fe}_x(\text{H}_2\text{O})_y(\text{OH})_z]^{(3x-z)+}$, and at pH larger than 3 the complexes are sufficient in size to render the solution opaque and gel-like. The hydrolysis is complete when the complex has no positive charge. The protons released from gels at pH = 4.5 by hydrothermal treatments indicate, however, that these gels still have a net positive charge and that proton transfer takes place from the gel to free water molecules in the paste. For the experiments where the solutions are precipitated to pH = 10, OH⁻ ions are present in the solution and possibly also trapped in the gel, and the hydrothermal crystallization proceeds very quickly. In the present case an increase in pH was found which is not in agreement with earlier measurements.¹ It is likely that an increase in pH took place in the gel during the drying and before the heating of the sample. At pH = 10 the crystallization results as well in formation of α -FeOOH. As the unit cell of this compound is much larger than that of α -Fe₂O₃ it is more difficult to observe individual peaks in the powder spectrum, and it was not possible to follow this process using neutron scattering. Likewise the intensity of the powder lines were not sufficiently strong to give information about any cluster formation prior to the crystallization of α -Fe₂O₃. We, therefore, plan to follow this process using neutron small angle scattering techniques and hydrogen deuterium mixtures to reduce the scattering from the water environment.

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