Kinetics of Rust Formation. A Small Angle Neutron Scattering Investigation on Iron(III) Hydroxide

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The aging of amorphous iron(III) hydroxide to α-Fe_2O_3 and α-FeOOH was studied by small angle neutron scattering techniques. The main parameters in determining the growth rate were pH of the solution, time and temperature of aging. The particles have a polydisperse size distribution which changes with time. The scattering density of the particles increases with time and each particle of the amorphous product produces a particle of α-Fe_2O_3 in acid solution. There is no indication of a process where the particles dissolve and reprecipitate.

The hydrolysis of iron(III) solutions with ammonia or sodium hydroxide solutions develops with the formation of the dimer complex $[(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{4+}$ followed by a series of polynuclear complexes.[1-5] When these complexes are sufficiently large in size, coagulation takes place and an amorphous gel-like precipitate of iron(III) hydroxide is formed. Aging of these precipitates at room temperature, at elevated temperatures, or under hydrothermal conditions results in the formation of crystalline products. In acid solutions hematite, α-Fe_2O_3, or possibly hydrohematite, is obtained from amorphous iron(III) hydroxide gels made from iron(III) nitrate solutions and ammonia or sodium hydroxide.[6,7] The rate of crystallization is increased by increasing temperature[6] or by the presence of oxalate in the gels.[7] However, the formation of the iron oxide hydroxides, α-FeOOH, γ-FeOOH and β-FeOOH has been reported from acid media containing nitrate, perchlorate and chloride ions, respectively.[7] Apparently, a number of factors including the presence and concentration of complex forming anions modifies the crystallization rate of amorphous iron(III) hydroxide gels and

the structure and composition of the crystalline products obtained.

In alkaline media iron(III) hydroxide gels are aged to goethite, α-FeOOH,[8] and under hydrothermal conditions α-Fe_2O_3 and α-FeOOH may be formed.[6] The formation of hematite rather than goethite is observed in the presence of hydroxicarboxylic acids,[9] or small concentrations of Al^{3+} ions.[10] Traces of aluminium eliminate the formation of goethite and favour the formation of hydrohematite when amorphous iron(III) hydroxide is treated hydrothermally.[11,12]

In contrast to the hydrolysis of aluminium(III) solutions where a polynuclear complex $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ is formed,[13] little is known about the nature of the polynuclear complexes and the particles formed in the hydrolysis of iron(III) solutions with respect to the sizes of the complexes and particles, or the growth rate of these species at different temperatures. To study this, it was decided to investigate the aging of iron(III) hydroxide gels obtained by hydrolysis using small angle neutron scattering.

The rate of hydrothermal crystallization of amorphous iron(III) hydroxide recently studied by on-line neutron powder diffraction showed that crystallization was complete within a few hours.[6] An investigation of the growth rate of the particles in the early stages of the crystallization of amorphous iron(III) hydroxides by on-line small angle neutron scattering experiments would thus be possible within an acceptable time period. To our knowledge, this on-line technique for small angle neutron scattering has not been used previously.
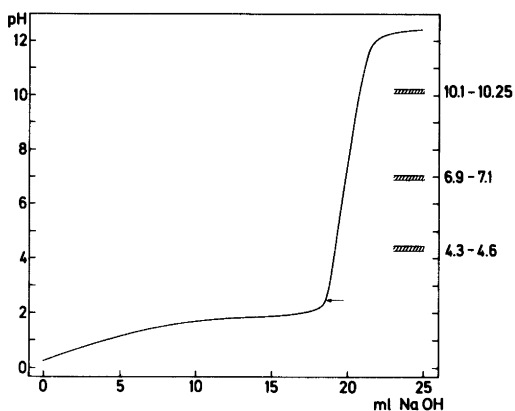
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Fig. 1. Titration curve of a 20 ml 1.5185 M iron(III) nitrate solution with 4.45 M NaOH. The arrow indicates where the heavy precipitate of iron(III) hydroxide is formed.

EXPERIMENTAL

Hydrolysis of iron(III) nitrate solutions. Solutions of iron(III) nitrate were made from $Fe(NO_3)_3.9H_2O$ (Merck *p.a.*), and solutions of sodium hydroxide were made from NaOH (Merck *p.a.*). A preliminary investigation of the hydrolysis of a 1.518 M iron(III) nitrate solution was made by titration with a solution of 4.45 M sodium hydroxide. The titration was made with a Radiometer REA 160 Titrigraph unit and pH of the solution was measured with a Radiometer PHM 64 pH-meter. Fig. 1 shows the

Table 1. Suspensions of iron(III) hydroxide in mother liquid (H_2O) kept at 20 °C. 1.5 M iron(III) nitrate solution precipitated with 4.5 M sodium hydroxide.

pH of mother liquid precipitation	after diffraction exp.	Age of the precipitate in days
6.91	7.44	40
7.04	6.56	4
10.25	12.64	40
10.13	10.20	36
10.15	9.96	32
10.20	9.97	28
10.22	10.00	24
10.10	9.71	20
10.21	10.22	16
10.15	9.64	12
10.10	9.58	8
10.10	9.84	4

Table 2. Suspensions of iron(III) hydroxide in mother liquid (H_2O) heat treated. 1.5 M iron(III) nitrate solution precipitated with 4.5 M sodium hydroxide to pH = 4.31.[a]

Heat treatment of sample Temp. °C	Time, min	pH of mother liquid after heat treatment
113	20	3.14
	40	2.75
	60	2.46
	80	2.39
	100	2.30
	120	2.24
107	20	3.20
	40	2.88
	60	2.58
	80	2.43
	100	2.35
	120	2.28
102	80	2.50
	160	2.29
	240	2.16
	320	2.03
	400	1.96
	480	1.92
	Time, h	
90	4	2.51
	8	2.34
	12	2.22
	16	2.16
	20	2.08
	24	2.02
94	1	
	3	
	5	
	7	
	9	
	11	
	13	
	14	
	16	
	18	
	20	
	22	

[a] Sample for kinetic scattering experiment (Fig. 10): 1.5 M iron(III) nitrate solution precipitated with 4.5 M sodium hydroxide pH = 11.45. The sample was used in an on-line diffraction experiment with the sample kept at 50 °C.

titration curve. In the first part of the titration the pH of the solution changes slowly with the volume of NaOH. When approximately 2.7 mmol OH⁻ per 1 mmol Fe^{3+} has been added the solution becomes suddenly very thick by a coagulation of the polynuclear complexes formed during the titration and the characteristic rust brown precipitate of iron(III) hydroxide is observed. Further addition of NaOH yields a relatively fast increase of pH of the suspension.

Preparation of iron(III) hydroxide samples for small angle neutron scattering experiments. Iron(III) hydroxide was precipitated by adding the sodium hydroxide solution dropwise to the iron(III) nitrate solution. During the precipitation the solution was stirred and pH was measured with a Radiometer PHM 64 Research pH-meter. The precipitations were interrupted at the pH values indicated in Fig. 1. Samples (15 ml) of the suspensions of the precipitated iron(III) hydroxide in the mother liquid were transferred to pyrex ampouls. These were sealed with rubber stoppers and kept at room temperature for the periods of time listed in Table 1, or were kept at higher temperatures in a thermostated oven at the experimental conditions listed in Table 2. After the diffraction experiments the pH of some of the suspensions were measured again.

Suspension of iron(III) hydroxide in the mother liquid are aged when kept for long periods of time at room temperature. This process may be observed as a change in pH of the solution. Fig. 2 shows the variation of pH with time for two series of iron(III) hydroxide precipitated to pH 6.9 – 7.1 and to pH 10.1 – 10.25, respectively. Both series show a drop in pH with time and for the precipitate with the initial pH 10.1 – 10.25 a clear change in colour is observed after approximately 30 days due to the formation of α-FeOOH. For the other series no colour change was observed. Precipitates of iron(III)
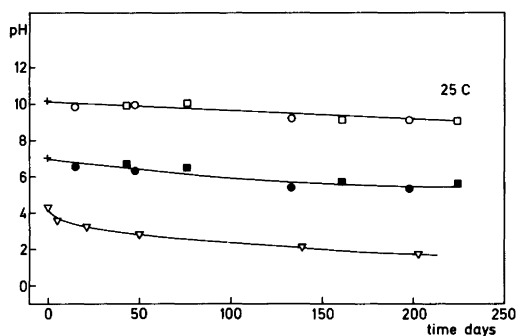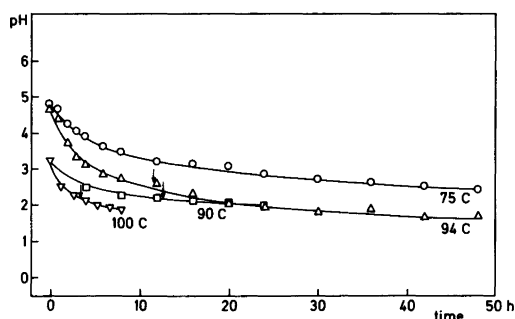

Fig. 3. Precipitates of iron(III) hydroxides aged by heat treatments. pH of the solutions are decreasing with time and with the temperature of the heat treatments. The arrows indicate where colour changes of the precipitates are observed.

hydroxide with an initial pH value of 4.3 show an even more drastic change in pH with time (Fig. 2). When precipitates of iron(III) hydroxide (pH = 3.3 and 4.8) are treated hydrothermally the aging is accelerated and crystalline products of hematite may be formed. The pH of the mother liquids measured after the hydrothermal treatments are displayed *vs.* time of treatment in Fig. 3 and show the same tendency as Fig. 2.

Small angle neutron scattering of iron(III) hydroxide specimens. The measurements were carried out on the neutron small angle diffractometer D11 of the Institut Max von Laue – Paul Langevin, Grenoble. The instrument is located at a neutron guide connected to the cold source, and the wave length was in the range from 10 to 16 Å. The detector consists of 64 × 64 elements of 1 cm^2, and was located either at 10 m or at 20 m from the sample. This gives typical maximum momentum transfer of $Q = 1.2 \times 10^{-2}$ to 1.5×10^{-2} Å^{-1} ($Q = 4\pi$ sin θ/λ). The samples were contained in quartz cuvettes of 1 mm path length and the cuvettes were mounted in a thermostated rack so that temperatures up to 100 °C could be obtained during the experiment. The size of the beam was between 0.5 and 1 cm^2.

The samples were either prepared beforehand for the long time treatment and measured at ambient temperature, or measured at reaction temperature for some of the fast reactions. In both cases the results are similar. The isotropic scattering curves were obtained by radial averaging over the detector surface, and in order to correct for background, a water spectrum was subtracted. Likewise, the detector response function was obtained using a water spectrum. This was done using standard ILL programs.[14]
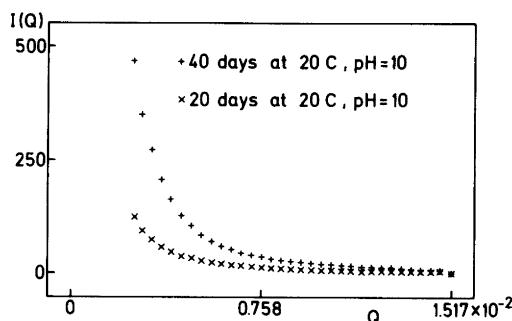

Fig. 2. Precipitate of iron(III) hydroxides aged at room temperature. pH of the solutions are decreasing with time.

I(Q)

Fig. 4. I(Q) vs. Q for two specimens of iron(III) hydroxide aged at room temperature in suspensions with pH = 10.

It was clear from the scattering curves that the particles belonged to a polydisperse size distribution (Fig. 4 and 5), and a simple model was therefore used. The basic equation for the calculation is

$$I(Q) \approx P(Q)S(Q)$$

where $I(Q)$ is the intensity scattered for momentum transfer Q, $P(Q)$ is the single particle form factor and $S(Q)$ is the inter-particle scattering function. Polydispersity is taken care of in $P(Q)$ which will be a sum, $\sum_i Pi(Q)$, of the form factors for the different particles. Polydispersity introduces a broadening in the interparticle correlation function and hence cross terms between $Pi(Q)$ and $S(Q)$, but these were neglected in the model. The particles are described as hard, uniform spheres with a size distribution according to a Gaussian distribution. The inter-action between spheres were taken into account using the Percus-Yevick [15] approximation. A least-squares fit was done employing the program SMALL,[16] and the parameters varied were the mean radius of gyration of the particle, the standard
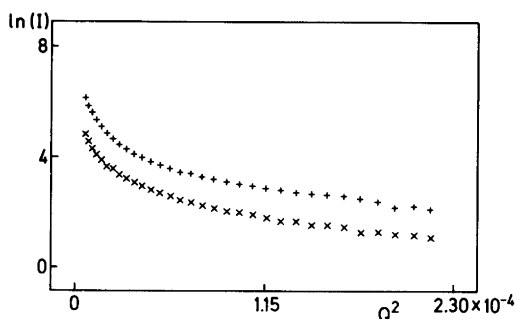
deviation of the distribution (σ), the volume fraction occupied by the particles (evf), and the scale factors. This last value gives the forward scattering $I(Q_o)$ and is proportional to the square of the integrated scattering density of the mean particle in excess of the scattering density of the solution.[17] In the present case, the solution is water, for which the neutron scattering density is nearly zero. The particle itself, consisting of iron hydroxides and bound water, has scattering density above zero, consisting of Fe and O with positive scattering lengths and H with negative scattering lengths. Moreover, as H (and H_2O) are ejected from the particle its scattering density will increase corre-sponding to an increase of $I(Q)$ which is discussed below.

The fits were good for the start and end products, i.e. for samples which are generally rather stable in time. One example of the quality of the fitting is given in Fig. 6. However, the agreement was less good, although acceptable, in the medium range, indicating some breakdown in the model. It was moreover found that the mean particle size was sensitive to the cutoff at low Q, so that the lower the cutoff the larger the particle. This is what would be expected where some of the particles are too large to give scattering within the geometry of the experimental set up. Typical particle sizes were in the range from 700 to 1000 Å, so in the analysis this limits the range of the particles that were seen.

A series of measurements was also done to study the kinetics of particle formation using hydrolysis of urea for pH control. Mixtures of Fe(III) nitrate and urea were heated to temperatures between 90 and 100 °C, and the scattering curves were recorded for constant intervals of time, typically 15 min. At these temperatures urea disintegrates into ammonia and carbon dioxide, and one can thus follow the formation of the polynuclear units from the dimer complex. No information could be obtained about
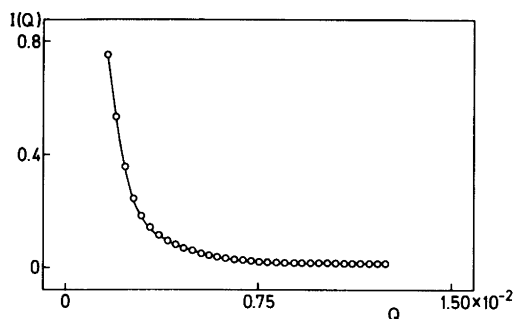

Fig. 5. ln(I) vs. Q^2 (Guinier plot) for the same specimens as shown in Fig. 4.

Fig. 6. Least-squares fit of data $I(Q)$ vs. Q to the model of a specimen (94 °C, 3 h, Table 2), showing a good fit of the scattering data to the model.

the size of the intermediate particles as the change from the dimer to the large particle was too rapid for the time scale of the measurement.

RESULTS AND DISCUSSIONS

The specimens listed in Table 1 were measured with a sample-detector distance of 10 m. For the two specimens where pH of the mother liquid was approximately 7 the two scattering profiles $I(Q)$ vs. Q were identical. The composition and size of the particles in these two specimens have thus not changed with time, and suspensions of amorphous iron(III) hydroxide in solutions with pH = 7 show no great tendency to produce crystalline products when kept at room temperature. In contrast to this, crystalline α-Fe-OOH is obtained from amorphous iron(III) hydroxide when kept at room temperature in solutions with pH = 10. At the time of the diffraction experiment a substantial fraction of the 40 days old specimen (Table 1) was converted to α-FeOOH, which was observed as a change in colour of the specimen. For this series of samples the scattering profiles $I(Q)$ vs. Q changes with the age of the samples. Fig. 4 displays $I(Q)$ vs. Q for two samples aged for 20 and 40 days, respectively. An interesting feature of the curves is the large increase of $I(Q)$ with time.

$I(Q)$ at zero angle of scattering $I(Q_o)$ is dependent on the number of particles in the specimen, on their size and atomic composition. The most likely process in the early stages of the aging is an expulsion of hydrogen ions from the particles, and as hydrogen has a scattering length of $b = -0.37\ 10^{-12}$ cm, $I(Q_o)$ will increase. Fig. 5 displays a Guinier plot, $\ln(I)$ vs. Q^2 for the same two specimens. It clearly shows the polydispersity of the specimens as the plots exhibit no linearity for low value of Q^2, and a single radius of gyration can thus not be found from the curves. However, the measurements (Fig. 6) may be fitted a curve describing a model for a polydisperse system from which the parameters $I(Q_o)$, effective volume fraction of the particles (evf), and a parameter (σ) for the particle distribution function may be found.[16] Fig. 7 displays the results obtained for the samples listed in Table 1. As mentioned previously, $I(Q_o)$ increases with time. The effective volume fraction decreases with time and σ goes through a minimum indicating that the particle size distribution changes with time. When the fraction of α-FeOOH in the specimen starts to be of
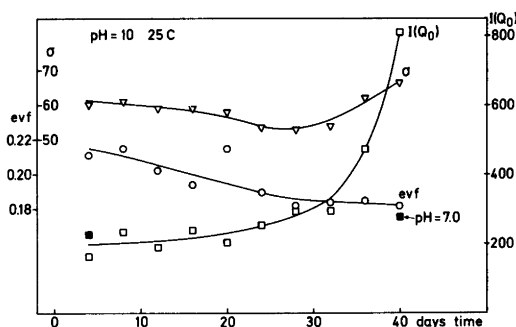
Fig. 7. $I(Q_o)$ effective volume fraction (evf) and σ for specimens with pH = 10 listed in Table 1.

significant magnitude, the values of σ increase gain.

The heat treatment of the iron(III) hydroxide specimens has an accelerating effect on the aging for the specimens precipitated to pH = 4.31 and heated to 90, 102, 107, and 113 °C, respectively (Table 2). This is observed as drop in pH which appears earlier for specimens treated at higher temperatures than for specimens heated at lower temperatures. The scattering profiles for all these specimens were recorded, and the values for $I(Q_o)$, evf, and σ were determined as described above. Fig. 8 displays the values obtained for the specimens which were heated to 90 and 102 °C, respectively. The characteristic feature is again an increase of $I(Q_o)$ with time, and that this increase comes much faster for the specimens treated at 102 °C than for those treated at 90 °C. In contrast to the results displayed in Fig. 7 where σ goes through a minimum and where the crystalline product obtained is α-FeOOH, the results displayed in Fig. 8 show only a decrease in σ for the two series of specimens. In this case the crystalline product is α-Fe$_2$O$_3$. It is also interesting to note that the effective volume fraction goes through a maximum in Fig. 8 and that this maximum appears when $I(Q_o)$ starts to increase significantly, and that a corresponding feature is not observed in Fig. 7.

The model used for describing the data is indeed very simple, giving as main information the scattering at zero angle $I(Q_o)$ with a simple interpretation. The explanation of the behaviour of the evf is less obvious. It is, however, to be expected that at the stage of aging when α-Fe$_2$O$_3$ is crystallized, water is expelled and the volume fraction decreases. This is observed when $I(Q_o)$ increases which coincides with the moment where a significant change in
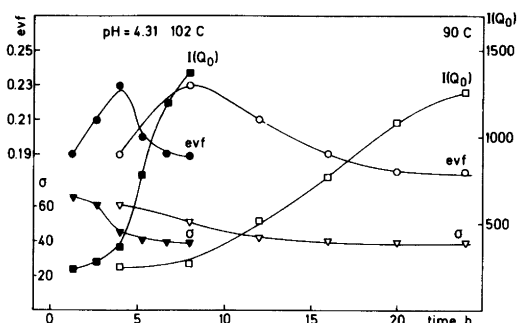
Fig. 8. $I(Q_o)$, evf, and σ for specimens aged at 90 °C (open symbols) and at 102 °C (filled symbols).

Fig. 10. $I(Q_o)$ evf and σ for on-line diffraction experiment with iron(III) hydroxide specimens at pH = 11.45 kept at 50 °C.

colour of the specimens is observed, indicating the formation of α-Fe_2O_3. The mechanism in the convertion of the polynuclear complexes to crystalline α-Fe_2O_3 must be that each particle of the polynuclear complex produces a particle of α-Fe_2O_3. There is no indication of a process where the particles dissolve and reprecipitate. In this time interval where the convertion of the polynuclear complex to α-Fe_2O_3 is dominant, the greatest drop in the value of σ is observed. It is also in this interval that the model calculation gives the poorest fit with the data. The model may be improved by introducing a σ-value for the polynuclear complex and a σ-value for the product, α-Fe_2O_3.

Fig. 9 displays the values of $I(Q_o)$, evf, and σ for the specimens of iron(III) hydroxide precipitated to pH = 4.60 and heat treated as listed in Table 2. (These data were measured with a 20 m distance betwéen sample and detector.) The results agree well with those displayed in Fig. 8. The specimens used in this series of experiments were precipitated to a pH-value of 4.60. Due to this higher value of pH,
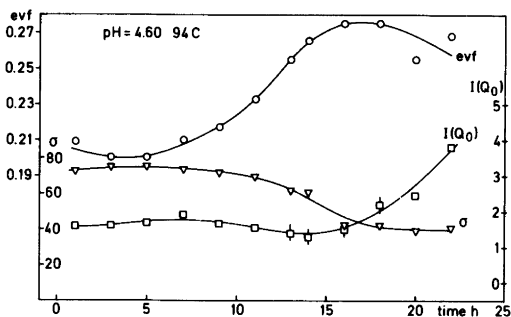

Fig. 9. $I(Q_o)$, evf and σ for specimens of iron(III) hydroxide with pH = 4.60 heated to 94 °C.
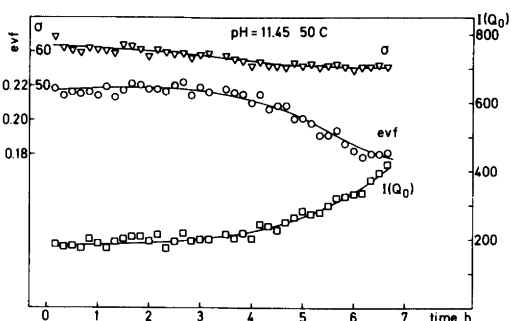
the crystallization starts at a much later time in this series of specimens heated to 94 °C than for the specimens with pH = 4.31 heated to 90 °C (Fig. 8). In addition to the temperature, pH of the gels thus plays an important role in the speed with which the aging of the iron(III) hydroxide gels proceeds.

In the on-line diffraction experiment, an iron(III) hydroxide sample with pH = 11.45 was housed in a cuvette kept at 50 °C and the neutron counts were collected every 10 min. For each measurement the $I(Q)$ vs. Q plots were fitted to the model described above and the results for $I(Q_o)$, evf and σ are are displayed in Fig. 10. As this experiment was made with a specimen of iron(III) hydroxide in an alkaline liquid the results of Fig. 10 may be compared with the results displayed in Fig. 7. The development in time of the three parameters show the same trend in the two sets of experiments. The on-line experiment was interrupted after 7 h. At that time the aging of the gel had advanced to a stage that roughly corresponds to that of a gel aged for 30 days at room temperature (Fig. 7).

In conclusion, it can be said that the speed of aging of amorphous iron(III) hydroxide gels may be studied by small angle neutron scattering and that it increases with temperature. For specimens in acid liquids the speed of aging increases with decreasing values of pH. For specimens with pH = 7, the speed of aging at room temperature is very low.

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