

FORMATION OF COLLOIDAL DISPERSIONS FROM SUPERSATURATED IRON(III) NITRATE SOLUTIONS V. SYNTHESIS OF MONODISPERSE GOETHITE SOLS

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ABSTRACT

Based on our knowledge of nucleation, growth and aging processes in supersaturated acid iron(III) solutions, methods are presented for the preparation of sols of monodisperse colloidal goethite particles having a well-defined crystal habit. One method involves controlled dialysis of dispersions of primary particles (amorphous iron hydroxide). This procedure yields monodisperse and stable sols provided the growth of the secondary particles (goethite) has not yet begun in the partially neutralized iron(III) solutions at the instant of dialysis. In another method, seeds of goethite crystals are added to supersaturated iron-bearing solutions. These experiments confirm an earlier observation that goethite grows in the [001] direction by incorporation of low-molecular-weight species from solution.

INTRODUCTION

For purposes of technical and industrial applications, but also as models for testing theories of colloidal behaviour, it is desirable to have at one's disposal a variety of colloidal dispersions in water which are well defined with regard to size distribution and particle shape [1–3]. The synthesis of monodisperse colloids of a variety of chemical compositions has been studied especially by Matijević [2, 3]. According to this investigator, the key to the preparation of uniform and monodisperse systems is the controlled generation of the reacting species which eventually result in the initiation of precipitation by one burst of nucleation. This objective is reached by building up the supersaturation at high temperatures and by the addition of complexing or oxidizing agents. The growth of these particles was supposed to be diffusion controlled. In the preparation of oxide dispersions, Matijević assumed that polynuclear metal hydroxo complexes act as precursors.

We have studied the development of goethite at temperatures below 100°C and low pH values by observing the relaxation of partially neutralized iron(III) nitrate solutions [4–6]. During the relaxation process a colloidal dispersion of primary particles, amorphous solids about 50 Å in size, initially formed and subsequent aging led to the growth of crystalline goethite. These

crystals were observed to grow preferentially in the [001] direction by uptake of low-molecular-weight polymeric species from solution to form units consisting of well-ordered needles. Crystals also formed by aggregation of primary particles followed by recrystallization. The final product always consisted of monocrystalline particles exhibiting a columnar habit with well-developed (110) and (001) crystal faces. The stability of these crystalline-colloidal dispersions at low pH (1–2) was noted to depend strongly on the ionic strength [7]. The sols destabilized by slow flocculation when the ionic strength was increased beyond 0.09 *M* by addition of sodium nitrate.

The experience acquired in our study of the precipitation of goethite via controlled nucleation and growth processes from homogeneous iron(III) nitrate solutions at 25°C enables us to propose methods for preparing well-defined goethite dispersions by influencing the growth conditions. The latter objective may be reached by the seeding of supersaturated solutions with goethite crystals and controlled dialysis. It will be shown that a variety of stable, quite monodisperse sols may be produced.

MATERIALS AND METHODS

Particle growth in partially neutralized acid solutions of iron(III) nitrate was controlled and influenced by a choice among three experimental methods. The first of these, dialysis, enables one to remove small ionic species from solution and to change the chemical regime (pH and ionic strength). This method can be used to stop the formation of the solid phase or to induce hydrolysis. As a second method, seeding of supersaturated iron(III) solutions with goethite particles was used to control the continued growth of these particles. Gel chromatography was used as a third technique to separate particles of distinctly different size in a sol.

The partially neutralized solutions were obtained by homogeneous base titrations according to procedures described previously [4]. In some experiments, these conditions were obtained by rapid mixing of equal volumes of sodium-hydroxide and iron(III)-nitrate solutions in a glass vessel after a design by Nielsen [8]. The two solutions were rapidly and tangentially injected into the mixing chamber.

The dialysis experiments were carried out using Visking membranes. Separation by gel chromatography was done with Sephadex G75 and G200 in columns 20–30 cm high having an inner diameter of 3 cm. The gel was first equilibrated with 10^{-3} *M* nitric-acid solutions. Aliquots of 50–100 ml of a sol were then placed on top of the column and eluted with nitric acid.

All chemicals used were of analytical grade. The dispersions were characterized by analytical ultracentrifugation (UC), electron microscopy (EM), photon correlation spectroscopy (PCS) and optical density (OD) measurements [4, 7]. Infrared spectroscopy was applied to establish the crystallinity of the precipitate [4].

RESULTS AND DISCUSSION

Rapid mixing experiments

Three different total iron(III)-nitrate concentrations, 0.125 *M*, 0.25 *M* and 0.5 *M*, were used in these experiments. Five aliquots of each iron(III) solution were rapidly mixed with equivalent volumes of sodium-hydroxide solutions of varying base concentration to obtain five different degrees of neutralization; 0.5, 1.0, 1.5, 2.0 and 2.5.

The degree of neutralization is specified by the ratio of the amount of base added per iron atom in the initial unneutralized solution. The ionic strength of all of the solutions of the same total iron(III) content was fixed by addition of sodium nitrate to the alkali solution before mixing. It was equal to 1.5 *M* in 0.125 *M* iron(III) nitrate, 3.0 *M* in 0.25 *M* iron(III) nitrate and 6.0 *M* in 0.5 *M* iron(III) nitrate solutions.

After mixing, relaxation set in immediately and the changes in optical density (OD) and pH with time were registered. A typical set of OD spectra recorded at different relaxation times is shown in Fig. 1 for a total iron(III) concentration of 0.125 *M* and at a degree of neutralization of OH/Fe = 1.0. The shapes of the absorption curves correspond roughly to those observed by Dousma and de Bruyn [9]. Immediately after mixing, the primary particles form and grow. After a few hours aging only negligible changes in the absorption curves occur for several tens of hours (about 50 h). After this lag time, the optical density of the system is seen to increase sharply over the

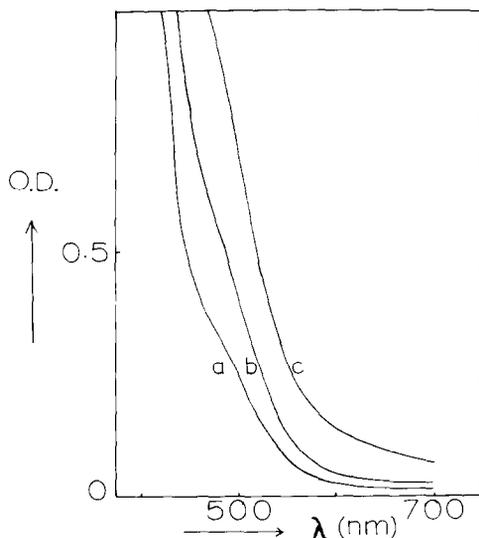


Fig. 1. Changes in optical density in the visible spectrum with time for a 0.125 *M* iron(III) nitrate solution, OH/Fe = 1, ionic strength 1.5 *M*. Curve a: 0–50 h; curve b: 70 h; curve c: 120 h.

entire spectrum (compare curve b with curve a in Fig. 1). The solution becomes turbid. This sudden increase in optical density is illustrated in Fig. 2, where the measured extinction at 700 nm is plotted as a function of time in 0.25 *M* total iron(III) solutions and the following OH/Fe ratios: 0.5, 1.5 and 2.5. Since the increased OD is obviously due to the increased scattering of incident light [10], this behaviour can only be accounted for by the formation of the larger secondary particles in the interim period. Indeed, within a few days (for small neutralization degrees) or a few weeks (for larger degrees of neutralization) a visible sediment formed.

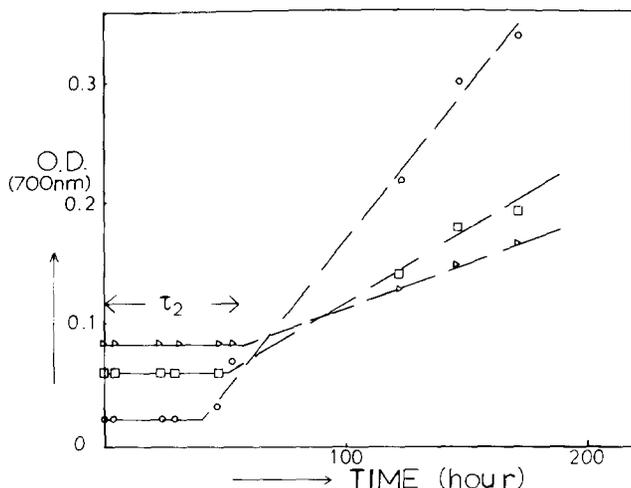


Fig. 2. Optical density at 700 nm as a function of time for 0.25 *M* iron(III) nitrate solutions (ionic strength 3 *M*) at varying degrees of neutralization (OH/Fe). (○) OH/Fe = 0.5; (◻) OH/Fe = 1.5; (△) OH/Fe = 2.5.

The steeper rise in OD at a lower, rather than a higher degree of neutralization (see Fig. 2) may be simply explained. In general, the turbidity of a sol is expected to increase more than linearly with an increase in the volume of the scattering particles. The observed changes in turbidity with degree of neutralization may therefore be accounted for if larger particles were to form at lower OH/Fe ratios than at higher OH/Fe ratios. Earlier observations [6] that at lower OH/Fe ratios large crystals are formed by the interaction of primary particles with free Fe^{III} ions in solution and that at higher OH/Fe ratios smaller (but more) goethite crystals form from the primary particles fully substantiate the above explanation. As the number of growing particles in the low OH/Fe sol is less than in a sol with a higher OH/Fe ratio, the steeper rise in turbidity in the former sol also indicates that growth is quite rapid.

In Fig. 3, the time lapse τ_2 between the start of the relaxation and the moment of sudden increase in OD (see Fig. 2) is plotted as a function of the

pH at this time for all experiments. We note, except at the lowest pH values, a constant value of about 50 h for τ_2 . This time lapse provides information on the processes preceding the growth of the secondary particles. It is an induction time during which the transformation from the amorphous to the crystalline state occurs. This transformation process involves the splitting off of water [11] to form oxo-bridges and other chemical and structural changes [12] during the first 24 h after the formation of the amorphous particles. Murphy et al. [13] also believe a decrease of the surface charge of these particles to be necessary for the formation of the secondary crystals. Recently, Musić et al. [14] traced the transformation of the amorphous particle to α -FeOOH structures via the formation of oxo-bridges by Mössbauer spectroscopy. The details of the mechanism of the transformation process are, however, still quite obscure. A quantitative understanding of the relation between the observed induction times τ_2 and this process must await further research.

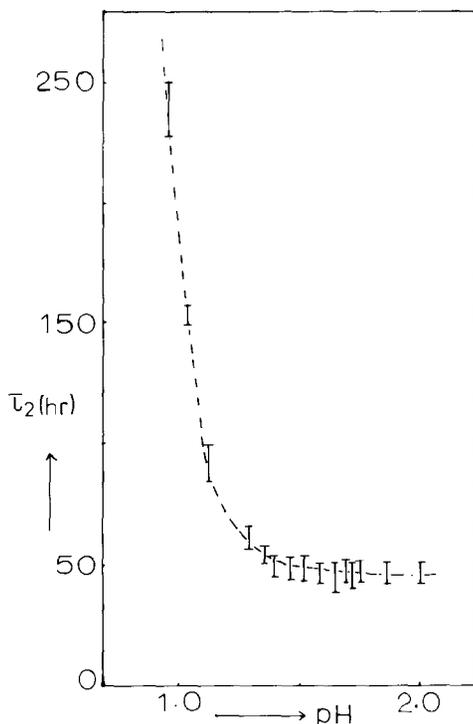


Fig. 3. Induction time τ_2 as a function of pH.

We may conclude from the results of the rapid mixing experiments that, rather early in the overall aging process, after approximately 2 days, goethite starts to grow from the amorphous colloids. This induction period during which the transformation from amorphous precursor to a crystalline particle

of essentially the same dimensions takes place is markedly independent of pH and ionic strength provided the pH of the sol is not extremely low.

Dialysis experiments

Dialysis of partially neutralized iron(III) nitrate solutions

Dialysis of partially neutralized solutions effectively stops nucleation and growth and leaves a sol of only primary particles. This manipulation also enables one to adjust the pH and ionic strength of the sol. Depending on the time at which the neutralized solution is dialysed, secondary particles may also be present in the sol. This will have far-reaching consequences for the stability of the monodisperse-goethite sol which forms afterwards. We illustrate here the importance of the length of the relaxation period preceding dialysis by the following experiment.

Three aliquot samples of an acidified solution ($6.25 \times 10^{-2} M \text{Fe}(\text{NO}_3)_3$, $I = 0.5 M$) titrated to a pH value of 2.12 and characterized by an induction period of 30 min [4] were dialysed 1, 3 and 5 days, respectively, after the start of the relaxation to obtain in each case solutions of pH 2.0 and ionic strength $0.05 M$. In the solutions which were dialysed after relaxation times of 3 and 5 days, the irreversible formation of a sediment consisting of aggregates about 200 nm long and 20 nm wide with a structure similar to the previously observed chain-like flocs [6] occurred within a few weeks.

In contrast, dialysis after 1 day results in the formation of a stable sol which, after a few months of aging, consisted of monodisperse cubic-goethite particles of edge-length 20 nm in addition to the primary particles. Both types of goethite particles, those in the stable sol and those in the flocculated systems, show the typical granular structure [6]. The induction period τ_2 referred to in the previous section was exceeded in the allowed relaxation times in the formation by dialysis of the two unstable sols. This implies that growth of secondary particles was already in progress in these two experiments, in contrast to the other experiment. To synthesize stable sols of goethite particles under the conditions chosen in this experiment, it is important to ascertain that growth of secondary particles has not yet started. We also note that the unstable sols produced here were essentially prepared under the same conditions as the B sols discussed in Ref. [6]. The dialysis experiments also confirm our previous suggestion [6] that the growth of goethite can occur via aggregation and recrystallization of amorphous particles in colloidal solutions.

By applying the dialysis method to partially neutralized acid iron(III)-bearing solutions, we are now able to produce stable monodisperse sols in a reproducible way and, by modifying the pH and the ionic strength, the particle size of these sols can also be controlled. Examples of such sols are listed in Table 1. These sols were obtained by dialysis, after 1 day of aging of a partially neutralized solution ($6.25 \times 10^{-2} M \text{Fe}(\text{NO}_3)_3$, $I = 0.5 M$, pH = 2.12), against a $10^{-3} M$ nitric acid solution. Parts of the dialysed solution

were then dialysed again at a constant ionic strength of 10^{-2} M (by addition of sodium nitrate) against 10^{-2} , 10^{-3} and 10^{-4} M nitric acid.

Goethite formed in all of these sols, and after aging for a few months at 25°C , UC and EM analyses show that a pseudo-equilibrium is reached between the primary and secondary particles. The colour of the solutions, initially dark brown, varies after the aging period from light brown at $\text{pH} = 2$ to dark brown at $\text{pH} = 4$. This is confirmed by UC analysis, which indicates that the fraction of strongly light-absorbing primary particles increases with increasing pH [6].

TABLE 1

Properties of sols obtained by dialysis after 1 day of a partially neutralized solution (6.25×10^{-2} M $\text{Fe}(\text{NO}_3)_3$, $\text{pH} = 2.12$, $I = 0.5$ M)

pH	Ionic strength (M)	S_{20} (S)		Final radius (nm) calculated from S_{20}	Linear dimension (nm) from EM	Radius (nm) calculated from PCS ^a
		Primary particles	Secondary particles			
2	10^{-2}	26	320	6.4	14	10
3	10^{-2}	32	485	7.8	16	12
4	10^{-2}	34	615	8.8	18	12
4 ^b	10^{-4}	30	905	10.5	24	—

^aPhoton correlation spectroscopy.

^bDialyzed against 10^{-4} M nitric acid.

Figure 4 illustrates the typical cubic habit of these secondary particles, the size of which varies from 14 nm at $\text{pH} = 2$ to 18 nm at $\text{pH} = 4$ (see Table 1). This small change in particle size with pH is real and is confirmed by UC analyses. The measured S_{20} values are also included in Table 1, as well as the calculated particle radii on assuming the Svedberg relation for spheres and a density of 4.3 g cm^{-3} (massive goethite). The agreement between EM observation and UC analysis is seen to be excellent.

Dialysis of the same solution against 10^{-4} M nitric acid and only $I = 10^{-4}$ M gives a sol with larger particles (Table 1). The concentration of sol particles is lower and they form at a slower rate. Only after 6 months aging could the secondary particles be detected by UC measurements. This observation confirms that the coagulation rate is one of the rate-controlling steps in the development of goethite from aged primary particles. The details of this process and its relation to recrystallization, also the role of pH and oriented flocculation need further experimentation.

Monodisperse sols of only secondary particles are obtained by separating the sols of mixed primary and secondary particles with Sephadex G75. This gel adsorbs the primary particles while the larger secondary goethite particles are eluted with the void volume.

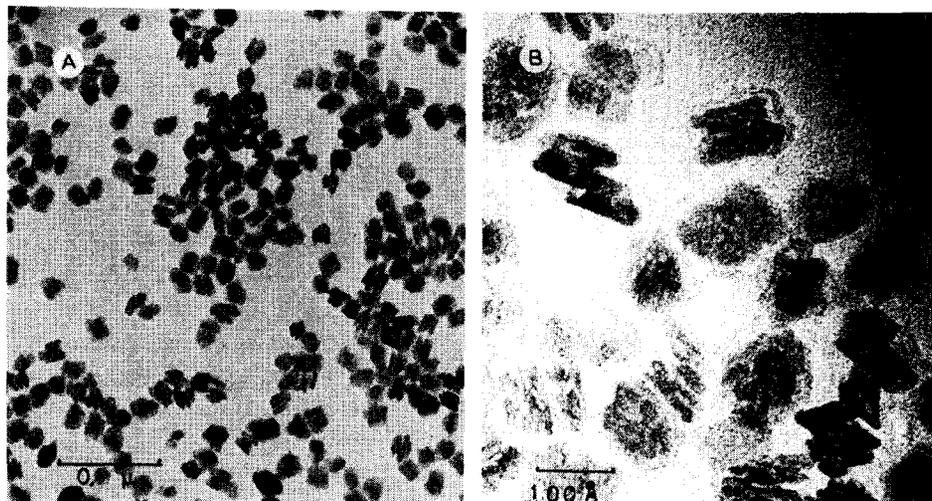


Fig. 4. Electron micrographs depicting the cubic crystals formed after dialysis at $\text{pH} = 2$, $I = 10^{-2} M$ of partially neutralized iron(III) solutions (see text). The secondary particles have been separated from the primary particles using gel-separation chromatography. (A) Sample showing the high degree of monodispersity. (B) Higher magnification than (A). The original micrograph clearly showed fringes with separation $4.5 \pm 0.5 \text{ \AA}$. The typical diamond-like shape of one of the faces suggests that the particles have faces (001) and (110) (Ref. [6]).

It should be stressed that the choice of the initial conditions (total iron(III) concentration, OH/Fe ratio) was quite arbitrary. Monodisperse sols of secondary particles are also obtained from dialysed solutions with different total iron(III) concentrations and varying degrees of neutralization as realized by homogeneous base titrations or careful addition of sodium bicarbonate.

Hydrolysis by dialysis

An acidified iron(III) solution can also be neutralized by dialysis against twice-distilled water. In such an experiment, the pH will change uniformly with time. Extended dialysis of a $1.0 M \text{ Fe}(\text{NO}_3)_3$ solution by this procedure produces a dark brown sol of $\text{pH} = 5.0$ which is free of soluble iron(III). After >6 months of aging, uniformly sized goethite crystals that can be separated from the primary particles by gel chromatography with Sephadex G200 are formed. This method of separation yields a dark yellow, rather monodisperse sol of rod-like goethite particles (Fig. 5) with a length of $110 \pm 10 \text{ nm}$ and a diameter of $10\text{--}20 \text{ nm}$.

Seeding of supersaturated solutions

In general, it has been argued that goethite seeds when added to a solution supersaturated with respect to this crystalline modification will tend to grow

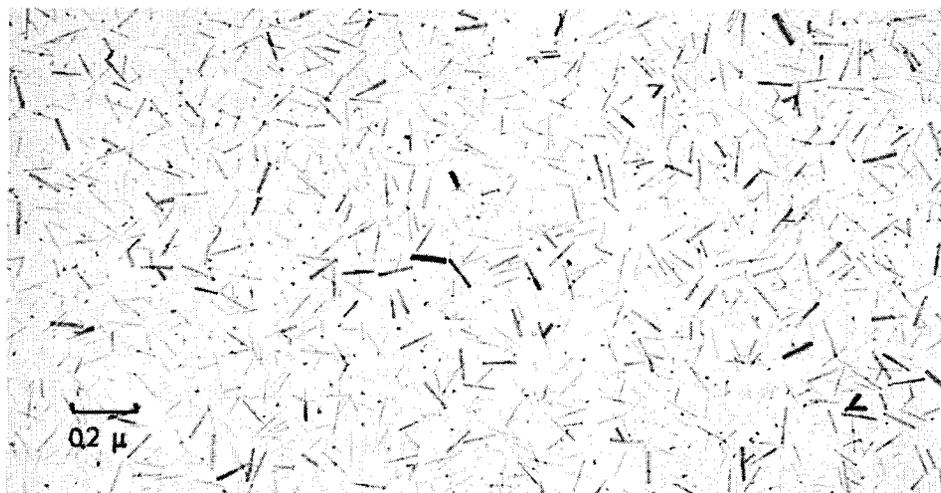


Fig. 5. Electron micrograph showing the development of particles with very large length dimension after dialysis of a 1 M $\text{Fe}(\text{NO}_3)_3$ solution (see text). In the electron microscope, fringes parallel to the long axis were observed and the EM study suggests that the particles again have faces (001), (120) and (010).

only in the [001] direction [6]. This implies that particles of a definite habit formed by various dialysis methods may be constrained to grow in only one direction.

This suggestion was tested by a series of experiments in which the starting solution was prepared in the following manner. A solution of 10^{-2} M $\text{Fe}(\text{NO}_3)_3$ was further acidified by adding nitric acid to prevent precipitation. The ionic strength increased to a value of approximately 0.09 M, just sufficient to prevent eventual flocculation [7]. While stirring this solution vigorously, its pH was then raised to a value of 2.05 by dropwise addition of 0.5 M NaHCO_3 . The solution is now supersaturated with respect to goethite but just undersaturated with respect to the amorphous phase, so that no solid phase forms spontaneously [4]. To aliquots of this test solution, various volumes of seed solutions containing only goethite particles of different size and habit and also solutions containing only primary particles were added. The change in particle size with time, after mixing, was then observed with the aid of electron microscopy. Some typical results of these time studies are summarized in Table 2. All seed particles, regardless of their origin, are seen to grow in one direction. A direct confirmation of our thesis that goethite grows via incorporation from solution of low-molecular-weight species in the [001] direction is provided by these experiments. In some cases, the length of the goethite particle is seen to increase quite drastically. This observation correlates with the total number of seed crystals added. The smaller the number of seeds the larger their length after growth is completed.

TABLE 2

Seed experiments. Changes in size of seed particles as observed in the electron microscope

Time of aging	1 ^a		2 ^b		3 ^c		4 ^d	
	Length (nm)	Width (nm)						
0	15	15	110	10–20	75	32	4	4
20 days	36	15	120	10–20	—	—	50–70	15–20
2½ months	45	15	150	10–20	133	33	84–100	15–20
4 months	64	15						

^aSeed solution obtained by dialysis of partially neutralized solutions (see text).^bSeed solution obtained by hydrolysis by dialysis (see text).^cSeed solution obtained by partial neutralization of a $6.25 \times 10^{-3} M$ $Fe(NO_3)_3$ solution up to pH = 2.22 (see Ref. [6]).^dSeed solution containing only primary particles.

Addition of primary particles to the test solution leads to a rapid formation of secondary particles. This finding provides definite proof for the precursor role of these particles in the development and further growth of goethite. This experiment can also provide a basis for future research on the factors that determine the crystal habit of the secondary goethite particles [6].

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