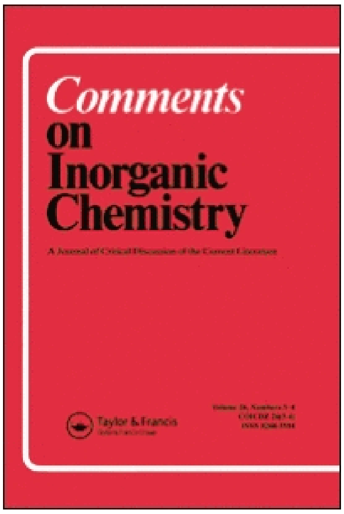

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Hydrolysis of Iron(III)...Chaotic Olation Versus Nucleation

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Hydrolysis of Iron(III)—Chaotic Olation Versus Nucleation

At moderate temperatures, a variety of sols, gels, amorphous or crystalline precipitates emerge from hydrolysis of iron(III) in aqueous solution. The product distribution reflects the interplay of fast proton transfer, olation and aggregation reactions. Polynuclear oxohydroxocomplexes with well-defined structures are formed under favorable circumstances in homogeneous solution. Polynuclear species with β-FeO(OH) structures have been identified in chloride solutions.

INTRODUCTION

Experimental studies on the hydrolysis of iron(III) usually start from rather acid solutions that contain the purple aquaion $Fe(H_2O)_6^{3+}$ or weak mononuclear complexes such as the yellow $FeCl(H_2O)_5^{2+}$ and $FeCl_2(H_2O)_4^{+}$. Subsequent base addition induces the first deprotonation step (1), which is immediately followed by the reversible dimerization (2):

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(OH)(H_2O)_5^{2+} + H_3O^+, \qquad (1)^*$$

$$2Fe(OH)(H_2O)_5^{2+} \rightleftharpoons [(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{4+} + 2H_2O. \quad (2)^*$$

Perchlorate solutions that contain the dinuclear $Fe_2(OH)_2^{4+}$ to about 10% of the total iron concentration can be kept unchanged for several

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[*] Inner-sphere water molecules will be omitted later in this text, that is, we will write Fe^{3+}, $FeOH^{2+}$, $Fe_2(OH)_2^{4+}$, H^+ for the species in Eqs. (1) and (2).

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for several weeks. This is by no means trivial, because they are supersaturated with respect to solid phases such as α-FeO(OH). There are reasons to believe that reactions (3) and (4) precede further steps in the nucleation of α-FeO(OH) in acid solution, and that they are quite endergonic:

$$Fe_2(OH)_2^{4+} + FeOH^{2+} + H_2O \rightarrow Fe_3(OH)_4^{5+} + H^+, \qquad (3)$$

$$Fe_3(OH)_4^{5+} + FeOH^{2+} \rightarrow Fe_4O(OH)_4^{6+} + H^+. \qquad (4)$$

If the molar ratio of base added per iron(III) exceeds a critical value, usually in the range 0.5–1, brown or reddish brown polynuclear species (5) are formed. Potentiometric methods can be used to determine average values $\bar{n}$ of q/p viz. $2r + s/p$[1]:

$$Fe_p(OH)_q^{3p-q} \qquad Fe_pO_r(OH)_s^{3p-(2r+s)} \qquad (5)$$

The species of type (5) compose the well-known colloidal solutions of iron(III) hydroxide from which precipitates emerge either spontaneously or by flocculation. "Iron hydroxides" obtained in this way may differ widely with regard to chemical composition, structure, particle size, size distribution, shape of particles and interfacial properties. In a final analysis, any product can only be understood in terms of the pathways of its formation. From the point of view of quantitative relationships, the set of relevant variables is virtually prohibitive. It includes all components of the primary solution and their concentration, the type of base added and its concentration, the rate of base addition including the size of drops, the rate of mixing, the temperature, the time and, last but not least, tiny traces of contaminants such as dust particles in the solution. However, in preparative procedures, the variables can be chosen in such a way that crystalline products are obtained, for example, α-FeO(OH),[2] β-FeO(OH),[3] α-Fe_2O_3 (Ref. 4) corresponding to the minerals goethite, akaganéite and hematite. In these procedures, quite often a thermal treatment induces a transformation of products emerging from a low-temperature stage. Thus traces of the primary pathways can be erased.

There are many problems of this type when iron(III) hydroxides are considered in the context of aquatic systems including sediments, in soils and in living organisms. In these systems, however, the aquaion $Fe(H_2O)_6^{3+}$ is quite rare. Hence, the network of reactions introduced above is confined to laboratory chemistry. On the other hand, the ferrous aquaion $Fe(H_2O)_6^{2+}$ is an important species in anoxic regions of lakes[5] and probably in biologic fluids.[6] Oxidation of Fe^{2+} to Fe^{3+} immediately induces hydrolysis unless selective ligands bind Fe(III) by forming mononuclear, highly stable complexes. The iron cycle in living organisms, chemically, involves the continuous competition of OH^- with other ligands. Transferrins prevent hydrolysis of iron(III) in the blood stream of vertebrates. In cells, however, iron hydroxide is encapsulated for storage by a protein shell in ferritin.[7] It is striking that, from the point of view of mechanisms, hydrolysis induced by oxidation has received, so far, much less attention than hydrolysis of Fe^{3+} starting from acidic media. The present account aims at elucidating the factors that govern hydrolysis of iron(III) and its products in the lower temperature region up to about 40°C, which is relevant to environmental and biologic chemistry.

PREEQUILIBRIA SPECIES AND SOLUBILITY PRODUCTS

There is a wealth of data about the set of equilibria (6). The compilation of Sylva[8] includes all investigations up to early 1971, whereas Baes and Mesmer[1] present selected values of stability constants in their excellent monograph:

$$\begin{array}{lll} & \text{25°C, 3 M NaClO}_4\text{(Ref. 9)} & \\ Fe^{3+} + H_2O \rightleftarrows FeOH^{2+} + H^+ & \log {}^*K_1 = -3.05 & \\ Fe^{3+} + 2\,H_2O \rightleftarrows Fe(OH)_2^+ + 2H^+ & \log {}^*\beta_{12} = -6.3 & (6) \\ 2\,Fe^{3+} + 2\,H_2O \rightleftarrows Fe_2(OH)_2^{4+} + 2H^+ & \log {}^*\beta_{22} = -2.3 & \end{array}$$

It was recognized many years ago that solutions containing $Fe_2(OH)_2^{4+}$ to a significant degree are supersaturated with respect to solid phases FeO(OH).[10] The successful determination of the constants ${}^*K_1$, ${}^*\beta_{12}$ and ${}^*\beta_{22}$ is bound to slow nucleation. From the data

TABLE I
Distribution of species in 0.05 M iron(III) perchlorate solution; 3 M $NaClO_4$, 25°C

Species	A^a (10^{-2}M)	B^b (10^{-2}M)
Fe^{3+}	3.48	1.92
$FeOH^{2+}$	0.20	0.02
$Fe(OH)_2^+$	0.01	negl.
$Fe_2(OH)_2^{4+}$	0.65	0.006
α-FeO(OH)	—	61% of total Fe(III)
pH	1.82	1.04

[a] Homogeneous solution prior to nucleation; concentrations calculated from Hedström's data (6).
[b] Equilibrium attained along with the precipitation of α-Fe(OH) from solution A; solubility product log $^*K_{so} = 1.4$.[11]

above, the distribution of species in Table I is calculated for a 0.05 M iron(III) perchlorate solution.

The solubility product that was used to calculate the concentration set B in Table I has been determined by equilibrating suspended α-FeO(OH) with perchloric acid. On the other hand, solutions of type A are obtained by neutralizing excess acid as described in the Induction. The first two solubility products in Table II were determined in this way, that is, by inducing precipitation. Actually, solution A is just about saturated with respect to amorphous FeO(OH) (log $^*K_{so} = 4.0$; Table II). Feitknecht and Michaelis[12] identified crystalline α-FeO(OH) in solution A after 7 weeks when the distribution of species was still far from situation B. Obviously, nucleation is a crucial factor in the transition A → B.

In the context of nucleation and crystal growth it is useful to consider kinetic properties of $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$. Water exchange from $FeOH^{2+}$ is about 10^3 times faster than from the aquaion (Table III).

TABLE II
Solubility products of FeO(OH) in 3 M $NaClO_4$, 25°C[a,11]

Solid phase	Age	Log $^*K_{so}$	$-$Log K_{so}
amorphous FeO(OH)	200 h	4.0 ± 0.1	38.7
amorphous FeO(OH)	1 yr	3.6 ± 0.1	38.3
α-FeO(OH)		1.4 ± 0.8	41.3

[a] $FeO(OH) + 3H^+ + H_2O \rightleftarrows Fe^{3+} + 3H_2O$; $^*K_{so} = [Fe^{3+}]/[H^+]^3$; $K_{so} = [Fe^{3+}] \times [OH^-]^3$; ionization constant of water $pK_w = 14.22$.

TABLE III
Kinetics of solvent water exchange on iron(III)[a,13]

	$Fe(H_2O)_6^{3+}$	$Fe(H_2O)_5OH^{2+}$
k (s^{-1}; 25°C)	$1.6 \cdot 10^{+2}$	$1.4 \cdot 10^{+5}$
ΔH^{a}($kJ \cdot mol^{-1}$)	64(±3)	42(±2)
ΔS^{a}($J \cdot mol^{-1}K^{-1}$)	12(±7)	5(±4)

[a] Concentration range Fe(III) 0.01–0.3 m, $HClO_4$ 0.3–4 m.

Moreover, solvent exchange rates and various ligand substitution rates are more consistent with dissociative activation for substitution on $FeOH^{2+}$ and associative activation for $Fe(H_2O)_6^{3+}$. The dinuclear $Fe_2(OH)_2^{4+}$ is formed at a fast rate, $k_{12} = 630\ M^{-1}s^{-1}$ (25°C; 3 M $NaClO_4$),[14]

$$FeOH^{2+} + FeOH^{2+} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} Fe_2(OH)_2^{4+}, \tag{7}$$

whereas the reverse reaction in (7) occurs in the range of seconds, $k_{21} = 0.4\ s^{-1}$. However, the decay (8) of the dinuclear is catalyzed by H_{aq}^{+} as seen from the rate expression (9) and the rate parameters:

$$Fe_2(OH)_2^{4+} + 2H^+ \rightarrow 2\ Fe^{3+}, \tag{8}$$

$$\{d[Fe_2(OH)_2^{4+}]\}/dt = (k_1 + k_2[H^+])\ [Fe_2(OH)_2^{4+}], \tag{9}$$

where $k_1 = k_{21}$ in (7), $k_2 = 3.1\ M^{-1}s^{-1}$. Hence, the half-time of decay in 1 M $HClO_4$ is 0.2 s, and formation of Fe^{3+} from $Fe_2(OH)_2^{4+}$ is by roughly 10 orders of magnitude slower than from $FeOH^{2+}$. Clearly, the rates of dissolution of polynuclears will be still slower if Fe(III) in the interfacial area is linked to neighboring centers by more than $2OH^-$ or O^{2-}. Hence, the study of dissolution rates in acid is expected to be an important tool in the investigation of polynuclears. However, surface reactions are complicated by effects of size and shape, in particular the surface-to-volume ratio. Effects of anion association are expected if polynuclears are polyelectrolytes, that is, if $(3p - q) > 0$ in Eq. (6). In view of these effects, the investigation of the kinetics of reaction (8) in chloride solution is very instructive.[15] In the concentration range $0 \leq [\mathrm{Cl}^-] \leq 1$ M, ionic strength 2 M ($NaClO_4$), the rate law (10a) has been found:

$$\{d[\mathrm{Fe_2(OH)_2^{4+}}]\}/dt = k_{\mathrm{obs}}\,[\mathrm{Fe_2(OH)_2^{4+}}],$$

$$\begin{aligned} k_{\mathrm{obs}} = {} & k_1 + k_2[\mathrm{H^+}] + k_4[\mathrm{H^+}][\mathrm{Cl^-}] \\ & + k_6[\mathrm{H^+}][\mathrm{Cl^-}]^2 + k_7[\mathrm{H^+}]^2[\mathrm{Cl^-}] \\ & + k_8[\mathrm{H^+}]^2[\mathrm{Cl^-}]^2, \end{aligned} \tag{10a}$$

$$k_{\mathrm{obs}} = \sum_{i,j=0}^{2} k_{ij}\,[\mathrm{H^+}]^i\,[\mathrm{Cl^-}]^j. \tag{10b}$$

Equation (10a) is identical to the series (10b) when terms $k_{01}[\mathrm{Cl}^-]$ and $k_{02}]\mathrm{Cl}^-]^2$ are neglected. The values of the parameters $k_1 = 0.3$ s^{-1}, $k_2 = 2.6$ $M^{-1}s^{-1}$ and $k_4 = 150$ $M^{-2}s^{-1}$ agree well with those reported by Sommer and Margerum.[16] The parameters $k_6 = 430$ $M^{-3}s^{-1}$, $k_7 = 30$ $M^{-3}s^{-1}$ and $k_8 = 350$ $M^{-4}s^{-1}$ show that the last three terms in Eqs. (10a) and (10b) determine the rate in 1 M HCl. Ion association of $\mathrm{Fe_2(OH)_2^{4+}}$ with Cl^- according to estimated formation constants $K_1 = 4$, $K_2 = 2$ M ($I = 2$ M) cannot account for the rates observed. There are conspicuous effects of concerted interaction of Cl^- and H^+ that also have been found in the dissolution kinetics of polynuclears formed in chloride solution.[15]

In fact, chloride seems to induce a particular type of solid phase in the hydrolysis of iron(III) at pH ≤ 3. Biedermann and Chow[17] determined the solubility product in the range $1.8 < \mathrm{pH} < 3.1$ according to reaction (11):

$$\mathrm{Fe(OH)_{2.7}Cl_{0.3}(s)} + 2.7\ \mathrm{H^+} \rightarrow \mathrm{Fe^{3+}} + 0.3\ \mathrm{Cl^-} + 2.7\ \mathrm{H_2O}, \tag{11}$$

$$\log {}^*K_{\mathrm{so}} = 3.04\ (25°\mathrm{C};\ 0.5\ \mathrm{M\ NaCl}).$$

The precipitate $\mathrm{Fe(OH)_{2.7}Cl_{0.3}}$ is the intermediate in the preparation of β-FeO(OH). Nitrate forms even less stable mononuclear complexes with $\mathrm{Fe^{3+}}$ than chloride, but in 1 M $NaNO_3$, the precipitate is

$Fe(OH)_2NO_3 \cdot aq$ as reported by Danesi et al.[18] who investigated the equilibrium (12):

$$Fe(OH)_2NO_3(s) + 2H^+ \rightleftarrows Fe^{3+} + NO_3^- + 2H_2O, \qquad (12)$$

$$\log {}^*K_{so} = 2.20\ (25°C;\ 1\ M\ NaNO_3).$$

The formation of both $Fe(OH)_{2.7}Cl_{0.3}$ and $Fe(OH)_2NO_3$ is kinetically controlled, and they are thermodynamically unstable with respect to phases FeO(OH).

HYDROLYSIS IN PERCHLORATE AND NITRATE SOLUTIONS

A variety of investigations that cover a broad range of composition has been carried out. Although it is impossible to summarize the results in terms of quantitative relationships, the type of phenomena observed and the dominant effects involved can be outlined in a concise way.

It is useful to consider, at first, a specific set of test solutions that are obtained by successive addition of $NaHCO_3$(1 M) to solution (13):

$$\left.\begin{array}{ll} Fe^{3+} & 0.06\ M \\ HClO_4 & 0.06\ M \end{array}\right\} a = -1 \qquad (13)$$

$$NaClO_4 \quad 2\ M.$$

We use a, defined as the molar ratio excess acid ($a < 0$) or base ($a > 0$) per Fe(III), to describe the analytic composition in the range $-1 \le a \le 3$. If $NaHCO_3$ solution is added rather slowly at a rate $\Delta a/\Delta t \approx 1\ h^{-1}$, the precipitation time $\tau(a)$ varies as shown in Figure 1. The rather arbitrarily defined time τ is the time elapsed before a Tyndall effect is observed. None of the solutions in the range $a \le a_{min}$ contain a detectable amount of polynuclear species when some visible precipitate has appeared. The precipitate is microcrystalline α-FeO(OH), whereas the solution only contains Fe^{3+}, $FeOH^{2+}$,

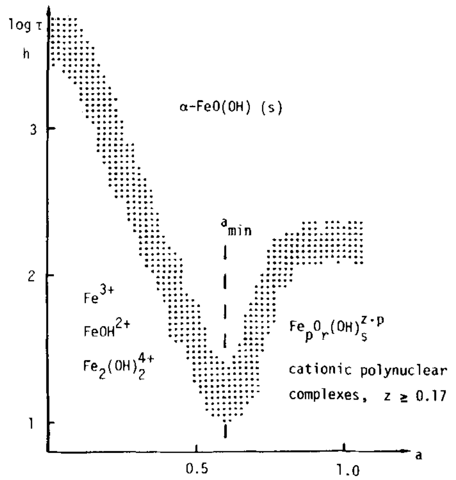


FIGURE 1 Variation of precipitation time τ with molar ratio $a = HCO_3$ /Fe(III) for 0.06 M iron(III) perchlorate solution. $I = 2$ M ($NaClO_4$); 25° C.[15,19]

$Fe_2(OH)_2^{4+}$. The decay time in strong acid solution was measured by stopped-flow methods to identify $Fe_2(OH)_2^{4+}$. Brown polynuclears form in the homogeneous solution if a is raised beyond a_{min} but kept below 2.8. The corresponding sols are stationary over a period from months up to several years. If, however, the rate $\Delta a/\Delta t$ is increased considerably, amorphous precipitates are formed instantaneously. Their transformation to α-FeO(OH) or α-Fe_2O_3 takes as much as several years. The stability of sols in the range $1 < a < 2.5$ depends on the type and concentration of anions. Perchlorate serves as a reference for weak interactions, whereas sulfate can be used to precipitate polynuclears instantaneously, indicating that the polynuclears are positively charged polyelectrolytes. In dilute solutions, NO_3^- is equivalent to ClO_4^-. Knight and Sylva[19] determined $\tau(a)$ for ClO_4^-, NO_3^- and Cl^-. Spiro et al.[20] isolated products with the composition $Fe(OH)_{3-x}(NO_3)_x(H_2O)_z$, $0.5 < x < 0.7$, from nitrate solutions (1 M; $a = 2$). We would have expected Danesi's product $Fe(OH)_2NO_3(s)$.[18] However, gel filtration on Sephadex was used to obtain the polymeric fraction free from the low molecular weight components, which involved severe changes in the activity of NO_3^-.

It is not easy to characterize polynuclears $Fe_p(OH)_q^{3p-q}$ with regard to their (p,q) distribution. Hsu[21] applied Na_2SO_4 precipitation in conjunction with chemical interactions, that is, the oxalate–oxalic acid (pH $\approx$ 3) extraction of more reactive amorphous fractions. In a very careful potentiometric study, Ciavatta and Grimaldi[22] investigated the polynuclears in clear solutions when the average number $\bar{n}$ of OH^- bound per Fe(III) was $2.3 < \bar{n} \leq 2.83$ and a well to the right of the minimum in the pertinent curve $\tau(a)$. The experimental data were interpreted in terms of the preequilibria species $FeOH^{2+}$, $Fe_2(OH)_2^{4+}$ and just one specific polynuclear $Fe_{12}(OH)_{34}^{2+}$. Steady-state pH was reached within 50 h, whereas precipitation times $\tau \geq$ 100 h were observed.

LOCAL PROCESSES AND HYDROLYSIS PRODUCT DISTRIBUTION

It has been pointed out by most authors that their data were only reproducible if base addition had been handled in a reproducible way. Actually, the product distribution reflects the rate of base addition including rates of mixing in conjunction with rates of processes on a molecular level. For the present purpose, it is useful to consider one drop of base immersed in a solution of Fe^{3+} (see Figure 2).

There is an enormous pH gradient at the interface of the drop and the bulk solution. The proton transfer reactions that produce mononuclear $Fe(OH)_i^{3-i}$ are extremely fast since the pertinent second-order rate constants are of the order $\geq 10^{+10}\ M^{-1}s^{-1}$. The relevant set of pK values (14) involves estimates as discussed in Ref. 1:

$$\begin{array}{lccccccccc} & Fe^{3+} & & FeOH^{2+} & & Fe(OH)_2^{+} & & Fe(OH)_3 & & Fe(OH)_4^{-} \\ pK & & 3 & & 3.3 & & \approx 6 & & \approx 9 & \end{array} \qquad (14)$$

There will be nonequilibrium distribution of species $Fe(OH)_i^{3-i}$ at the boundary of the drop of base. Of course, subsequent fast protonation (15) will occur on the acid side of the interfacial layer,

$$Fe(OH)_i^{3-i} + H^+ \rightarrow Fe(OH)_{i-1}^{4-i} + H_2O, \qquad (15)$$

$$\begin{array}{c}\mathrm{Fe(OH)}_i^{3-i} + \mathrm{Fe(OH)}_j^{3-j} \rightarrow \mathrm{Fe_2(OH)}_{i+j}^{6-(i+j)} \\ \downarrow \\ \mathrm{Fe}_p\mathrm{(OH)}_q^{3p-q}\end{array} \qquad (16)$$

Equation (16) is a loose way to indicate the fast formation of polynuclears that interferes with the proton transfer reactions (15). Any polynuclear will also be exposed to proton attack, but the rates will

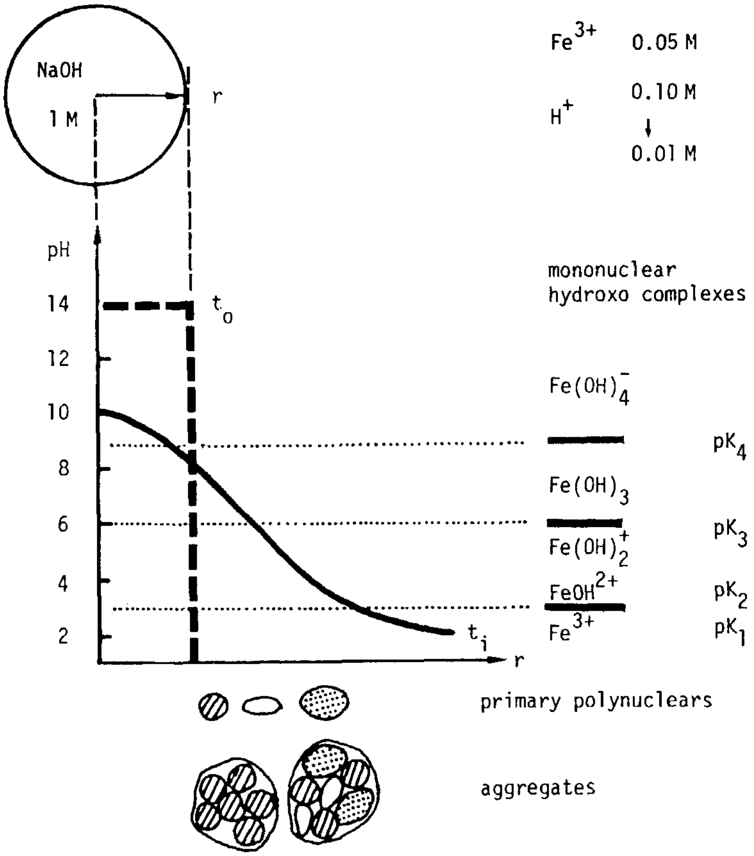


FIGURE 2 Fast reactions on the time scale of mixing a drop of NaOH solution with bulk iron(III) solution. Consecutive reactions (products) are deprotonation $[\mathrm{Fe(OH)}_i^{3-i}]$, olation $[\mathrm{Fe}_p\mathrm{(OH)}_q^{3p-q}]$ and aggregation of olation products.

diminish with increasing values of p as outlined earlier in this Comment. There can be no doubt that the lability of water will increase considerably along the series (14). Consequently, rate constants pertinent to the olation reactions of type (16) may well reach, or even exceed, about 10^7 $M^{-1}s^{-1}$.

When the mixing is complete, either of three distinctly different situations may arise:

1. No polynuclear persist while the preequilibria are shifted, just as in the experiments of Hedström[9] [see Eq. 6] who used $NaHCO_3$ solution instead of NaOH to keep pH gradients low.
2. The acidity of the bulk solution is too low to bring about acid decomposition of the stochastically formed polynuclear aggregates.
3. Nuclei have been generated that induce the growth of crystalline polynuclears in solution.

Situation (2) is rather disturbing since amorphous products will hardly transform to well-defined phases by intramolecular processes.[12] Lower activation energies are provided by pathways involving complex formation at the solid–solution interface, for example, by hydroxycarboxylic acids.[23] An efficient monodentate ligand is hydroxide itself in the preparation of α-FeO(OH), which involves heating of the amorphous product in alkali–hydroxide solution.[2]

The arguments presented here also apply to the homogeneous injection technique as used by Dousma and De Bruyn.[24] However, nearly perfectly homogeneous base addition was achieved by Magini[25] who extracted HNO_3 with an organic solution of a primary amine to prepare a rather concentrated hydrolyzed iron(III) nitrate solution. The colloidal solution transformed into a gel, and a structural continuity between species in solution and solidified product had been established.

HYDROLYSIS IN CHLORIDE SOLUTION

Synthetic β-FeO(OH) and Akaganéite

It is well known that yellow powders precipitate from hot iron(III) chloride solutions.[3] Depending on the conditions, the composition will be Fe(OH)$_{2-x}$Cl$_x$ with x in the range $0 < x \leq 0.3$. The structural parameters persist over all the range of x.[26] The limiting value $x \rightarrow 0$ is reached in a preparation by warming up primary products ($0.1 < x < 0.3$) in excessive dilute ammonia solution. The structure of β-FeO(OH)[26,27] is shown in Figure 3. Natural β-Feo(OH), akaganéite was detected in 1959 as a seemingly rare mineral. However, it was reported in 1976 that β-FeO(OH) is a major form of iron in various secondary iron-containing minerals in a selection of New Zealand soils and iron manganese soil concretions.[28] This suggests that β-FeO(OH) is probably present in similar soils in other parts of the world.

Crystal Growth in Solution

A variety of methods has been applied recently to elucidate the time evolution of the size (p), the shape and the structure of polynuclears at all stages[29] between the well-defined dimer Fe$_2$(OH)$_2^{4+}$ and precipitates. In a qualitative sense, precipitation times τ depend on a as shown in Figure 1. Large polynuclears are formed only in the range $a > a_{\text{min}}$. Microcrystalline precipitates were obtained by flocculation with sodium paratoluene sulfonate. The composition FE(OH)$_{2.7}$Cl$_{0.3}$ was independent of a and age of the solution. Magnetic susceptibility of these precipitates was virtually identical in the temperature range 77–300 K. Mössbauer spectra[30] of frozen solutions were identical with respect to isomer shift, quadrupole splitting and magnetic hyperfine splitting parameters. Similarly, x-ray powder diagrams of flocculated polynuclears confirmed β-FeO(OH) structure.[15] Flocculated polynuclears were easily soluble in NaClO$_4$ solution, pH $\approx$ 1.5, and could be reprecipitated by adding NaCl. Aging processes in perchlorate solutions proceed very slowly. These characteristics, altogether, provide ample evidence for a well-defined structure of the polynuclears in solution.

Small angle laser light-scattering methods were applied to determine the weight average p_w of the coefficient p in (17),

$$\text{Fe}_p\text{O}_r(\text{OH})_s^{3p-s} \quad < 2r + s/p > \; = 2.7, \tag{17}$$

and the translational diffusion coefficients of the macromolecular polynuclears.[31] The last type of information is restricted to rather monodisperse particle systems.

The results of an extended study in the concentration ranges (15),

$$\begin{array}{lll} \text{Fe (III)} & : & 0.05 - 0.4\ \text{M} \\ \text{Cl}^- & : & 0.2 - 1.5\ \text{M} \\ a & : & 0 - 2.4, \end{array} \tag{18}$$

provided a rather clear picture of the phenomena all the way from Fe^{3+} to polynuclears in solution ("colloidal particles") and, finally, to precipitates. The conclusions are summarized in the order of consecutive phenomena:

Nucleation is localized with respect to time and space, that is, it occurs at the inlet of base solution within the time of intermixing with the bulk solution. The concentration of nuclei formed in this way is reflected in the concentration of polynuclears emerging from subsequent growth. Depending on the base added at strictly reproducible conditions to identical educt solutions, polynuclear size varies from $p_w = 1000$ to 60,000 at the limit of primary growth, which is indicated by virtually stationary pH values. Carbonate CO_3^{2-} differs from bases OH^-, NH_3, imidazol and pyridine by provoking relatively high degrees of supersaturation. Nucleation is heterogeneous at values of a close to zero but homogeneous if $a > a_{\min}$. Nucleation can be induced by dust particles or by crystals of NaCl and $CaCl_2$.

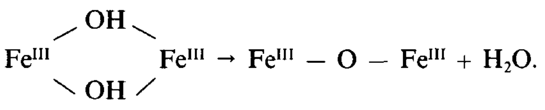
Anisotropy of growth dominates the evolution of polynuclears in the primary stage of formation. The length 700 Å was reached when the width of crystalline needles was about 30 Å.

Growth rates of polynuclears in the primary stage close to supersaturation are compatible with average rate constant $\bar{k}$ of intrinsic steps (19),

$$PN(p) + FeOH^{2+} \xrightarrow{\bar{k}} PN(p+1), \tag{19}$$

in the order of $10^2 M^{-1}s^{-1}$.

Aging of polynuclears does not involve the transformation of hydroxobridges into oxobridges (20) but rather a change of their shape,



$$Fe^{III}\!\begin{array}{c}\diagup OH \diagdown \\ \\ \diagdown OH \diagup\end{array}\!Fe^{III} \rightarrow Fe^{III} - O - Fe^{III} + H_2O. \tag{20}$$

The specific surface is reduced by decrease of length in favor of an increase in width. The kinetics of the net process is defined by the rates of dissociation reactions producing mononuclear Fe^{3+} from the terminal sites of the needles in conjunction with growth in the center part.

Precipitation of polynuclears yielding products that contain 0.3 Cl per Fe(III) is reversible. The solubility depends on the size, shape and chloride concentration, as well as on ionic strength.

Chloride effects are operating at all levels, that is, in nucleation, growth, aging and acid decomposition that is accelerated quite considerably by chloride. The effect of chloride in nucleation is removed if sodium hydroxide at a concentration level of about 1 M is used instead of Na_2CO_3 or $NaHCO_3$ solution. Feitknecht et al.[32] reported that there is a memory effect in amorphous primary precipitates that transforms into crystalline phases α-FeO(OH) and β-FeO(OH) on aging. The fraction of α-FeO(OH) increases if both a and the concentration of NaOH are increased. The observation time was 15 years! Cationic polynuclears with β-FeO(OH) structure do not enclose chloride ions, as shown by tracer exchange experiments with ^{36}Cl.[33]

Expulsion of chloride from precipitates is achieved by raising the pH and washing out the chloride gradually. The linewidth of x-ray powder patterns increases significantly toward stoichiometric β-FeO(OH) obtained in this way. There is no agreement as yet on the mechanism of this substitution.

Structural Aspects

It is easy to accept that the chloride content can be reduced to any desired value. However, it is rather a challenge to rationalize the limiting value $x = 0.3$ as provided by Biedermann's solubility product (11) and by chemical analysis of precipitates. The fragment shown in Figure 6 exhibits the correct stoichiometry by structural constraints, and it fits the β-FeO(OH) structure as indicated in Figure 4. In this linear array, the limiting value for $p \rightarrow \infty$ is $\bar{n} = 2.67$, but $\bar{n} = 2.65$ is obtained for p as low as 300, whereby the length of the array is about 300 Å. The limiting composition $Fe_3O_2(OH)_4$ of the structural embryo is maintained if embryos are combined in the way indicated in Figure 4, that is, by merely removing water ligands from the embryos. The cross section in Figure 4 just about matches the width of polynuclears as derived from dynamic light-scattering data.

Of course, these considerations do not explain real growth mechanisms, but they are useful to define the problem, particularly with regard to nucleation. The chemical potential of polynuclear oxohydroxocomplexes as a function of p is expected to pass a maximum region that certainly contains polynuclears such as $Fe_6O(OH)_9^{7+}$ ($\bar{n} = 1.83$) indicated in Figure 6 in which the total array is $Fe_{15}O_7(OH)_{21}^{10+}$ ($\bar{n} = 2.33$). If the first stage of growth is a cycle involving three steps, the unit shown in Figure 6 would possibly represent a situation beyond the critical size. The position of chloride is indicated in the projection of the embryo in Figure 5. Chloride ions are assumed to be rather localized on the basis of model calculations of the electrostatic potential in the environment of the polynuclears.[34] Finally, we return to Eqs. (3) and (4) in which $Fe_3(OH)_4^{5+}$ and $Fe_4O(OH)_4^{6+}$ were suggested to represent early members $p = 3;4$ in the formation of polynuclears in acid solution.

The local environment in α-FeO(OH), as well as in β-FeO(OH), is facial-$FeO_3(OH)_3$.[35] Since structural transformations from amorphous material to α-FeO(OH) are known to require high activation energies, oxide bridges have to be formed at an early stage in nucleation. Moreover, the chain $Fe[(OH)_2Fe]_{p-1}$, $\bar{n} = 2$, has never been found to be an intermediate in Fe(III) hydrolysis. As a conclusion, the structures in Figure 7 are assigned to species $p = 3;4$, which possibly are predecessors to further small polynuclears involved in nucleation.

SUMMARY AND CONCLUSIONS

At moderate temperatures, the variety of products that can emerge from hydrolysis of iron(III) solutions is virtually unrestricted with respect to morphologic properties and distributions of local units $FeO_i(OH)_j(H_2O)_k$ with constant coordination number $(i + j + k) = 6$. This variety reflects the properties of mononuclear complexes $Fe(OH)_i^{3-i}$ in conjunction with pH and its rate of change in the solution as a function of space and time. Structurally well-defined polynuclear oxohydroxocomplexes $Fe_pO_r(OH)_2^{3p-(2r+s)}$ can be obtained in highly supersaturated solutions under conditions that secure

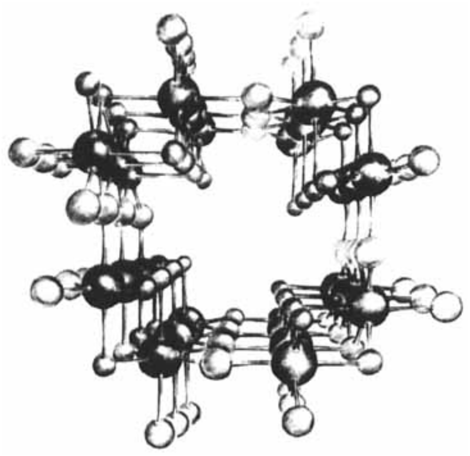


FIGURE 3 The idealized structure of β-FeO(OH) in a perspective view along the fourfold axis of the unit cell $a = b = 10.44$ Å, $c = 3.01$ Å.[27]

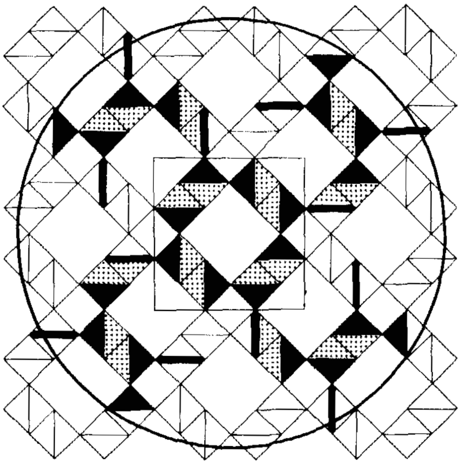


FIGURE 4 Projection of a hypothetic crystalline polynuclear composed of structural embryos. Face sharing of octahedrons involves loss of water from embryos but constancy of $\bar{n} = 2.67$. The diameter of the circle is 30 Å.

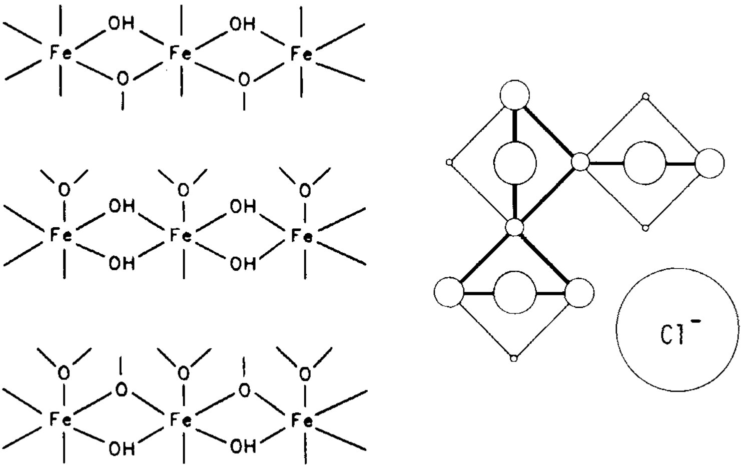


FIGURE 5 Chains of octahedrons with limiting stoichiometries $\bar{n}$ = 2.33, 2.67 and 3.00 and the projection of the structural embryo, $\bar{n}$ = 2.67 (Figure 5). Outer sphere Cl^- is shown at the minimum energy position.

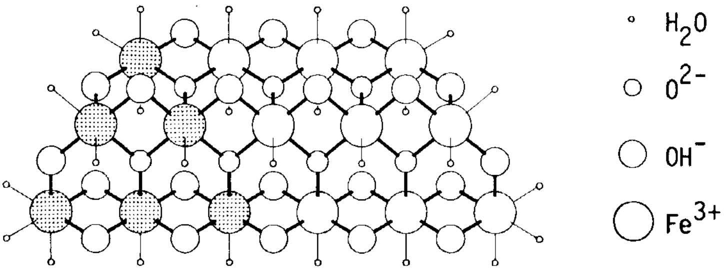


FIGURE 6 The polynuclear $Fe_{15}O_7(OH)_{21}^{10+}$, $\bar{n}$ = 2.33, as a part of a structural embryo $[Fe_3O_{2/3}(OH)_{4/3}]_p^{0.33p}$; $p \rightarrow \infty$; $\bar{n} \rightarrow 2.67$.

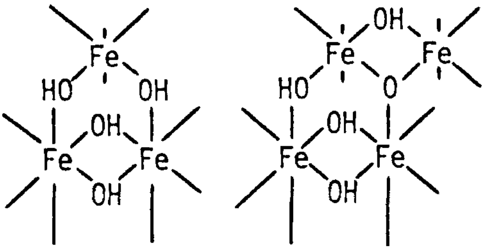


FIGURE 7 Structures assigned to $Fe_3(OH)_4^{5+}$ and $Fe_4O(OH)_4^{6+}$.

homogeneous nucleation. Heterogeneous nucleation is prevailing in the low supersaturation range in which Fe^{3+}, $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$ are preponderant species. Nucleation and growth of crystals or cationic polynuclears are very much affected at pH $\leq$ 5 by general and specific anion effects, showing that any moderately strong ligand will perturb pathways of hydrolysis. Nucleation phenomena and interfacial properties call for attention. Hydrolysis induced by oxidation of Fe^{2+} and ligand interactions are important topics in aquatic chemistry,[5] soil chemistry,[23] biogeochemistry,[36] biochemistry[7,37] and technology.[38]

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