

Hydrolysis of Inorganic Iron(III) Salts

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I. Introduction

The importance of iron chemistry in geological, environmental, metallurgical, industrial, and biological contexts makes understanding of iron chemistry of fundamental significance. In connection with metallurgical interest in the behavior of Fe(III) in weakly acid solutions, literature on the hydrolysis and precipitation of Fe(III) was retrieved. The amount of literature since 1960 pertaining to the processes of hydrolysis and precipitation of Fe(III) justified production of a review on the subject. The work of Spiro et al.,¹⁻⁴ Hsu et al.,⁵⁻⁷ Quirk et al.,⁸⁻¹⁰ and De Bruyn et al.¹¹⁻¹⁵ are especially noteworthy. Thermodynamic data on Fe(III) hydrolysis have been reviewed or compiled by Langmuir,¹⁶ Sylva,¹⁷ Baes and Mesmer,¹⁸ and Smith and Martell.¹⁹

The scope of this review includes studies on the hydrolysis and precipitation of Fe(III) from aqueous solutions of its inorganic salts, chiefly the nitrate, perchlorate, chloride, and sulfate. After a survey of structural and thermodynamic properties of the relevant Fe(III) species, this review examines the reactions



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of hydrolysis and precipitation in aqueous Fe(III) solutions. These reactions, most of which occur slowly, include the formation, aging, and agglomeration of a red cationic hydrolytic polymer.^{1-4,8-15} The constitution of the slowly precipitated hydrated oxide products is also examined. For comparison, the constitution and aging of rapidly precipitated hydrated iron(III) oxides is briefly surveyed. Techniques employed in the study of Fe(III) hydrolysis and precipitation include pH measurement, visible and infrared spectroscopy, ultracentrifugation, electron microscopy, and X-ray diffraction. Electrokinetic properties and thermal dehydration of precipitated iron oxides are not considered. Iron(III) oxides, hydrated oxides, or related compounds formed via oxidation of elemental iron or iron(II) compounds, or via other redox reactions, are not considered.

II. Structural Data

A. Crystalline Iron(III) Oxides and Hydrated Oxides

The characterized crystalline iron(III) oxides and hydrated oxides are Fe_2O_3 and $FeO(OH)$, each of which is polymorphic. The phases important in the hydrolysis and precipitation of Fe(III) salts are listed in Table I.²⁰⁻³² Their crystal structures are illustrated schematically in Figure 1. The structures of α - and β -

TABLE I. Crystalline Iron(III) Oxides and Hydrous Oxides

Fe(III) compound	isomorphs	structural formula	ref
α -Fe ₂ O ₃ (hematite)	α -Al ₂ O ₃ (corundum)	FeO _{6/4}	20-22
α -FeO(OH) (goethite)	α -AlO(OH) (diaspore)	<i>fac</i> -FeO _{3/3} (OH) _{3/3}	23-25
β -FeO(OH) (akaganeite)	M' _x MnO ₂ (hollandite) ^a	<i>fac</i> -FeO _{3/3} (OH) _{3/3}	26-28
γ -FeO(OH) (lepidocrocite)	γ -AlO(OH) (boehmite)	<i>cis</i> -FeO _{4/4} (OH) _{2/2}	23, 29-32

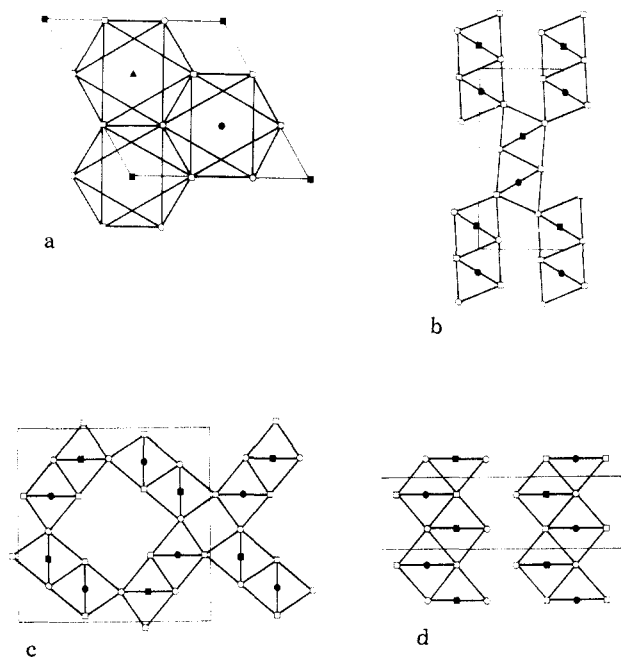
^a M' = K, Ba, etc.

Figure 1. Schematic crystal structures: (a) Hematite (α -Fe₂O₃) (R3c, Z = 6; a = 503, c = 1375 pm); projection along [001], (●) Fe at z = 0, 1/6, 1/2, 2/3; (Δ) Fe at z = 0, 1/3, 1/2, 5/6; (■) Fe at z = 1/6, 1/3, 2/3, 5/6; (○) O at z = 1/12, 5/12, 3/4; (□) O at z = 1/4, 7/12, 11/12. (b) Goethite (α -FeO(OH)) (Pbnm, Z = 4; a = 464, b = 998, c = 303 pm); projection along [001], (●) Fe at z = 1/4; (■) Fe at z = 3/4; (○) O at z = 1/4; (□) O at z = 3/4. (c) Akaganeite (β -FeO(OH)) (I4/m, Z = 8; a = 1048, c = 302 pm); projection along [001], (●) Fe at z = 0; (■) Fe at z = 1/2; (○) O at z = 0; (□) O at z = 1/2. (d) Lepidocrocite (γ -FeO(OH)) (Bbmm, Z = 4; a = 1253, b = 388, c = 307 pm); projection along [001], (●) Fe at z = 0; (■) Fe at z = 1/2; (○) O at z = 0; (□) O at z = 1/2.

FeO(OH) are built of double chains of edge-shared Fe(O,OH)₆ octahedra; this feature is also discernible in the structure of γ -FeO(OH). The double-chain structural element is illustrated in Figure 2. In contrast, the structure of α -Fe₂O₃ does not contain this double-chain element.

B. Aqueous Iron(III) Species

Of interest here are the species Fe³⁺, Fe(OH)²⁺, Fe(OH)₂⁺, and Fe₂(OH)₂⁴⁺ or Fe₂O⁴⁺ that exist in aqueous Fe(III) salt solutions.¹⁶⁻¹⁹ The Fe³⁺ ion has been shown to exist as the octahedral [Fe(OH₂)₆]³⁺ complex in Fe(NO₃)₃·9H₂O,³³ in the alums, e.g., CsFe(SO₄)₂·12 H₂O,³⁴ and in solution.³⁵⁻³⁷ The Fe(OH)₂⁺ and Fe(OH)₂⁺ species derived by deprotonation of [Fe(OH₂)₆]³⁺ are expected to possess the structures [Fe(OH₂)₅(OH)]²⁺ and *cis*- or *trans*-[Fe(OH₂)₄(OH)₂]⁺, respectively. The dimeric species Fe₂(OH)₂⁴⁺ or Fe₂O⁴⁺ has been structurally characterized only in the form of complexes with organic ligands. In one complex, the structure is [L₅-FeOFeL₅] where L₅ is a pentadentate amine.³⁸ Of the three other complexes, one is [L₃(H₂O)₂FeOFe(OH₂)₂-L₃]³⁹ and the other two are [L₃(H₂O)Fe(OH)₂Fe(OH₂)L₃]^{40,41} in all three L₃ is a substituted picolinate.

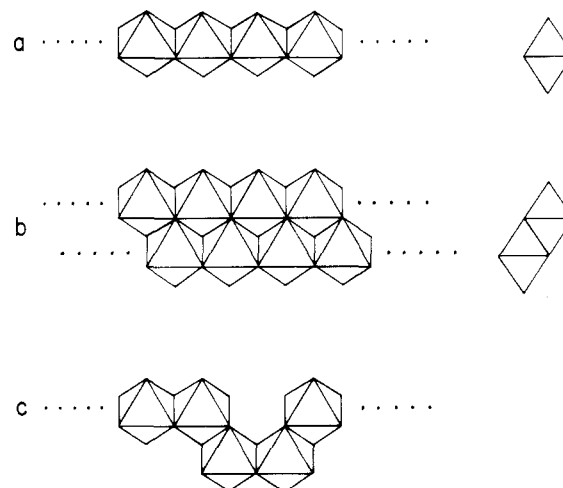


Figure 2. Chains of Fe(O,OH,H₂O)₆ octahedra: (a) Single straight chain, *trans*-FeX₂X_{4/2}; side and end views. (b) Double straight chain, *cis-fac*-FeXX_{2/2}X_{3/3}; side and end views. (c) Single kinked chain, *trans*- and *cis*-FeX₂X_{4/2}.

TABLE II. Gibbs Energy Data for Fe(III) Species

species	ΔG_f° , kJ/mol	ref
Fe ³⁺ (aq)	-17 ± 1 ^a	16, 54-59
(1/2) α -Fe ₂ O ₃ (hematite)	-371 ± 1	16, 49, 50, 51
α -FeO(OH) (goethite)	-489 ± 1	50, 52, 53
α -FeO(OH) (goethite)	-491 ± 1	16

^a Based on ΔG_f° [Fe²⁺(aq)] = -91 ± 1 kJ/mol.^{16,54-58}

The existence of both Fe(OH)₂Fe and FeOFe forms with similar ligands suggests that the energy difference between Fe^{III}(OH)₂Fe^{III} and Fe^{III}OFe^{III} + H₂O is small, and the presumed species [(H₂O)₄Fe(OH)₂Fe(OH₂)₄]⁴⁺ and [(H₂O)₅FeOFe(OH₂)₅]⁴⁺ may exist in equilibrium in solution. However, assessments of magnetic, infrared, and kinetic data on aqueous Fe(III) solutions indicate that the dimeric species should be formulated Fe₂(OH)₂⁴⁺ rather than Fe₂O⁴⁺.^{42,43}

C. Coordination of Iron(III) by O²⁻, OH⁻, and H₂O

In all the species cited above, Fe(III) is octahedrally coordinated by O²⁻, OH⁻, or H₂O. A survey of Fe(III) coordination in oxides, hydroxides, and aquo species by the author⁴⁴ shows that Fe(III) in acidic oxide environments, including aqueous solutions, is octahedrally coordinated. Only in basic environments does Fe(III) occur in tetrahedral coordination to a significant extent; examples include β -NaFeO₂,⁴⁵ Na₅FeO₄ and related compounds,⁴⁶ BaFe₂O₄,⁴⁷ and the rare-earth iron garnets Ln₃Fe₅O₁₂⁴⁸ (Ln = rare-earth element) in which three-fifths of the Fe(III) ions are tetrahedrally coordinated.

III. Thermodynamic Data

Gibbs energy data for Fe₂O₃, FeO(OH), and Fe³⁺-(aq)^{16,49-53} are given in Table II. The value for Fe³⁺(aq)

TABLE III. Solubility Products of Fe(III) Oxides and Hydrated Oxides at 25 °C and 0 Ionic Strength

$(1/2)\text{Fe}_2\text{O}_3(\text{s}) + (3/2)\text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 3\text{OH}^-$ $\text{FeO}(\text{OH})(\text{s}) + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 3\text{OH}^-$		
solid phase	$-\log K_{\text{so}}^a$	ref
$(1/2)\alpha\text{-Fe}_2\text{O}_3$ (hematite)	41.7 ^b	Gibbs energies (Table II)
	42.7	19
	$\leq 41.9 \pm 0.4$	16
$(1/2)\gamma\text{-Fe}_2\text{O}_3$ (maghemite)	$\geq 38.8 \pm 0.5$	16
$\alpha\text{-FeO}(\text{OH})$ (goethite)	41.7 ^b	Gibbs energies (Table II)
	41.5	17-19
	$\leq 41.2 \pm 0.4$	16
$\beta\text{-FeO}(\text{OH})$ (akaganeite)	$36 + x^c$	18, 60
$\gamma\text{-FeO}(\text{OH})$ (lepidocrocite)	$\geq 38.7 \pm 0.5$	16
"Fe(OH) ₃ " (amorphous)	37.1-39.0 ^d	16-19

^a Uncertainties are ± 0.1 to 0.2 in most cases. ^b Based on $\Delta G_f^\circ[\text{Fe}^{3+}(\text{aq})] = -17$ kJ/mol (see text) and CODATA values for $\text{H}_2\text{O}(\text{l})$ and $\text{OH}^-(\text{aq})$.⁶¹ ^c Estimated from data given for $\text{Fe}(\text{OH})_2\text{Cl}_{0.3}$ in references, with correction for chloride complexation from data in ref 19, and estimation of a correction of ~ 1 log K unit^{18,19} to convert from ionic strength 0.5 to 0. The term x is log K for the reaction $\beta\text{-FeO}(\text{OH})(\text{s}) + \text{H}_2\text{O} + 0.31\text{Cl}^- \rightarrow \beta\text{-Fe}(\text{OH})_{2.7}\text{Cl}_{0.3}(\text{s}) + 0.3\text{OH}^-$. ^d Range for fresh to aged precipitate.

is based on the value for $\text{Fe}^{2+}(\text{aq})$ ^{49,50,54-58} and the standard reduction potential E° ($\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$) of $+0.77$ V.⁵⁹ Recent data favor a value of -91 ± 1 kJ/mol^{18,54-58} rather than -79 kJ/mol^{49,50} for $\Delta G_f^\circ[\text{Fe}^{2+}(\text{aq})]$.

Table III gives solubility product data for Fe_2O_3 , $\text{FeO}(\text{OH})$, and amorphous hydrous iron(III) oxides.^{16-19,60,61} Both direct determinations and values calculated from Gibbs energy data (Table II) are included.

Equilibrium data for the hydrolysis reactions of Fe(III) are given in Table IV.^{18,19,62} The species Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, and $\text{Fe}_2(\text{OH})_4^{4+}$ are well characterized. The species $\text{Fe}_3(\text{OH})_4^{5+}$ was reported in one

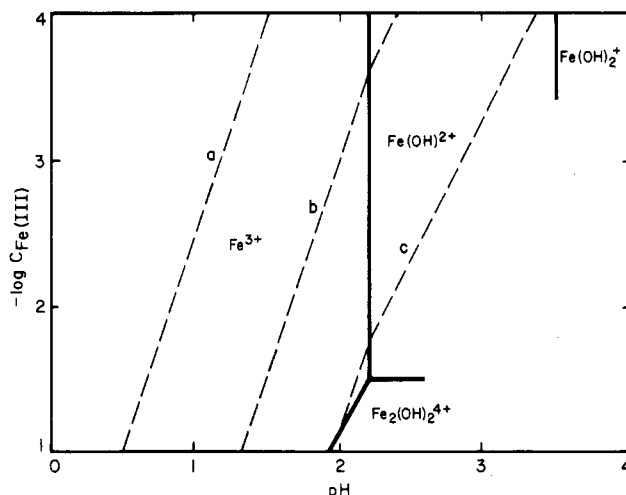
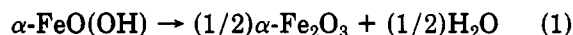


Figure 3. Approximate predominance-area pH vs. log $C_{\text{Fe(III)}}$ (M) diagram, 25 °C, ionic strength 0. The dashed lines labeled a, b, and c are the saturation lines for goethite, aged amorphous hydrous oxide, and fresh amorphous hydrous oxide, respectively.

study.^{18,19} The claim for a species $\text{Fe}_{12}(\text{OH})_{34}^{2+}$ ⁶³ has been refuted.¹¹ A pH vs. log $C_{\text{Fe(III)}}$ diagram, calculated from the data in Tables III and IV, is given in Figure 3; $C_{\text{Fe(III)}}$ is the total concentration of dissolved Fe(III). Table V gives pH values for Fe(III) salt solutions and shows that unacidified Fe(III) salt solutions are unstable with respect to precipitation of $\alpha\text{-Fe}_2\text{O}_3$ or $\alpha\text{-FeO}(\text{OH})$ at all concentrations with the possible exception of very high concentrations. Solutions are unstable to precipitation of amorphous hydrous oxide at concentrations $< 10^{-2}$ mol/L.

The stability of $\alpha\text{-FeO}(\text{OH})$ relative to $\alpha\text{-Fe}_2\text{O}_3$ and water is uncertain; ΔG°_{298} for reaction 1 is 0 ± 1 kJ/mol,



based on the data in Table II. Langmuir⁶⁴ has analyzed the dependence of ΔG of reaction 1 on particle size and

TABLE IV. Equilibrium Constants for Fe(III) Hydrolysis Reactions^a

temperature, °C	25	25	25	25	80
ionic strength, M	0	1.0	2.67	3.0	2.67
$-\log K$ for reaction					
$\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^{2+} + \text{H}^+$	2.2	2.8	2.9	3.0	2.1
$\text{FeOH}^{2+} + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_2^+ + \text{H}^+$	3.5	3.2	2.8	3.3	1.1
$\text{Fe}(\text{OH})_2^+ + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + \text{H}^+$	6				
$\text{Fe}(\text{OH})_3 + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_4^- + \text{H}^+$	10				
$2\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{Fe}_2(\text{OH})_4^{4+} + 2\text{H}^+$	2.9	2.7	3.2	2.9	2.5
$3\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3(\text{OH})_4^{5+} + 4\text{H}^+$	6.3			5.8	
ref	18, 19	18, 19	62	18, 19	62

^a Values are rounded averages because uncertainties are generally ± 0.1 - 0.2 .

TABLE V. pH Values of $\text{Fe}(\text{NO}_3)_3$ Solutions, 20-25 °C

$C_{\text{Fe(III)}}$, M	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
pH values					
no precipitation ^a	1.5	2.3	3.0	3.8	4.7
saturation with ^a					
hematite ^b	0.4	0.7	1.1	1.4	1.8
goethite ^c	0.5	0.8	1.2	1.5	1.9
aged amorphous hydrous oxide ^d	1.3	1.7	2.1	2.5	3.0
fresh amorphous hydrous oxide ^e	2.1	2.5	2.9	3.5	4.3
titration data, $\text{Fe}(\text{NO}_3)_3$ by NaOH ^f					
pure $\text{Fe}(\text{NO}_3)_3$ solution	1.5	2.3	3.2		
minimum for polymer formation	1.3	2.1	2.8		
minimum for immediate relaxation ^g	1.6	2.3	3.0		
plateau	2.0	2.5	3.2		

^a Calculated with equilibrium constants in Tables III and IV. ^b $\text{p}K_{\text{so}} = 41.7$. ^c $\text{p}K_{\text{so}} = 41.5$. ^d $\text{p}K_{\text{so}} = 39.0$. ^e $\text{p}K_{\text{so}} = 37.1$. ^f Interpolated from data of De Bruyn et al.^{11,12} ^g pH_B ; see text, section IVF1.

concludes that the effect of particle size on ΔG becomes significant (exceeding 5 kJ/mol) for particle sizes $<10^{-1}$ μm .

IV. The Hydrolysis Reactions

The hydrolysis of inorganic Fe(III) solutions consists of several steps: (1) formation of low-molecular-weight species; (2) formation of a red cationic polymer; (3) aging of the polymer, with eventual conversion to oxide phases; and (4) precipitation of oxide phases directly from low-molecular-weight precursors. After a summary of investigative techniques, the hydrolysis steps, especially the formation, structure, and chemistry of the polymer, are described.

A. Investigative Techniques

Most of the hydrolysis studies have been conducted on solutions of Fe(III) nitrate, perchlorate, or chloride in the concentration range 10^{-3} – 10^{-1} M, at room temperature. The behavior of hydrolyzed Fe(III) solutions depends on the nature and mode of addition of basic reagents.^{1,11,65–67} Ordinary mixing of solutions of alkali hydroxide or ammonia with Fe(III) solutions results in immediate formation of a precipitate; if the amount of base added corresponds to ≤ 2.5 mol base per mole iron, the precipitate redissolves.

For reliable characterization of the hydrolysis process, it is necessary to add base so that precipitation does not occur. This has been accomplished by slow addition with rapid mixing of a weak base such as an alkali bicarbonate,^{1–10,65–67} slow addition of base solution with very rapid mixing in a specially designed vessel,^{11–15,68} or solvent-extraction removal of acid liberated by hydrolysis.⁶⁹ The solvent-extraction technique has the advantages of being homogeneous and avoiding introduction of extraneous ions into the solution.

Characterization of the hydrolysis reactions requires employment of a variety of modern experimental techniques, preferably concurrently. Most investigations satisfying this requirement have been conducted by four groups of investigators. Hsu et al.^{5–7} studied hydrolyzed $\text{Fe}(\text{ClO}_4)_3$ solutions by pH measurement, chemical analysis, turbidimetry, and ultrafiltration. Although they referred to the hydrolysis product in solution as colloidal ferric hydroxide, their data are concordant with the data of the other investigators, and indicate that their solutions contained the hydrolytic polymer. Quirk et al.^{8–10} employed pH measurement, chemical analyses, ultracentrifugation, and electron microscopy on hydrolyzed Fe(III) nitrate, perchlorate, and chloride solutions. De Bruyn et al.^{11–15} examined hydrolyzed Fe(III) nitrate, chloride, and sulfate solutions by visible spectrophotometry, light scattering, pH measurements, ultracentrifugation, and electron microscopy. Spiro et al.^{1–4} isolated the polymer from hydrolyzed $\text{Fe}(\text{NO}_3)_3$ solutions and characterized it by chemical analysis, ultracentrifugation, visible spectrophotometry, X-ray diffraction, infrared spectroscopy, and Mössbauer spectroscopy.

B. Low-Molecular-Weight Hydrolysis Products

The low-molecular-weight hydrolysis products, $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, and $\text{Fe}_2(\text{OH})_2^{4+}$, were discussed above in regard to their structures and equilibria. Their

equilibria are established rapidly, although the reactions involving $\text{Fe}_2(\text{OH})_2^{4+}$ are significantly slower than the reactions involving only monomers. Baes and Mesmer¹⁸ have reviewed the kinetics of the decomposition of $\text{Fe}_2(\text{OH})_2^{4+}$ by acid. The rate law is

$$-d[\text{Fe}_2(\text{OH})_2^{4+}]/dt = (k_1 + k_2[\text{H}^+])[\text{Fe}_2(\text{OH})_2^{4+}] \quad (2)$$

At 25 °C $k_1 \sim 0.4 \text{ s}^{-1}$ and $k_2 \sim 3 \text{ mol}^{-1} \text{ L s}^{-1}$. At 35 °C the rate constants are higher by a factor of about 2.

C. Formation of the Hydrolytic Polymer

Addition of base at room temperature to Fe(III) nitrate, perchlorate, or chloride solutions in amounts insufficient to precipitate hydrous oxide results in relatively rapid formation of the red hydrolytic polymer.^{1–4,8–15} Similar treatment of $\text{Fe}_2(\text{SO}_4)_3$ solutions also produces polymer; however, precipitation occurs at lower pH values and at a greater rate than in solutions of salts with the monovalent anions.^{14,66} Both Hsu and Ragone⁵ and this author⁶⁶ have observed that addition of sulfate salts to polymer formed by adding NaHCO_3 to solutions of Fe(III) perchlorate or nitrate causes rapid precipitation.

De Bruyn et al.^{11,12} titrated 6×10^{-4} – 6×10^{-1} M $\text{Fe}(\text{NO}_3)_3$ solutions with homogeneously added NaOH.⁶⁸ They observed titration curves consisting of three regions. In the first region, OH^-/Fe mole ratio 0 to ~ 1 , the pH increases. In the second region, OH^-/Fe mole ratio ~ 1 to 2.5, the pH curve is flattened to a plateau. In the third region, OH^-/Fe mole ratio ≥ 2.5 , the pH increases steeply and precipitation occurs. Table V gives pH values for pure $\text{Fe}(\text{NO}_3)_3$ solutions and for the plateau part of the titration curve derived by plotting the published data vs. Fe(III) concentration $C_{\text{Fe(III)}}$ and interpolating to round values of $C_{\text{Fe(III)}}$.

De Bruyn et al.¹³ also examined the effect of Cl^- on the titration of Fe(III) solutions by base. Results were similar to those obtained with $\text{Fe}(\text{NO}_3)_3$ solutions; however, in the plateau region the pH actually decreased slightly during the titration.

D. Composition of the Polymer

Spiro et al.^{1,3} and Quirk et al.⁸ isolated the hydrolytic polymer as amorphous solids from 0.02–0.3 M Fe(III) nitrate and chloride solutions by gel filtration and lyophilization and obtained chemical analyses. The solids dissolve readily in water or salt solutions, giving solutions that remain clear for several days. Hsu and Ragone⁵ analyzed the precipitates obtained by adding sodium sulfate solution to hydrolyzed 0.01 M $\text{Fe}(\text{ClO}_4)_3$ solutions. The derived OH^-/Fe ratios, given in Table VI, indicate that the polymer is cationic. One would expect that the OH^-/Fe mole ratio in the polymer would increase or possibly remain constant as OH^-/Fe mole ratio in the preparation solution is increased. The data of Spiro et al.^{1,3} agree with this expectation, but the data of Hsu and Ragone⁵ contradict it. Possible reasons for the contradictory data are that the sulfate precipitates were washed with alcohol–water mixtures during isolation, during which loss of sulfate as H_2SO_4 may have occurred; or that the precipitates may have contained colloidal hydrous oxide in addition to the polymer. The data show that the OH^-/Fe ratio in the polymer increases with age; this observation is con-

TABLE VI. Selected Data on the Composition of Isolated Polymers

anion in polymer	ref	initial $C_{\text{Fe(III)}}$ in prepn soln, M	OH^-/Fe in prepn soln	age, days	OH^-/Fe in isolated polymer
NO_3^-	1	0.3	2.0	<1	2.52
		0.3	1.0	<1	2.27
NO_3^-	8	0.1	2.0	0.1	2.45
		0.1	2.0	14	2.75
Cl^-	8	0.1	2.0	0.1	2.25
		0.1	2.0	14	2.9
SO_4^{2-} (pptn from soln of ClO_4^- salt)	5	0.01	1.0	<1	2.74
		0.01	2.0	<1	2.65
		0.01	1.0	12	2.81
		0.01	2.0	12	2.75

sistent with the pH decrease observed on aging of solutions containing the polymer (see section IVF). The lower OH^-/Fe ratio in fresh chloride polymer relative to that in fresh nitrate polymer may be due to coordination of some Cl^- to Fe(III) in the polymer. The greater increase in OH^-/Fe ratio with age in chloride polymers relative to that in nitrate polymers may be caused by replacement of coordinated Cl^- by OH^- . Additional evidence for the cationic nature of the polymer is its uptake, though slow, by cation-exchange resin,¹ and the metathetical replacement of nitrate by acetate.³ The fact that in the addition of base to Fe(III) salt solutions the maximum OH^-/Fe ratio obtainable without precipitation is about 2.5^{1,8-13,66,67} is also consistent with the above analytical data.

In contrast to these properties of the polymer, hydrous Fe_2O_3 precipitate (filtered, washed, and dried in air at room temperature) consists of hard glassy fragments which do not undergo dispersion or reversion to gel on contact with water.

E. Structure of the Polymer

Evaluation of the structural data indicates that the iron atoms in the polymer have coordination number 6, $\text{Fe}(\text{O},\text{OH},\text{H}_2\text{O})_6$. The infrared spectra and chemical metathesis observations reported by Spiro et al.³ indicate that NO_3^- is not coordinated to the iron in the polymer. X-ray diffraction data have been reported by Spiro et al.³ on solutions of the isolated polymer and by Magini⁶⁹ on hydrolyzed 2.8 M $\text{Fe}(\text{NO}_3)_3$ solutions. The published radial distribution functions are very similar, Magini's data showing better resolution. Spiro interpreted his data in terms of tetrahedral coordination of iron by oxygen at 0.21 nm and a nearest Fe-Fe separation of 0.35 nm. Magini interpreted his data in terms of octahedral coordination with Fe-O separation 0.20–0.21 nm, with a minimum Fe-Fe separation of 0.34–0.35 nm. However, Spiro et al.³ indicated that their optical spectra were more consistent with octahedral than tetrahedral coordination of Fe(III) . Comparison of observed Fe-O distances in the polymer with Fe-O distances in crystals supports octahedral coordination in the polymer. In crystals Fe-O distances are 0.20–0.21 nm for octahedral coordination^{48,70} and 0.18–0.19 nm for tetrahedral coordination.⁴⁶⁻⁴⁸ As noted above under structural data, tetrahedral Fe-O coordination in Fe(III) species in acidic aqueous media has not been observed. Magini⁶⁹ noted a continuity of structure from polymer-containing solution to precipitated hydrous oxide, further supporting octahedral Fe-O coordination.

The presumed $\text{Fe}(\text{O},\text{OH},\text{H}_2\text{O})_6$ octahedra in the polymer are most likely connected by sharing vertices or edges. Expected Fe-Fe distances are 0.38–0.41 nm for octahedra sharing vertices and about 0.30 nm for octahedra sharing edges.^{20-32,38-41} A minimum Fe-Fe distance of 0.34–0.35 nm was deduced by Spiro et al.³ and Magini⁶⁹ from their radial distribution functions; the contributions due to Fe-Fe interactions are not well resolved from those due to O-O interactions. Hence the data are inconclusive regarding the mode of linking of the FeO_6 octahedra in the polymer; edge and vertex sharing may both be present.

Electron microscopy^{10,12,13} has shown that the hydrolytic polymer in nitrate, perchlorate, or chloride solutions consists of spheres 2–4 nm in diameter at ages less than a few days. Spiro et al.¹ reported spheres of diameter ~ 7 nm, but their results have been criticized.^{10d} The density of the polymer isolated by gel filtration and lyophilization is about 3.5 g cm^{-3} .^{1,8} Molecular weight data reported by Spiro et al.,^{1,2} derived from the size of the spheres and density, composition, and sedimentation data, were criticized and reanalyzed by Quirk et al.^{10d} who calculated a molecular weight of $\sim 10^4$, an order of magnitude lower than Spiro's value. On the basis of a monomer formula $\text{Fe}(\text{OH})_{2.5}$ ^{0.5+} the number of iron atoms per polymer particle is $\sim 10^2$. The high molecular weight of the polymer is also shown by its separability from low-molecular-weight Fe(III) species by gel chromatography, where the elution volume of the polymer approximates the void volume of the gel column, and the elution volume of the low-molecular-weight Fe(III) approximates the total volume of the column.^{1,9}

In summary, the polymer consists of spheres 2–4 nm in diameter, containing $\sim 10^2$ Fe(III) ions, most likely in octahedral $\text{Fe}(\text{O},\text{OH},\text{H}_2\text{O})_6$ coordination. These $\text{Fe}(\text{O},\text{OH},\text{H}_2\text{O})_6$ octahedra are condensed most probably by sharing edges or vertices; as suggested by Spiro et al.³ for their tetrahedral interpretation, they may form long chains or ribbons which are coiled and to some extent crosslinked.

F. Aging of the Polymer

Hydrolyzed Fe(III) solutions containing the red polymer are not at equilibrium, as shown by changes that at 25 °C become evident in hours and continue for months to years. At higher temperatures the aging processes are accelerated. At 90 °C the lifetime of the polymer is very short,^{4,11} at least when formed from Fe^{3+} during titrations at that temperature. The changes observed on aging solutions containing the polymer

TABLE VII. pH Values of Fe(III) Solutions (Nitrate or Perchlorate)^a

initial $C_{\text{Fe(III)}}$, M OH ⁻ /Fe mole ratio	0.1 0	0.5	1.0	1.5	2.0	2.5	0.01 0	0.5	1.0	1.5	2.0	2.5
from observations ^b												
fresh (<1 day)	1.5	1.9	2.1	2.1	2.2	2.4	2.3	2.5	2.6	2.6	2.6	2.8
plateau (~10 days)	1.5	1.6	1.7	1.7	1.8	2.0	1.9	1.9	2.0	2.1	2.2	2.4
final (>100 days)	1.4	1.4	1.4	1.5	1.5	1.6	1.8	1.8	1.8	1.9	2.0	2.1
calcd, no precipitation or polymerization	1.5	2.0	3.0				2.3	2.6				
calcd, with precipitation												
goethite ^c	0.5	0.5	0.6	0.6	0.7	0.8	0.8	0.9	0.9	0.9	1.0	1.1
aged amorphous hydrous oxide ^d	1.3	1.4	1.4	1.4	1.5	1.6	1.7	1.7	1.8	1.8	1.9	2.0

^a Probable accuracy ± 0.1 unit. ^b Interpolated from data of De Bruyn et al.,^{11,12} Hsu and Ragone,⁵ and Quirk et al.⁸
^c $pK_{s0} = 41.5$. ^d $pK_{s0} = 39.0$.

include changes in chemical composition,^{5,8} decrease in pH,^{5-8,11-15} increase in light absorption,^{4,12-14} increase in turbidity or light scattering,^{5,12,65} increase in sedimentation coefficients,^{1,4,9,10,12,13} increase in particle size by electron microscopy,^{10,12,13} and decrease in the rate of degradation of the polymer by acid.⁴

The following paragraphs describe the aging of the red polymer obtained at room temperature in Fe(III) nitrate or perchlorate solutions. The aging behaviors of the polymers obtained in nitrate and perchlorate solutions are very similar, and are described together. The effects of chloride and sulfate on the aging of the polymer are considered separately.

1. pH

The pH of hydrolyzed Fe(III) solutions is observed to decrease with time. The progress of the pH changes depends on $C_{\text{Fe(III)}}$ and the OH⁻/Fe mole ratio. De Bruyn et al.^{11,12} observed that in 6×10^{-4} – 6×10^{-1} M Fe(NO₃)₃ solutions there is a minimum initial pH, referred to as pH_B, above which the pH decrease (relaxation) begins immediately after preparation of the solution. The pH_B corresponds to a OH⁻/Fe mole ratio of about 0.5. At pH values below pH_B, the pH begins to decrease only after an induction period. The induction period increases indefinitely at progressively lower initial pH values at constant $C_{\text{Fe(III)}}$. Hsu et al.^{5,7} also observed these two modes of pH variation in 2×10^{-4} – 6×10^{-2} M Fe(ClO₄)₃ solutions, although they did not report pH_B. Hsu⁶ observed that seeding solutions exhibiting the induction period with aged colloidal hydrous iron(III) oxide sol (or polymer solution, OH⁻/Fe = 1.0) markedly decreased the induction period. The pH decrease after the induction period continues at a decreasing rate and levels off at >100 days.

The rate of decrease in pH occurring in solutions titrated with NaOH to pH > pH_B is 0.2–0.5 pH unit per day in 0.01 M Fe(ClO₄)₃ and 0.2–0.3 pH unit per day in 0.06 M Fe(NO₃)₃ during the first day of aging, and then decreases.^{5,12} The data of Hsu and Ragone for 0.01 M Fe(ClO₄)₃,⁵ which extend to 300 days, show that the pH nearly levels off at time $t = 1$ –10 days, then decreases again with further aging to $t > 100$ days. This behavior suggests that two aging processes are occurring. The pH data of De Bruyn et al.¹² and the sparser pH data of Quirk et al.⁸ in 0.02–0.3 M Fe(III) solutions, if plotted against log t , likewise show that the pH levels off at $t = 1$ –10 days and subsequently decreases to $t > 100$ days. De Bruyn et al.^{12,14} and Spiro et al.^{1,4} proposed that the aging process consists of at least two steps (see section F9).

The pH values of hydrolyzed solutions at selected Fe(III) concentrations and OH⁻/Fe mole ratios are presented in Table VII. Approximate pH values calculated without precipitation or polymerization and with precipitation are also tabulated. The tabulated values derived from observations were obtained by plotting all reported observations and interpolating to the tabulated Fe(III) concentrations and OH⁻/Fe mole ratios. The final observed pH values (>100 days) agree well with the pH values calculated for precipitation of aged amorphous hydrous iron(III) oxide. The final pH values differ considerably from pH values calculated for goethite precipitation and indicate that the solutions may have not reached equilibrium. Alternatively, the difference of observed and calculated final pH values can be rationalized by particle-size considerations. The difference of 2.5 units in log K_{s0} values of goethite and aged amorphous hydrous iron(III) oxide is equivalent to a difference of -14 kJ/mol = $(\Delta G_f^\circ_{298}[\text{FeO}(\text{OH})] - \Delta G_f^\circ_{298}[\text{FeO}(\text{OH})]_{\text{aged amorphous}})$. This difference in Gibbs energy is attributable to particle size effects.⁶⁴ Magini⁶⁹ suggests that the aged amorphous precipitate may consist of microcrystals.

2. Optical Spectra and Light Scattering

Spectrophotometric and light-scattering observations were conducted by De Bruyn et al.¹² on hydrolyzed 0.06 M Fe(NO₃)₃ solutions, and by Spiro et al.⁴ on polymer separated from hydrolyzed 0.3 M Fe(NO₃)₃ solutions by gel chromatography. Turbidity measurements were also reported by Hsu et al.⁵⁻⁷ and Feitknecht and Michaelis.⁶⁵

The visible spectrum of the polymer consists of absorption increasing monotonically with decreasing wavelength from >800 to <400 nm. A shoulder at about 470 nm with an absorbance of 70–80 mol⁻¹ L cm⁻¹ was observed in solutions of separated polymer⁴ but not in the unseparated solutions.¹²

De Bruyn et al.¹² observed that solutions with pH < pH_B showed no change in absorbance and no turbidity until after the end of the induction period. Subsequently, the absorbance was reported to increase, and turbidity developed. Hsu et al.⁵⁻⁷ observed a rapid development of turbidity commencing at the end of the induction period.

In solutions with pH > pH_B (OH⁻/Fe 0.5–2.0) light absorption at 400–800 nm was reported to increase during several days.^{4,12} Observations were terminated because of development of turbidity. The rate of increase of light absorption decreases with time and apparently approaches zero by age 14 days. Further in-

crease in absorption reported at 14–23 days may have been caused primarily by light scattering.

Knight and Sylva⁶⁷ observed the time required for the appearance of turbidity, t_T , in hydrolyzed 0.03–0.25 M Fe(III) solutions. The variation of t_T with OH^-/Fe mole ratio showed a sharp minimum at $\text{OH}^-/\text{Fe} = 0.5\text{--}0.6$, which is close to the OH^-/Fe ratio at pH_B determined by De Bruyn et al.^{11,12} These data agree with observations reported previously by Feitknecht and Michaelis.⁶⁵

3. Ultracentrifugation and Electron Microscopy

Quirk et al.¹⁰ and De Bruyn et al.¹² conducted extensive studies of hydrolyzed Fe(III) solutions by ultracentrifugation and electron microscopy. Spiro et al.¹⁴ reported briefer observations. In hydrolyzed solutions with $\text{pH} < \text{pH}_B$ the concentration of polymer particles was too low for determination of the sedimentation coefficient S .¹² A low concentration of much heavier particles was detected in those solutions, even during the induction period. Hydrolyzed solutions with initial $\text{pH} > \text{pH}_B$ aged less than 1 day contain particles with small S values. Electron microscopy shows spherical particles 2–4 nm in diameter. During aging for 1–10 days, the S values increase slowly. Beginning at ages longer than 1–10 days, the S values undergo a large increase. Concurrent electron microscopy observations show that the polymer spheres agglomerate to rods, which in turn agglomerate to rafts. At ages >10 days, the spheres composing the rods and rafts lose their identity. During a period of months the rafts slowly flocculate to form a precipitate. Increased ionic strength accelerates the agglomeration of the rods to rafts.¹⁰

4. Composition of the Solutions

Quirk et al.⁸ monitored hydrolyzed 0.02–0.3 M Fe(III) nitrate and perchlorate solutions with initial $\text{pH} > \text{pH}_B$ by chemical analysis. The fraction of iron present as low-molecular-weight species remained nearly constant from 2 to 750 days. The fraction of iron present as precipitate was significant at 30 days and usually exceeded 50% at 750 days. The fraction of iron present as polymer decreased correspondingly, as expected if the polymer is precursor to the precipitate.

Hsu et al.^{5,7} determined total polymeric and colloidal iron in hydrolyzed 0.01 M $\text{Fe}(\text{ClO}_4)_3$ solutions by precipitation with Na_2SO_4 and found that the fraction of iron precipitated was nearly constant at ages 30–300 days for solutions with OH^-/Fe mole ratio 1.0 or 2.0 ($\text{pH} > \text{pH}_B$). For solutions with OH^-/Fe mole ratio 0 ($\text{pH} < \text{pH}_B$), no precipitate was obtained with Na_2SO_4 until after an induction period ranging up to several days. This behavior correlates with the data described above on solutions exhibiting an induction period for pH decrease.

Hsu and Ragone⁵ analyzed their solutions by ultrafiltration and showed that formation of large ($>10^2$ nm) particles occurred slowly during a period of months.

The constancy of the fraction of iron existing as low-molecular-weight species in solutions with initial $\text{pH} > \text{pH}_B$ at ages > 2 days indicates that polymer aging occurs without significant net uptake or release of low-molecular-weight iron species. The low-molecular-weight species may play a role in the aging mechanisms.

In solutions with initial $\text{pH} < \text{pH}_B$, Hsu and Ragone's⁵ ultrafiltration and precipitation data indicate that the concentration of low-molecular-weight iron species decreases after the induction period.

5. Degradation of the Polymer by Acid

Spiro et al.⁴ investigated the rate of degradation by HNO_3 of the polymer separated from hydrolyzed 0.3 M $\text{Fe}(\text{NO}_3)_3$ solutions with $\text{OH}^-/\text{Fe} = 2.0$ as a function of polymer age. They deduced a rate equation for degradation by acid:

$$d[\text{Fe}(\text{polymer})]/dt = -k[\text{Fe}(\text{polymer})]^m[\text{H}^+]^n \quad (3)$$

They determined $m = 1.0$ and $n = 1.0$ for HNO_3 concentrations <1 M for polymer aged ≤ 8 hours at 24–25 °C. For polymer separated, aged, and degraded at 24–25 °C, $k = 4 \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}$ for polymer aged 0.4 h, decreasing at a rate greater than exponential to $4 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$ for polymer aged 100–200 h.

Addition of polymer aged ≥ 1 day to excess 1–2 M HNO_3 results in immediate precipitation of an undetermined fraction of the iron.^{14,67} X-ray diffraction shows that the precipitate consists of microcrystalline goethite.⁶⁷

Hsu and Ragone⁵ also observed a slow reaction of hydrolyzed species with added acid.

6. Final Products of Aging

The hydrolyzed Fe(III) solutions begin depositing precipitates in days to weeks; precipitation continues for months. X-ray diffraction and infrared spectroscopy^{5–8,10,11,65,67} demonstrated that the precipitates formed from nitrate and perchlorate solutions consist of $\alpha\text{-FeO}(\text{OH})$ (goethite). Some $\gamma\text{-FeO}(\text{OH})$ (lepidocrocite) was also observed to form from solutions with low $C_{\text{Fe(III)}}$ and low OH^-/Fe ratios.^{5,8–10,65,67} The quantities and rates of formation of goethite and lepidocrocite indicate that goethite is the product of aging of the polymer, and lepidocrocite is formed directly from low-molecular-weight species.^{8,10d} Increasing ionic strength accelerates the precipitation rate of goethite but inhibits formation of lepidocrocite.^{8,10,12} Spiro et al.⁴ observed that the rate of precipitation is faster in solutions of polymer separated by gel filtration than in unseparated solutions and attributed this behavior to inhibition of agglomeration by low-molecular-weight species.

7. Effects of Chloride Ion

The effect of Cl^- on polymer aging was examined by Quirk et al.^{8,10} and De Bruyn et al.¹³ Polymer produced in chloride solutions consists of spherical particles like those obtained in nitrate or perchlorate solutions. The course of pH changes on aging is accelerated by the presence of Cl^- . This was indicated particularly by a decrease in pH during titration of chloride solutions on entering the plateau region of the titration curve.^{8,13} Substitution of Cl^- by OH^- in the polymer may contribute to the accelerated pH decrease.¹³ The sedimentation coefficients S for polymer in chloride solutions indicate earlier formation of large particles than in nitrate or perchlorate solutions.¹⁰ The S distributions in chloride solutions at ages 0.1–7 days were bimodal, in contrast to the unimodal distributions in nitrate or

TABLE VIII. Summary of Observations on Aging of Hydrolyzed Fe(III) Nitrate or Perchlorate Solutions^a

	pH < p <i>H</i> _B	pH > p <i>H</i> _B
approximate range of OH ⁻ /Fe mole ratio for C _{Fe(III)} ~ 10 ⁻¹ M	< 0.5	0.5 to 2.5
pH	<i>t</i> < <i>t</i> ₁ : no change <i>t</i> > <i>t</i> ₁ : decreases; levels off at <i>t</i> > 100 days	decreases; levels off at <i>t</i> = 1–10 days, subsequent decrease, levels off at <i>t</i> > 100 days
concentration of low-molecular-weight Fe(III) species	<i>t</i> < <i>t</i> ₁ : no change <i>t</i> > <i>t</i> ₁ : decreases; levels off at <i>t</i> > 100 days	little or no change from <i>t</i> = 2 to <i>t</i> > 100 days
light absorption (400–800 nm) and scattering	<i>t</i> < <i>t</i> ₁ : no change <i>t</i> > <i>t</i> ₁ : turbidity develops rapidly	increase in light absorption, leveling off by <i>t</i> = 14 days; turbidity subsequently develops
particle sizes by ultracentrifugation and electron microscopy	concentration of particles < 100 nm too low for characteriza- tion	initially spheres 2–4 nm diameter; agglomeration of spheres to rods at <i>t</i> = 1–10 days; subsequent agglomeration of rods to rafts continuing to <i>t</i> > 100 days
precipitation	precipitation begins at <i>t</i> > <i>t</i> ₁ , continuing slowly to <i>t</i> > 100 days	precipitation begins at <i>t</i> > 10 days, continuing slowly to <i>t</i> > 100 days

^a *t* = time; *t*₁ = induction period.

perchlorate solutions of the same ages. Electron microscopy observations on polymer in chloride solutions also showed faster agglomeration of the spheres. At 3–4 h rods were evident in chloride solutions but not in nitrate or perchlorate solutions.¹⁰ Agglomeration of rods to rafts was slower in chloride solutions than in nitrate or perchlorate solutions.

The principal effect of Cl⁻ on aging of the polymer is that the final precipitated product is β-FeO(OH) (akaganeite) rather than α-FeO(OH) (goethite).^{8,10b,13,26,60,67,71–73}

Quirk et al.^{10d} examined the effects of addition of Cl⁻ at different times during aging of the polymer obtained from nitrate solutions. Addition of Cl⁻ to 2-h-aged polymer from nitrate solutions resulted in sedimentation behavior analogous to that observed in hydrolyzed FeCl₃ solutions. Addition of Cl⁻ to 1-day-aged polymer had much less effect on the subsequent sedimentation behavior, which resembled that of polymer in nitrate solutions.

8. Effects of Sulfate Ion

De Bruyn et al.¹⁴ reported briefly on the effect of SO₄²⁻ on the hydrolysis and precipitation of Fe(III). Sulfate complexes strongly with Fe(III)^{19,62} and results in complex behavior depending on the SO₄²⁻/Fe ratio in the solutions. The presence of SO₄²⁻ results in precipitation at a greater rate and at lower pH values or OH⁻/Fe mole ratios than in solutions with only uninegative anions. Hematite and goethite were identified in the solids precipitated from sulfate solutions, but no sodium jarosite (approximately NaFe₃(OH)₆(SO₄)₂) was observed.

9. Summary of Aging Observations

Table VIII gives a summary of the observations pertaining to the aging of hydrolyzed Fe(III) nitrate or perchlorate solutions. The behavior is determined by the value of the initial pH relative to p*H*_B.

Spiro et al.^{1,4} inferred a two-step aging process of the polymer spheres from their data, which include kinetics of degradation by acid. The first stage consists of "hardening" of the polymer spheres, and the second, of

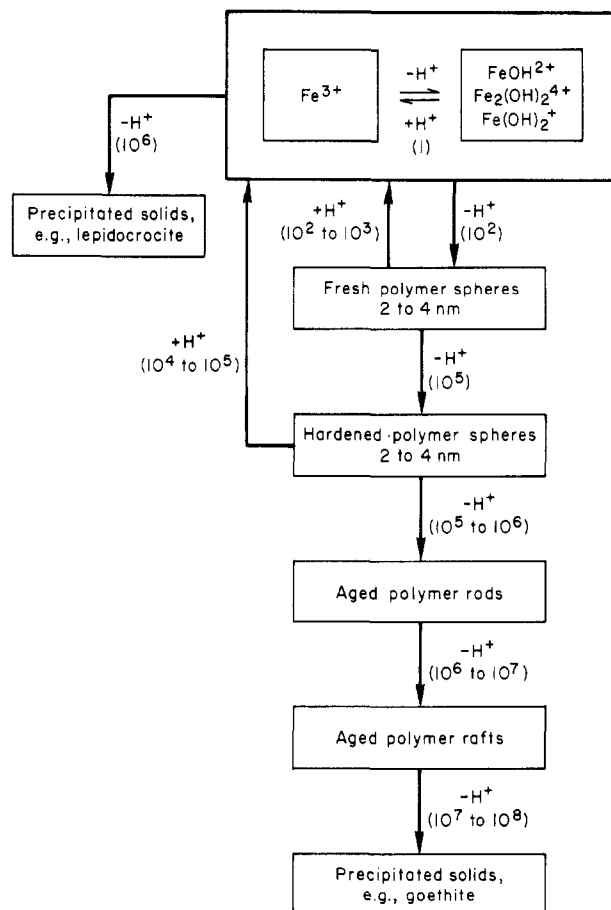


Figure 4. Hydrolysis processes in Fe(III) solutions. Numbers in parentheses give reaction times (s) at 25 °C.

agglomeration of the spheres. De Bruyn et al.^{12,14} from their data inferred a three-step hydrolysis process consisting of formation of the polymer spheres from low-molecular-weight species, aggregation of the spheres, and subsequent precipitation. The present review of the data justifies discerning a four-step hydrolysis process, depicted in Figure 4. The four-step process combines the schemes proposed by De Bruyn et al. and Spiro et al., namely polymer formation, hardening, aggregation to rods and rafts, and precipi-

tation. Also shown in Figure 4 is the formation of solids, e.g., lepidocrocite, directly from low-molecular-weight species.^{5,8,10,65,67} Mechanisms of these steps are discussed below in section I.

G. Products of High-Temperature Hydrolysis

The course of hydrolysis of Fe(III) solutions at high temperatures was examined briefly by De Bruyn et al.¹¹ The lifetime of the polymer decreases with increasing temperature, so that titrations conducted at 90 °C result in precipitation without formation of soluble polymer.

Several investigators have studied the solids precipitated during high-temperature hydrolysis without addition of base⁷⁴⁻⁷⁹ by X-ray diffraction, infrared spectroscopy, and Mössbauer spectroscopy. The sensitivity of the effects of Fe(III) concentration, anion identity and concentration, acidity, heating rate, temperature, and time on the nature of the products has been emphasized by Matijevic and Scheiner.⁷⁷ Matijevic et al.^{76,77} have prepared monodisperse colloidal solutions of various Fe(III) hydrolysis products by rigorously controlled high-temperature hydrolysis. The products obtained from nitrate, perchlorate, or bromide solutions are goethite or hematite.^{11,74,77-80} In the presence of chloride or fluoride, akaganeite is produced; goethite and hematite also form, especially after a long time.^{74,75,77,79,80} In the presence of sulfate, a variety of sulfate-containing products are formed in addition to goethite or hematite.^{14,74,76,79,80} The particle sizes of the colloids are 10²–10³ nm,^{76,77} 2 orders of magnitude larger than the polymer spheres discussed above.

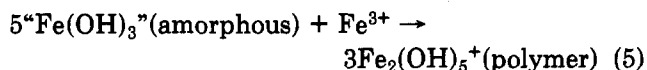
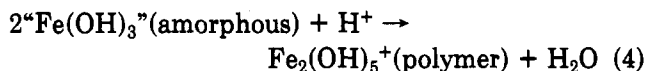
H. Constitution and Aging of Precipitated Hydrous Iron(III) Oxide Gels

There have been several recent reinvestigations of the constitution and aging of precipitated hydrous iron(III) oxide gels.^{65,69,73,81-97} The precipitates obtained by addition of bases to Fe(III) solutions under a wide variety of conditions are amorphous to X-rays and are not stoichiometric hydroxides. X-ray diffraction and radial distribution functions and infrared and Mössbauer spectroscopy indicate short-range order; interpretations of the data are conflicting.^{69,73,81-86}

Aging of the amorphous gels requires years at room temperature, and hours to days at 100 °C. The products formed are goethite or hematite and depend on solution compositions, temperature, time, and the details of preparation and pretreatment of the gel.^{65,78,83,87-95} A mixture of goethite and hematite often is obtained. There is a strong tendency toward production of goethite in solutions with pH > 10 and hematite in solutions with pH < 4. This is true even in the presence of Cl⁻, where akaganeite if formed is converted to goethite or hematite.^{83,87,88,92,94,96} Lepidocrocite is also converted to goethite or hematite.^{96,97}

The author made semiquantitative observations at 26–28 °C on the dissolution of amorphous hydrous iron(III) oxide which shed more light on its constitution.⁶⁶ Amorphous hydrous iron(III) oxide precipitated from unhydrolyzed or polymer-containing hydrolyzed Fe(NO₃)₃ solutions redissolved when treated with an amount of HNO₃ or Fe(NO₃)₃ solution calculated to give a final OH⁻/Fe = 2.0. The red solutions obtained apparently contain the hydrolytic polymer formed ac-

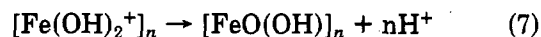
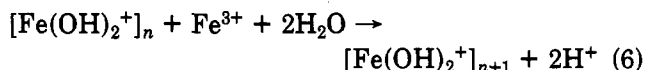
cording to the simplified reactions (eq 4 or 5). For fresh



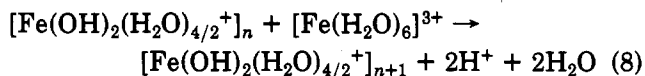
precipitates dissolution times were several seconds for reaction 4 and a few minutes for reaction 5 at reagent concentrations ~10⁻¹ mol/L. Dissolution times were observed as a function of ages of the precipitates and of the polymer-containing solution, OH⁻/Fe = 2.0, from which the precipitates were prepared. For constant polymer age and increasing precipitate age, dissolution times increased as expected. For constant precipitate age and increasing polymer age to ~8 days, dissolution times decreased by a factor of 2–3. For polymer ages 8–14 days, precipitate dissolution times increased modestly. The behavior observed in chloride solutions was similar to that observed in nitrate solutions. These observations suggest that the precipitated hydrous oxide may consist of aggregates of polymer spheres or structural entities from which the polymer is readily reformed. The decreased dissolution time of precipitates obtained from polymer solutions with ages up to 8 days is consistent with the hardening stage of polymer aging described above. In precipitate formed from hardened polymer, bonding between the presumed polymer-like entities is perhaps weaker than in precipitate formed from fresh polymer. If the dissolution mechanism consists of scission of the bonds connecting the polymer entities and regeneration of dissolved polymer, precipitate dissolution time should decrease with increasing polymer age during the hardening period, in agreement with the observations.

I. Discussion of Possible Reaction Mechanisms

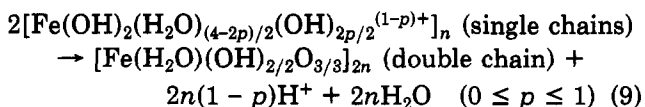
Mechanisms suggested for formation and aging of the hydrolytic polymer involve condensation of monomeric [Fe(H₂O)_{6-n}(OH)_n]⁽³⁻ⁿ⁾⁺ to form polymers in which Fe(III) ions are bridged by OH⁻ groups (olation, reaction 6) or O²⁻ ions (oxolation, reaction 7).^{11-14,98} The ololation



reaction 6 can be expressed in accordance with Figure 2 as



The oxolation reaction 7 is considered to be much slower than the ololation reactions 6 or 8.^{11-14,98} The representation of oxolation by reaction 7 suggests straightforward deprotonation, which should be fast and reversible. A more plausible representation of oxolation is reaction 9, which represents it as a condensation-



deprotonation of two single chains of edge-linked $\text{Fe}(\text{OH}, \text{H}_2\text{O})_6$ octahedra to double chains of $\text{Fe}(\text{O}, \text{OH}, \text{H}_2\text{O})_6$ octahedra (Figure 2). Considering the probable displacement of coordinated H_2O , OH^- , or other ligands and the steric requirements, a low rate for the oxolation reaction is not surprising.

Condensation of the double chains by elimination of water could ultimately result in the structures of goethite or akaganeite, as shown by comparing Figures 1b, 1c, and 2. Formation of lepidocrocite or hematite cannot proceed simply from the double chains (Figures 1d, 1a). This proposal is consistent with formation of goethite or akaganeite from the polymer and lepidocrocite from low-molecular-weight species in accord with the observations and proposals of Spiro et al.,¹⁴ Quirk et al.,¹⁰ and De Bruyn et al.^{11,14} Whether hematite forms via a process involving the polymer, or forms mainly from low-molecular-weight species, is not clear. Kinked chains (Figure 2) may be involved because the structure of hematite (Figure 1a) cannot be built from straight single or double chains.

The presence of Cl^- during hydrolysis results in formation of akaganeite from the polymer instead of goethite. The observations by Quirk et al.^{10d} on the effect of addition of Cl^- on aging of the polymer indicate that Cl^- is incorporated in the early stages of polymer formation and hardening, though some Cl^- is probably subsequently released. Consistent with this hypothesis is the presence of Cl^- in the resultant akaganeite.^{26,60,71,72,73,99,100}

The fact that the presence of F^- during hydrolysis also results in akaganeite formation, while goethite is obtained in nitrate, bromide, and perchlorate solutions, is consistent with the order of ionic volumes, namely, $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{ClO}_4^-$.

V. References

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