Applied Geochemistry, Vol. 9, pp. 23–36, 1994
Printed in Great Britain.

0883–2927/94 $6.00 + .00
Pergamon Press Ltd

Reactivity of aquatic iron(III) oxyhydroxides—implications for redox cycling of iron in natural waters

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(*Received* 22 *September* 1992; *accepted in revised form* 1 *July* 1993)

Abstract—The reactivity of iron(III) oxyhydroxides as reflected by their tendency to dissolve is of great importance in the redox cycling of iron and the bioavailability of iron to phytoplankton in natural waters. In this study, various iron(III) oxyhydroxides were produced by oxygenation of iron(II) in the presence of solutes, such as phosphate, sulfate, bicarbonate, valeric acid, TRIS, humic and fulvic acids, and in the presence of minerals, such as bentonite and δ-Al_2O_3 under conditions encountered in aquatic systems. The reactivity of the different iron(III) oxyhydroxides was subsequently assessed by means of a reductive dissolution using ascorbate and non-reductive dissolution using HQS (8-hydroxyquinoline-5-sulfonic acid) or oxalate. The experimental results show that the iron(III) oxyhydroxides with a low degree of polymerization exhibit higher reactivity than those with a high degree of polymerization or with high crystallinity. The quantity of active surface sites and the coordination arrangement of the functional groups at the surface of the iron(III) oxyhydroxides, especially the extent of the endstanding -OH groups per iron(III) ion determine the reactivity of iron(III) oxyhydroxides toward dissolution.

Surfaces, such as clay and aluminum oxides, not only accelerate the oxygenation reaction of iron(II), but also induce the formation of iron(III) oxyhydroxides which are more active toward the dissolution reactions. Polymerization of iron(III) oxyhydroxides on the surfaces occurs predominantly in two dimensions rather than in three dimensions.

In a laboratory experiment, the iron(III) oxyhydroxide formed in the presence of TRIS can be reduced by fulvic acid in a closed system under the following conditions: $Fe(OH)_3(s)$ 0.01 g/l, fulvic acid 5 mg/l, pH 7.5, 20°C. The kinetics of the reaction depend on the reactivity of iron(III) oxyhydroxide and reducing power of fulvic acid. Although reductants other than fulvic acid may be of importance in natural waters, this result provides the laboratory evidence that the $>Fe^{III}$-OH/Fe(II) is able to act as an electron transfer mediator for the oxidation of natural organic substances, such as fulvic acid, by molecular oxygen either in the absence of microorganisms or as a supplement to microbial activity.

INTRODUCTION

Reactivity of iron-rich particles, as reflected by their tendency to dissolve, has drawn much attention because the dissolution of aquatic iron(III) oxyhydroxides promotes the redox cycling of iron and facilitates the uptake of iron by phytoplankton in natural waters (Davison, 1985; Sulzberger *et al.*, 1989, 1990; Rich and Morel, 1990; Martin and Gorden, 1988; Candfield and Berner, 1987). Laboratory studies (Stumm *et al.*, 1985; Deng, 1992; Miller *et al.*, 1986; von Gunten and Schneider, 1991) have shown the variation in the dissolution rate of iron(III) oxyhydroxides between the various highly crystalline and amorphous particles as well as oligomeric colloids. Generally, the dissolution rate of highly crystalline iron(III) oxyhydroxides is lower than that of the poorly crystalline iron(III) oxyhydroxides. As suggested by Wehrli *et al.* (1990), the reactivity of a surface metal-centre is likely to increase with the number of terminal ligands or groups. In the case of iron(III) oxyhydroxides, the terminal (or endstanding) groups such as $>Fe(OH)_2$ and >Fe-OH are more active toward the interactions occurring at the solid–water interface than >Fe-OH-Fe< groups.

The occurrence of a large number of iron-rich particles has been widely observed in marine and freshwater systems (Wells and Goldberg, 1991; Buffle *et al.*, 1988; Laxen and Chandler, 1983; Tipping *et al.*, 1981). As reported by Wells and Goldberg (1991), the iron-rich colloids <120 nm in size accumulated near the oxic–anoxic boundary in the water column of the marine system. The iron-rich particles most probably originate from mononuclear $Fe^{III}(OH)_i^{(3-i)}$ produced by oxygenation of iron(II) in the oxic zone of natural waters and readily reduce to soluble iron(II) when they settle into the anoxic zone of natural waters (Davison, 1985; Davison *et al.*, 1980; Wersin *et al.*, 1991). The process of the oxygenation of iron(II) occurring at the oxic–anoxic boundary was recently simulated in a laboratory by von Gunten and Schneider (1991). They have produced highly reactive iron(III) colloids with a low nuclearity (1.0 nm $\leq$ radius $\leq$ 20 nm) by oxygenation of iron(II) in the presence of TRIS (Tris–(hydroxymethyl)-aminomethane, 0.1–0.5 M, pH 7.5) and in the presence of oxygen between 1.0×10^{-6} and 5.0×10^{-6} M. These conditions (O_2 and pH)

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are close to those at the oxic–anoxic boundary in natural waters (Berner, 1981). The iron(III) colloids produced can be readily dissolved by a reductive phenanthroline medium (0.025% phenanthroline, 0.4% hydroxylamine hydrochloride, acetate buffer pH 4.7). Although the TRIS medium is unrealistic with regard to natural waters because such a substance does not occur, it can act as an effective scavenger of the primary hydrolytic products formed by the oxygenation of iron(II) (von Gunten and Schneider, 1991; Schneider and Schwyn, 1987).

The studies on characterization of iron-rich particles collected from natural waters have shown that the particles are largely associated with inorganic species, organic materials and minerals (Buffle *et al.*, 1988; Tipping *et al.*, 1981; Perret *et al.*, 1990, ref. therein). The inorganic and organic components associated with the iron(III) particles are likely to affect the surface structure of iron(III) oxyhydroxides, or modify the iron(III) oxyhydroxides to a considerable depth (Hochella, 1990, ref. therein). As a consequence, the reactivity of the modified iron(III) oxyhydroxides may be quite different in comparison to pure iron(III) oxyhydroxides.

The complexity of characterizing iron-rich particles collected from natural waters has been addressed by Perret *et al.* (1990). The most important problems are linked to sampling and fractionation by using filtration and centrifugation techniques. The application of such techniques results in denaturation of the particles in terms of size, structure, morphology etc., before their characterization. Thus, the physico-chemical properties of the particles obtained after these operations may not fully represent those of the particles existing in the water column of natural waters. In this study, we have tried to avoid using the techniques which may denature the iron(III) oxyhydroxides. An attempt was made to obtain the chemical properties of the solid phases through chemical reactions, such as determination of the rate of dissolution.

This study was undertaken in order to better understand the redox cycling of iron in natural waters and assess the relationship between the formation of iron(III) oxyhydroxides by oxygenation of iron(II) and their reactivity to subsequent dissolution. The objectives of this study were: (1) to investigate whether solutes in natural waters (such as humic and fulvic acids, phosphate, sulfate, fatty acid) and surfaces of minerals (such as bentonite and aluminum oxide) could assist in real natural water systems in the formation of iron(III) oxyhydroxide as reactive as those formed in the presence of TRIS; (2) to test the reactivity of iron(III) oxyhydroxides by measuring the rate of a non-reductive dissolution using a complex former HQS (8-hydroxyquinoline-5-sulfonic acid) or oxalate, and the rate of a reductive dissolution using ascorbate; (3) to compare the rates of reductive dissolution by ascorbate for two different iron(III) oxyhydroxides (i.e. those formed in the presence of TRIS–imidazole medium and those formed in the presence of imidazole medium). In this context, an attempt was made to measure the redox potential of the iron(III) oxyhydroxide/iron(II) couple in order to see whether the reactivity could be related to the stability of the iron(III) oxyhydroxides; and (4) to estimate the net rate of the overall redox cycling of iron(III) oxyhydroxide/iron(II) coupled with fulvic acid in the absence of light and microorganisms.

EXPERIMENTAL

Materials

δ-Al_2O_3 (Degussa Company, Germany) and bentonite (montmorillonite, Aldrich-Chemie Company, Switzerland) are commercial products with a surface area of 113 m^2/g (Degussa Company, 1977) and 100 m^2/g (geometry estimation by R. Giovanoli, University of Bern), respectively. 8-Hydroxyquinoline-5-sulfonic acid monohydrate and humic acid were obtained from Aldrich-Chemie Company and EGA-Chemie Company, respectively. Fulvic acid was obtained from the International Humic Substances Society prepared from the Suwannee River, Georgia, U.S.A. The main chemical properties of this fulvic acid were reported elsewhere (Thurman and Malcolm, 1983). The purity of N_2 used in this study was 99.999%. The trace amount of O_2 contained in the N_2 was further removed by passing the N_2 through a solution of V(II) with amalgamated zinc (Wersin, 1990).

Analytical techniques

1. *Measurement of pH.* The pH measurement was conducted using a pH meter (Metrohm 605) with a combined pH electrode (Metrohm). The pH electrode was previously calibrated using standard buffer solutions of pH 4 and 7 (Merck).

2. *Determination of iron.* The formation of iron(III)–HQS complexes is used to monitor the non-reductive dissolution of iron(III) oxyhydroxide formed in the presence of TRIS. The absorbance maximum of Fe^{III}–HQS complexes was observed at λ = 570 nm in a pH range of 6.5–7.5 (ε = 5600 $M\ cm^{-1}$, Deng, 1992). The stoichiometry of Fe^{III}–HQS complexes in solution can be determined from the observed plateau in concentration of iron(III)–HQS complex with increasing HQS concentration at a fixed iron concentration (1.0×10^{-4} M). It appears that the 1:3 complex $Fe^{III}(HQS)_3$ predominates in the concentration range of HQS 3.0×10^{-4}–6×10^{-4} M.

The determination of ferrous and total iron was carried out by using the phenanthroline method (Tamura *et al.*, 1974). The measurement of ferrous iron was completed within 5 min in order to minimize the slow reduction of ferric iron by phenanthroline.

3. *Determination of phosphate.* The heteropoly blue method was used to determine phosphate (Clesceril *et al.*,

1989). The absorbance maximum of the color complex is at $\lambda = 710$ nm ($\varepsilon = 16700$ M cm^{-1}, Deng, 1992).

Preparation of iron(III) oxyhydroxides

In order to produce different iron(III) oxyhydroxides, several procedures were used in this study.

1. *Precipitation of the iron(III) oxyhydroxide from a homogeneous solution.* The general concept of precipitation from a homogeneous solution is that the precipitant is not added but is slowly generated by a homogeneous chemical reaction. In this study, the precipitation of the iron(III) oxyhydroxide from a homogeneous solution takes place when precipitant iron(III) is slowly generated by the oxygenation of iron(II). A slow precipitation process allows an equilibrium to be established between the surface of the iron(III) oxyhydroxide and the solution. The procedure is described as follows:

Pure CO_2 (PCO_2 = 1 atm) was bubbled through a solution containing 2.5×10^{-4} M $NaHCO_3$ and 0.01 M $NaNO_3$ until a pH value of 4.5 was attained. Subsequently, a small amount of solid $Fe(ClO_4)_2 \cdot 6H_2O$ was added to give an initial iron(II) concentration of 1.0×10^{-4} M. The solution was kept in the dark and exposed to the air. The precipitation occurred in this system when the pH increased in infinitesimally small increments as the CO_2 diffused out of the solution and at the same time, O_2 was introduced.

2. *Oxygenation of iron(II) in the presence of different solutes.* A solution (500 ml) containing 1.0×10^{-2} M $NaClO_4$ and 3.0×10^{-4} M $NaHCO_3$ was bubbled with pure CO_2 (PCO_2 = 1 atm) until a pH value of 4.5 was attained, then 0.0183 g $Fe(ClO_4)_2 \cdot 6H_2O$ and the required amount of solutes was added. The initial concentration of iron(II) was 1.0×10^{-4} M. Oil-free air (PO_2 = 0.2 atm) was then bubbled through the stirred solution until pH 5 was achieved. The pH of the solution was adjusted to pH 7 by addition of imidazole buffer (pK_a=7, Smith and Martell, 1975). The final concentration of imidazole was 1.0×10^{-2} M. The oxygenation of iron(II) (PO_2 = 0.2 atm) proceeded rapidly at about pH 7. The formation of iron(III) oxyhydroxide in the presence of TRIS followed the same procedure as described for imidazole buffer. The oxygenation of iron(II) in the presence of TRIS (0.5 M) occurred at pH 7.5–7.7. The stability constants of iron(II)–imidazole complexes ($\log K_1 = 3.2$, $\log K_2 = 3.17$ in 0.058 M KCl at 25°C, Sillen and Martell, 1964) show that imidazole has a weak tendency of complexation with iron(II). However, no stability constants are available for the iron(II, III)–TRIS complexes.

The characterization of the iron(III) oxyhydroxides was carried out by Prof. R. Giovanoli (University of Bern) using electron microscopy (Hitachi H-600-2). The electron micrograph suggested that the structure of the particles formed in the presence of the imidazole medium looked like lepidocrocite because of the aggregated thin platelets. They appeared quite porous and gave unsatisfactory X-ray diffraction pattern. The geometry of the particles was estimated as $40 \times 3.4 \times 2.0$ nm^3 (Deng, 1992). The iron(III) oxyhydroxide produced in TRIS medium could not be studied with the electron microscope because the colloids were too small to be seen.

3. *Oxygenation of iron(II) in the presence of suspensions.*

(1) *Preparation of the suspensions.* 0.625 g of δ-Al_2O_3 or bentonite was added into a 240 ml solution containing 1.0×10^{-2} M $NaClO_4$ and 3.0×10^{-4} M $NaHCO_3$ and equilibrated with the bulk solution overnight at room temperature with stirring.

(2) *Preparation of iron(II) solution.* A 250 ml solution containing 1.0×10^{-2} M $NaClO_4$ and 3.0×10^{-4} M $NaHCO_3$ was purged with pure CO_2 (PCO_2 = 1 atm) until a pH value of 4.5 was achieved and 0.0183 g $Fe(ClO_4)_2 \cdot 6H_2O$ was then added. The concentration of iron(II) in solution was 2.0×10^{-4} M.

(3) *Procedure of the oxygenation of iron(II).* The suspension of δ-Al_2O_3 or bentonite (240 ml) was purged with pure CO_2 (PCO_2 = 1 atm.) until a pH value of 4.5 was attained. Subsequently, the suspension (240 ml) and the solution of iron(II) (2.0×10^{-4} M, 250 ml) were mixed at 4.5. The mixture was then bubbled with the oil-free air (PO_2 = 0.2 atm) until pH 5 was attained. The pH was adjusted to pH 7 by adding 10 ml 0.5 M imidazole buffer. The initial concentration of iron(II) in the mixture was 1.0×10^{-4} M. The concentration of δ-Al_2O_3 or bentonite suspension was 1.25 g/l. The oxygenation of iron(II) proceeded rapidly at about pH 7.

Dissolution of iron(III) oxyhydroxides

The dissolution experiments were carried out in a glass vessel in the absence of light (wrapped with aluminum foil). All experiments were carried out at a constant temperature (20°C ± 0.1) by keeping the vessel in a thermostated water bath. During the dissolution experiments, the pH was kept constant by addition of $HClO_4$ with a pH stat (Metrohm). For the reductive dissolution, the suspension of the freshly formed iron(III) oxyhydroxide [0.01 g/l $Fe(OH)_3(s)$] was first deoxygenated by nitrogen for 15 min before the required quantity of ascorbate solution (freshly prepared) was added. The initial concentration of ascorbate was 4.8×10^{-2} M. For the experiment of a non-reductive dissolution, stock solution of HQS (2.5×10^{-3} M) was directly added into the suspension of the freshly formed iron(III) oxyhydroxide ($Fe(OH)_3(s)$ 0.01 g/l). The initial concentration of HQS was 5.0×10^{-4} M. After addition of ascorbate or HQS, aliquots of the suspension were withdrawn periodically by a syringe and filtered through a 0.1 μm cellulose nitrate membrane. The concentration of ferrous and total iron were determined in the filterable fraction with the phenanthroline methods described in the section on analytical techniques.

Dissolution of iron(III) oxyhydroxide formed in the presence of TRIS ($(Fe(II))_0$ 1.0×10^{-4} M, TRIS 0.5 M, pH 7.5, PO_2 = 0.2 atm, 20°C) by fulvic acid was carried out in a closed system under the following conditions: 0.01 g/l $Fe(OH)_3(s)$, pH 7.5, 5 mg/l fulvic acid, 20°C. The procedure of the dissolution is described as follows. The suspension of the iron(III) oxyhydroxide (28.5 ml) was transferred into a flask with a full volume of 30 ml. The suspension was carefully purged with nitrogen for about 10 min to eliminate dissolved oxygen. Then 1.5 ml fulvic acid (0.1 mg/ml, freshly prepared) was added and mixed well with the suspension. The flasks with the same experimental conditions (i.e. 0.01 g/l $Fe(OH)_3(s)$, pH 7.5, 5 mg/l fulvic acid, 20°C) were carefully capped to avoid entrapment of air and immersed in water in a dark container to minimize the oxygenation of ferrous iron.

A glove-box filled with nitrogen (nitrogen was circulated into the box for about 1 h before sampling) was used for sampling in order to prevent oxygenation of ferrous iron. The sampling was carried out at intervals during the dissolution experiment. Each sample was taken from one of the flasks immersed in water in the dark container and each

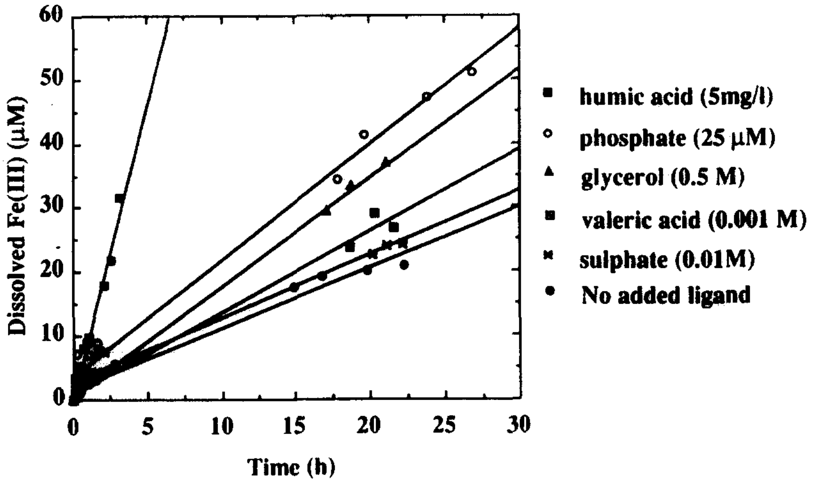

FIG. 1. HQS promoted dissolution of the iron(III) oxyhydroxides formed in the presence of different solutes. The conditions for the formation of the iron(III) oxyhydroxides: $Fe(II)_0$ 1.0 × 10^{-4} M, imidazole 0.01 M, $NaHCO_3$ 3.0 × 10^{-4} M, $NaClO_4$ 1.0 × 10^{-2} M, PO_2 = 0.2 atm, pH 7.0 ± 0.2, 20°C. The conditions for the dissolution: $Fe(OH)_3(s)$ 0.01 g/l, HQS 5.0 × 10^{-4} M, pH 7.3 ± 0.1, 20°C.

flask in the dark container was used for only one sampling. The concentrations of iron(II) and total iron in the samples were determined by the phenanthroline method.

Measurement of the electrode potential for the iron(III) oxyhydroxide/iron(II) redox couple

A recent study (GRENTHE *et al.*, 1992) has demonstrated that a stable and reproducible redox potential can be measured in the system of iron(III) oxyhydroxide/iron(II) by using an inert electrode (i.e. Pt, Au or glassy carbon) combined with a reference electrode such as calomel. In this study, the electrode potentials for the iron(III) oxyhydroxide/iron(II) redox couple were measured at 25°C under a nitrogen atmosphere.

1. *Preparation of Fe(II) solution* (1.0 × 10^{-3} *M*, 100 ml). The preparation of iron(II) solution followed the procedure described in the section on the oxygenation of iron(II) in the presence of a suspension.

2. *Procedure of electrode potential measurement.* A platinum electrode (Metrohm) (saturated calomel electrode as reference) was used to measure the electrode potential of the iron(III) oxyhydroxide/iron(II) couple. The electrode (in conjunction with a pH meter) was calibrated by a redox standard solution (+250 mV, Metrohm). One hundred millilitres of an iron(III) oxyhydroxide suspension (those formed in the presence of TRIS and in the presence of imidazole, $Fe(OH)_3(s)$ 0.01 g/l) was purged with pure CO_2 (PCO_2 = 1 atm) for about 1.5–2 h in order to eliminate dissolved oxygen and to reach a pH value of 5.0–5.5. The freshly prepared iron(II) solution (5.3 ml, 1.0 × 10^{-3} M) was then mixed with the Fe(III) oxyhydroxide suspension to give an iron(II) concentration of 5.0 × 10^{-5} M. Then, CO_2 was substituted by N_2 to keep out O_2 and to drive CO_2 out of the suspension. This resulted in a pH increase. The electrode potentials for the iron(III) oxyhydroxide/iron(II) redox couple in the presence of imidazole or in the presence of TRIS were measured at different pH values.

RESULTS AND DISCUSSION

Dissolution of iron(III) oxyhydroxides formed in the presence of different solutes by a complex former (HQS)

Figure 1 shows the dissolution of iron(III) oxyhydroxides formed freshly in the presence of different solutes by HQS (5.0 × 10^{-4} M, pH 7.3±0.1, 20°C) in the period of 25 h. The dissolution rate of these iron(III) oxyhydroxides was obtained in the range of 10^{-8} M/min–10^{-7} M/min by taking the slope of the curves in Fig. 1. Figure 2 illustrates that iron(III) oxyhydroxide formed in the presence of TRIS (TRIS 0.5 M, PO_2 = 0.2 atm, $Fe(II)_0$ = 1.0 × 10^{-4} M, pH 7.5) is also dissolved by HQS (5.0 × 10^{-4} M) at pH 7.4. About 50% of the total iron(III) oxyhydroxide ($Fe(OH)_3(s)$ 8.6 × 10^{-3} g/l or Fe(III) total 8.0 × 10^{-5} M) is readily dissolved within 25 s with a dissolution rate of 9.6 × 10^{-5} M/min. Comparison of Fig. 1 and Fig. 2 shows that the dissolution rates of the iron(III) oxyhydroxides vary to a different extent depending on the conditions of their formation. The reactivity of the iron(III) oxyhydroxides is observed to decrease in the following sequence in terms of the solutes present during the formation of iron(III) oxyhydroxides by the oxygenation of iron(II): TRIS ≫ humic acid > phosphate, glycerol > valeric acid, sulfate, no added ligand.

The intention of this study was to investigate whether solutes of natural waters such as humic acid, phosphate, sulfate and valeric acid, could assist in a real system in the formation of a similarly reactive oxyhydroxide which was produced by VON GUNTEN and SCHNEIDER (1991). No substances used in this study were found to have such an influence on en-

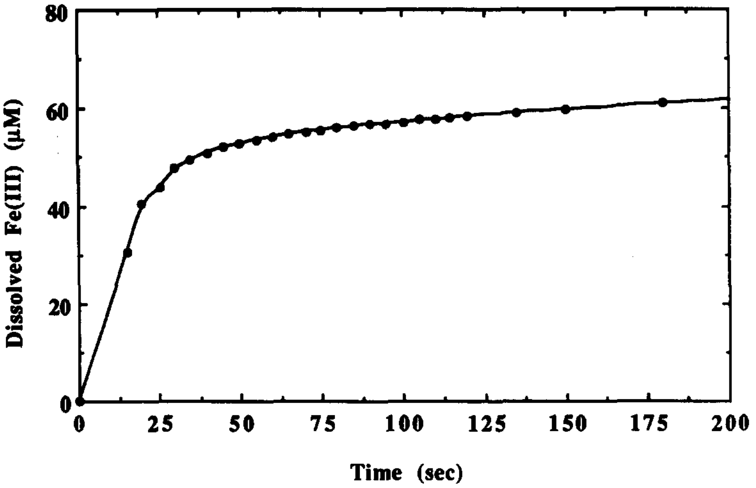

Fig. 2. Dissolution of the iron(III) oxyhydroxide formed in the presence of TRIS by HQS: formation of iron(III) oxyhydroxide: $Fe(II)_0$ 1.0×10^{-4} M, TRIS 0.5 M, $NaHCO_3$ 3.0×10^{-4} M, $PO_2 = 0.2$ atm, $NaClO_4$ 1.0×10^{-2} M, pH 7.5, 20°C; dissolution of iron(III) oxyhydroxide: $Fe(OH)_3(s)$ 8.6×10^{-3} g/l, HQS 5.0×10^{-4} M, pH 7.4, 20°C.

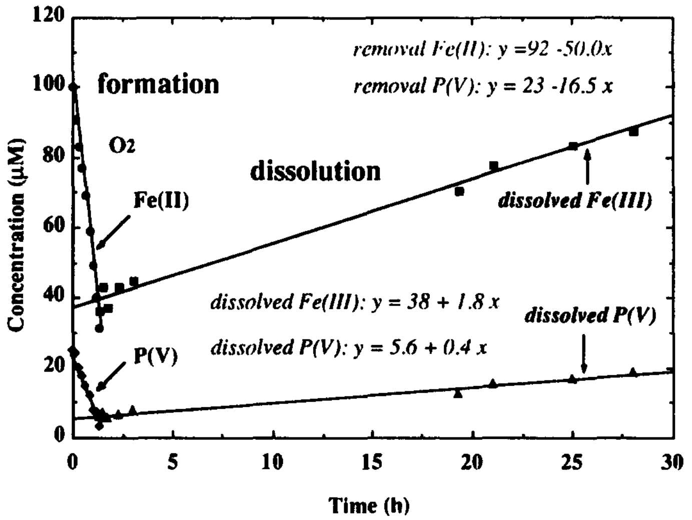

Fig. 3. Iron(III) oxyhydroxide formed by the oxygenation of iron(II) in the presence of phosphate. The freshly formed iron(III) oxyhydroxide was subsequently dissolved by a non-reductive dissolution using HQS. Formation of iron(III) oxyhydroxide: $Fe(II)_0$ 1.0×10^{-4} M, NaH_2PO_4 2.5×10^{-5} M, imidazole 1.0×10^{-2} M, $NaHCO_3$ 3.0×10^{-4} M, $NaClO_4$ 1.0×10^{-2} M, $PO_2 = 0.2$ atm, pH 6.9, 20°C; dissolution of the iron(III) oxyhydroxide: $Fe(OH)_3(s)$ 0.01 g/l, HQS 5.0×10^{-4} M, pH 7.4, 20°C.

hancing the reactivity of oxyhydroxide as that found by the effect of TRIS. The iron(III) oxyhydroxide formed in the presence of TRIS shows the highest reactivity among the iron(III) oxyhydroxides tested. As reported by von Gunten and Schneider (1991), an oligomeric iron(III) oxyhydroxide was formed where extensive polymerization can be prevented by TRIS which most likely forms outer-sphere complexes on the surface of iron(III) colloids. Such iron(III) colloids showed a much higher affinity towards phosphate than do crystalline iron(III) oxyhydroxide. The molar ratios (P/Fe) for the adsorption of phosphate are 0.25 for the iron colloids formed in TRIS medium and only 0.02 for goethite (von Gunten and Schneider, 1991). Thus, the high reactivity observed for the iron(III) oxyhydroxides formed in the TRIS medium is plausibly explained by their large surface area (1 nm ≤ radius ≤ 20 nm, von Gunten and Schneider, 1991) with a high proportion of active terminal -OH groups, such as $>Fe(OH)_2$, >Fe-OH on the surface. Correspondingly, a higher dissolution rate of this iron(III) oxyhydroxide can be expected when a high quantity of the surface complex with the suitable coordination arrangement is achieved (Wieland *et al.*, 1988).

Figure 3 shows that the iron(III) oxyhydroxide is

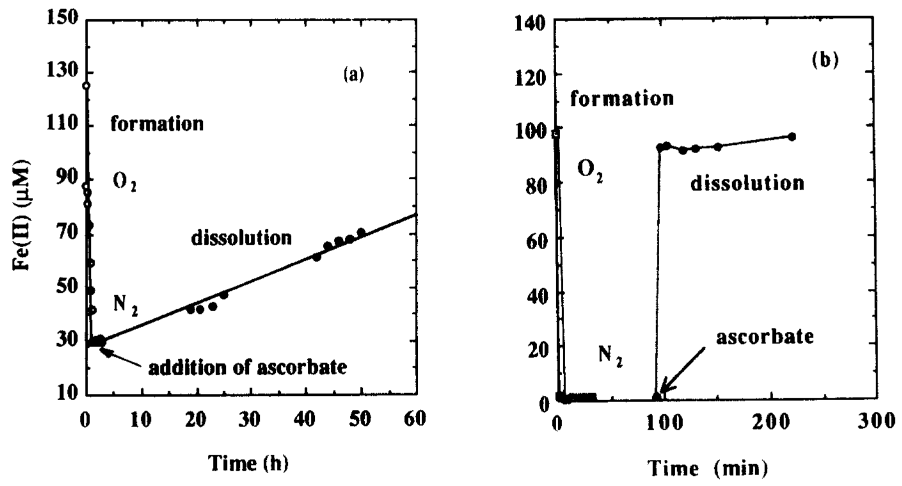

FIG. 4. Effect of TRIS on the formation of iron(III) oxyhydroxide and its dissolution by ascorbate at 20°C. (a) Formation of iron(III) oxyhydroxide: $Fe(II)_0$ 1.0 × 10^{-4} M, imidazole 1.0 × 10^{-2} M, $NaHCO_3$ 3.0 × 10^{-4} M, $NaClO_4$ 1.0 × 10^{-2} M, PO_2 = 0.2 atm, pH 6.7; dissolution of freshly formed iron(III) oxyhydroxide: $Fe(OH)_3(s)$ 0.01 g/l, ascorbate 4.8 × 10^{-2} M, pH 7.0 ± 0.2, N_2. (b) Formation of iron(III) oxyhydroxide: $Fe(II)_0$ 1.0 × 10^{-4} M, imidazole 1.0 × 10^{-2} M, TRIS 0.5 M, $NaHCO_3$ 3.0 × 10^{-4} M, $NaClO_4$ 1.0 × 10^{-2} M, PO_2 = 0.2 atm, pH 7.7; dissolution of freshly formed iron(III) oxyhydroxide: $Fe(OH)_3(s)$ 0.01 g/l, ascorbate 4.8 × 10^{-2} M, pH 7.5, N_2. A similar rapid dissolution was observed in the pH range of 4–8.

formed by the oxygenation of iron(II) in the presence of phosphate ($Fe(II)_0$ 1.0 × 10^{-4} M, $(NaH_2PO_4)_0$ 2.5 × 10^{-5} M, imidazole 0.01 M, PO_2 = 0.2 atm, pH 6.9). During the formation of the iron(III) oxyhydroxide, on the one hand, both concentrations of iron(II) and phosphate decreased as a function of time. The molar ratio P(V)/Fe(II) for the removal phosphate and ferrous iron from the solution is 0.33. The freshly formed iron(III) oxyhydroxide was subsequently dissolved by HQS (5.0 × 10^{-4} M, pH 7.4). During the dissolution of the iron(III) oxyhydroxide, on the other hand, the iron(III) and phosphate were gradually released from the solid phase. Obviously, phosphate has become incorporated into the iron(III) oxyhydroxide, rather than being simply adsorbed on the surface of the oxyhydroxide. The ratio P(V)/Fe(III) in the solid phase is 0.22 based on the dissolution result; this ratio is quite close to the 0.25±0.06 reported for iron-rich particles collected from natural waters by BUFFLE *et al.* (1988).

In view of the ratio P(V)/Fe(III) = 0.22 obtained during the dissolution of the solid phase, the composition of the solid phase would not be expected to be merely a pure iron(III) oxyhydroxide because the phosphate is slowly released from the solid phase during the dissolution. The solid phase would also not be expected to be a pure ferric phosphate ($FePO_4 \cdot 2H_2O$, log K_{s0} = −26 at 25°C, STUMM and MORGAN, 1981) because the ratio P(V)/Fe(III) obtained from the dissolution of the solid phase was 0.22 rather than 1. As to the precipitation of ferrous phosphate ($Fe_3(PO_4)_2$, logK_{s0} = −32 at 25°C, STUMM and MORGAN, 1981), the process may not have occurred because no ferrous iron was released during the dissolution.

Dissolution of iron(III) oxyhydroxides formed in the presence of imidazole and TRIS–imidazole medium by ascorbate

Figure 4(a) shows that the iron(III) oxyhydroxide is produced in the presence of imidazole (imidazole 0.01 M, $Fe(II)_0$ 1.25 × 10^{-4} M, PO_2 = 0.2 atm, pH 6.7). The freshly formed iron(III) oxyhydroxide ($Fe(OH)_3(s)$ 0.01 g/l) is subsequently dissolved by ascorbate (4.8 × 10^{-2} M, pH 7 ± 0.2, N_2). The reductive dissolution rate is calculated as 8.2 × 10^{-7} M/h by taking the slope of the dissolution curve in Fig. 4(a). Figure 4(b) illustrates that iron(III) oxyhydroxide ($Fe(OH)_3(s)$ 0.01 g/l) is formed by the oxygenation of iron(II) in the presence of the TRIS–imidazole medium ($Fe(II)_0$ 1.0 × 10^{-4} M, TRIS 0.5 M, imidazole 0.01 M, pH 7.7, PO_2 = 0.2 atm). The freshly formed iron(III) oxyhydroxide is subsequently dissolved by ascorbate (4.8 × 10^{-2} M, pH 7.5, N_2). As illustrated in Fig. 4(b), almost 100% of the iron(III) oxyhydroxide formed in the TRIS–imidazole medium was rapidly dissolved by ascorbate at pH 7.5 within a minute. Based on this observation, the rate of dissolution of the iron(III) oxyhydroxide formed in the TRIS–imidazole medium is estimated as 6 × 10^{-3} M/h. A similar rapid dissolution of this iron(III) oxyhydroxide was observed in the pH range of 4–8. Comparison of Fig. 4(a) and (b) shows that the dissolution kinetics of these two iron(III) oxyhydroxides differ markedly depending on the conditions of their formation.

To improve the understanding of the difference in the dissolution kinetics of the two iron(III) oxyhydroxides, an attempt was made to measure the redox potential of the iron(III) oxyhydroxide/iron(II)

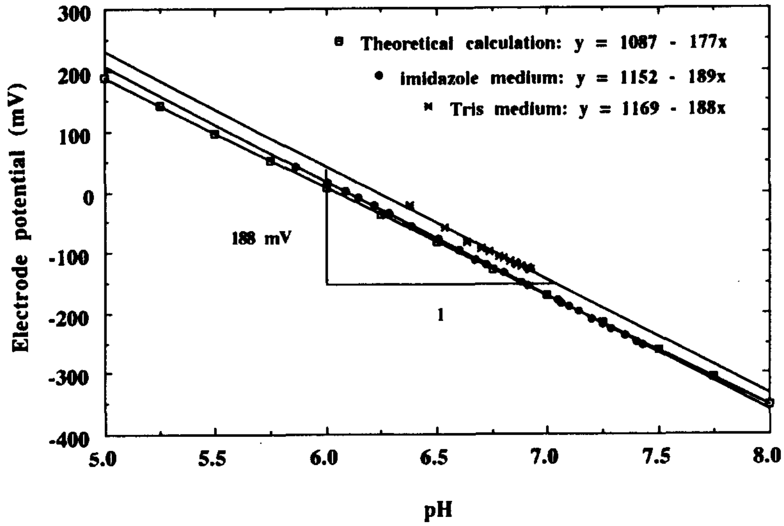

FIG. 5. Dependence of the electrode potential of the iron(III) oxyhydroxide/iron(II) redox couple on pH ($Fe(OH)_3(s)$ 0.01 g/l, Fe(II) 5.0 × 10^{-5} M, N_2, 25°C): formation of $Fe(OH)_3(s)$: $Fe(II)_0$ 1.0 × 10^{-4} M, $NaHCO_3$ 3.0 × 10^{-4} M, $NaClO_4$ 1.0 × 10^{-2} M, $PO_2 = 0.2$ atm, imidazole 1.0 × 10^{-2} M (pH 7), or TRIS 0.5 M (pH 7.5).

Table 1. Standard redox potential of iron(III) oxyhydroxide/iron(II) redox couple and solubility product for two different iron(III) oxyhydroxides

System	E^0_H(V)*	log K_{s0}†
$Fe(OH)_3$(s)/Fe(II) (TRIS)	1.0	−38
$Fe(OH)_3$(s)/Fe(II) (imidazole)	1.0	−38

*Calculation of the standard redox potential (E^0_H) (see Appendix I).

†Values are estimated based on the E^0_H (see Appendix II).

couple in order to see whether the reactivity of iron(III) oxyhydroxides could be related to the stability of the iron(III) oxyhydroxides. Figure 5 shows the electrode potential of the system consisting of the iron(III) oxyhydroxide/iron(II) ($Fe(OH)_3(s)$ 0.01 g/l, Fe(II) 5.0 × 10^{-5} M) redox couple. The redox potentials are measured by a Pt electrode (calomel electrode as reference) as a function of pH. The slope obtained from experimental data is in agreement with that of the theoretical calculations [Fig. 5 and Eqn (2)]. The potential decreases gradually as the pH increases in accord with Eqn (2) given below.

The half redox reaction for reductive dissolution of iron(III) oxyhydroxide can be generally described as follows:

$$Fe(OH)_3(s) + 3H^+ + e = Fe^{2+} + 3H_2O \quad (1)$$

According to the Nernst equation, the half redox reaction can be expressed as:

$$E_H = E^0_H + 0.059 \log [H^+]^3/[Fe^{2+}]$$
$$= E^0_H - 0.059 \log [Fe^{2+}] - 0.177\text{pH} \quad (2)$$

The standard redox potential for the iron(III) oxyhydroxide/iron(II) couple can be calculated by the Nernst equation based on the experimental result (see Appendix I). As depicted in Table 1, the difference in the experimentally estimated standard redox potentials and the solubility product (see Appendix II) for iron(III) oxyhydroxides formed in TRIS medium and imidazole medium is not significant. The dissolution rates of these two kinds of iron(III) oxyhydroxides by ascorbate (shown in Fig. 4), however, differ markedly. This observation indicates that the difference in reactivity of these two iron(III) oxyhydroxides is controlled by the surface structure. The coordination arrangement of the functional groups at the surface of iron(III) oxyhydroxides, especially the extent of end-standing -OH per iron(III) center, such as >Fe-OH, $>Fe(OH)_2$ determine that reactivity toward dissolution.

Dissolution of the iron(III) oxyhydroxide produced from the homogeneous solution by oxalate

It is known that iron(III) oxyhydroxides can usually be produced in the laboratory by adding a base or a buffer to an iron(III) solution. The result of following this procedure is that the products of iron(III) hydrolysis (such as dinuclear and further polynuclear species) appear rapidly no matter what mixing technique is applied during the formation of iron(III) oxyhydroxide. This phenomenon is due to the fact that the rates of mixing are slow on the time scale of diffusion-controlled proton transport reactions (SCHNEIDER and SCHWYN, 1987). Thus, the polynuclear species were instantaneously produced where a high pH value is created locally by addition of a base or a buffer. It is believed that the mononuclear $Fe(OH)_i^{3-i}$ is the primary product of hydrolysis of iron(III) and may be active in terms of dissolution. In this study, we attempt to obtain the mono-

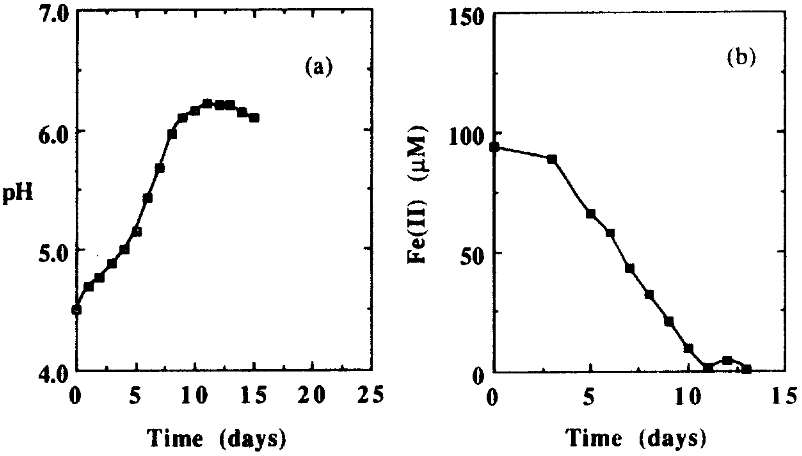

FIG. 6. Variation of pH (a) and iron(II) (b) as a function of time during the oxygenation of iron(II) in the Fe(II)-HCO_3^--CO_2-O_2-H_2O system: $Fe(II)_0$ 1.0×10^{-4} M, $[HCO_3^-]/[Fe(II)_0] = 2.5$ ($[Fe(II)_0]$ and $[HCO_3^-]$ are the initial concentrations of Fe(II) and bicarbonate, respectively), ionic strength: 1.0×10^{-2} M $NaNO_3$, 20°C.

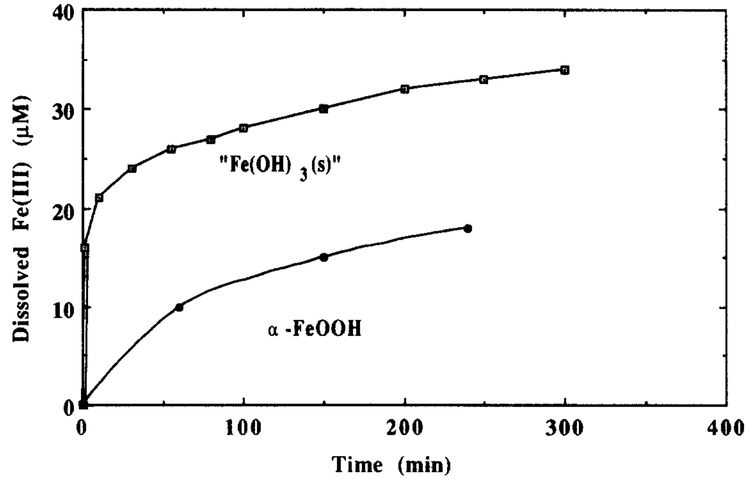

FIG. 7. Comparison of dissolution kinetics of iron(III) oxyhydroxide produced from the homogeneous solution and goethite (α-FeOOH) by oxalate (1.0×10^{-3} M, 25°C) at pH 3.0: $Fe(OH)_3(s)$ 0.01 g/l; α-FeOOH 0.46 g/l. One part of the $Fe(OH)_3(s)$ reacts very rapidly in an initial phase, the remaining $Fe(OH)_3$ (s) dissolves at a much slower rate.

nuclear $Fe(OH)_i^{3-i}$ or the iron(III) oxyhydroxide with a low degree of polymerization by means of precipitation from a homogeneous solution (see experimental section for details of the procedure). Figures 6(a) and (b) show that the pH and the concentration of Fe(II) change as a function of time. The results indicate that pH increased as CO_2 diffused out of the solution and at the same time, iron(II) is oxidized to iron(III) as O_2 is introduced slowly into solution. No localized high pH values occur during the formation of oxyhydroxide. The reactivity of the iron(III) oxyhydroxide produced from the homogeneous solution was assessed by a non-reductive dissolution using oxalate (1.0×10^{-3} M) at pH 3.0. As shown in Fig. 7, the initial rate of the dissolution of iron(III) oxyhydroxide is very fast. About 25% of the total iron in the iron(III) oxyhydroxide ($Fe(OH)_3(s)$ 0.01 g/l) is readily dissolved within 10 min. Apparently, the iron(III) oxyhydroxide produced from a homogeneous solution exhibits higher reactivity (initial dissolution rate) than that of a highly crystalline iron(III) oxyhydroxide such as goethite (data of the dissolution for goethite are from SUTER *et al.*, 1991). As has been discussed earlier in this paper, such a difference in the reactivity may also be plausibly caused by the difference in the degree of polymerization of the oxides and in the quantity of the active functional groups with various coordination arrangements on the surfaces of the two iron(III) oxyhydroxides.

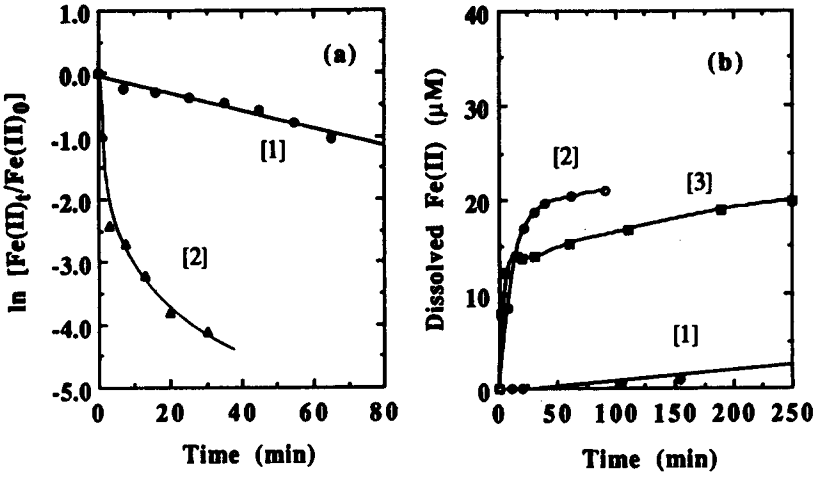

FIG. 8 (a). Formation of iron(III) oxyhydroxides (1) in the absence of a suspension and (2) in the presence of bentonite suspension 1.25 g/l (Fe(II))$_0$ 1.0 × 10^{-4} M, imidazole 1.0 × 10^{-2} M, $NaHCO_3$ 3.0 × 10^{-4} M, $NaClO_4$ 1.0 × 10^{-2} M, PO_2 = 0.2 atm., pH 6.8 ± 0.1, 20°C). (b) Dissolution of the iron(III) oxyhydroxides by reductive dissolution with ascorbate (4.8 × 10^{-2} M, 20°C, N_2) at pH 7.2. For the curve (3), the conditions for the formation of iron(III) oxyhydroxide were: Fe(II)$_0$ 1.0 × 10^{-4} M, imidazole 1.0 × 10^{-2}M, δ-Al_2O_3 1.25 g/l, $NaHCO_3$ 3.0 × 10^{-4}M, $NaClO_4$ 1.0 × 10^{-2}M, PO_2 = 0.2 atm, pH 7.0, 20°C.

Dissolution of iron(III) oxyhydroxides formed in the presence of bentonite and δ-Al_2O_3 by ascorbate

Figure 8(a) shows the kinetics of the oxygenation of iron(II) in the absence of suspension (curve 1) and in the presence of bentonite (1.25 g/l) (curve 2). The conditions for the oxygenation of iron(II) in these two systems were as follows: Fe(II)$_0$ 1.0 × 10^{-4} M, imidazole 0.01 M, PO_2 = 0.2 atm, pH 6.8. The oxygenation of iron(II) is apparently accelerated in the presence of a solid phase such as bentonite. Similar enhancement has been reported in the oxygenation of iron(II) in the presence of goethite or hornblende (TAMURA *et al.*, 1980, WHITE and YEE, 1985). It has been known that hydroxo complexes of iron(II) are oxidized faster by oxygen than the corresponding aqueous ion. As shown by WEHRLI and STUMM (1988), the adsorption of iron(II) onto a hydroxo functional group of an oxide surface can enhance the oxygenation of iron(II) in a way similar to hydrolysis. This phenomenon can be explained by the fact that the coordination of iron(II) by surface hydroxyl groups or by OH^- in solution increases the electron density at the iron(II) center and facilitates the electron transfer from the iron(II) center to O_2 (LUTHER, 1990). Figure 8(b) shows the comparison of dissolution kinetics of iron(III) oxyhydroxides formed in the absence of a suspension (curve 1) and in the presence of a suspension, such as bentonite (curve 2) and δ-Al_2O_3 (curve 3) (the conditions for the formation of iron(III) oxyhydroxide in the presence of δ-Al_2O_3 were: δ-Al_2O_3 1.25 g/l, Fe(II)$_0$ 1.0 × 10^{-4} M, PO_2 = 0.2 atm, imidazole 0.01 M, pH 7.0). The initial dissolution rates of iron(III) oxyhydroxides formed in the presence of a suspension are much higher than that of iron(III) oxyhydroxide formed in the absence of the suspensions. The active iron(III) oxyhydroxide produced on the surface of the suspensions may be assumed to be polymerized predominantly in two dimensions rather than in three dimensions. Thus, the high reactivity of the iron(III) oxyhydroxide produced on the surfaces can be plausibly interpreted as being the result of a low degree of polymerization and a high quantity of active surface sites.

Dissolution of the iron(III) oxyhydroxide formed in the presence of TRIS by fulvic acid

It is interesting, and perhaps more important for natural waters, to know how reactive the iron(III) oxyhydroxide will be in terms of the reductive dissolution by naturally occurring organic substances, such as fulvic acid. In order to simulate conditions similar to those encountered at the oxic–anoxic boundary in natural waters, the dissolution of iron(III) oxyhydroxide ($Fe(OH)_3(s)$ 0.01 g/l) formed in a TRIS medium (TRIS 0.5 M, pH 7.5, PO_2 = 0.2 atm, 20°C) was performed in a closed system at pH 7.5 in the presence of 5 mg/l fulvic acid. The kinetics of the conversion of iron(III) colloids to iron(II) was followed by measuring the ferrous iron produced (Fig. 9). The rate of the conversion is 60 nM/h obtained from the slope of the curve in Fig. 9 during a period of 25 d.

A reaction sequence with regard to the redox cycle of iron coupled with natural organic substances has been proposed by STUMM and MORGAN (1981). The iron(III)–iron(II) couple is able to act as an electron-transfer catalyst for the oxidation of natural organic substances such as fulvic acid by oxygen:

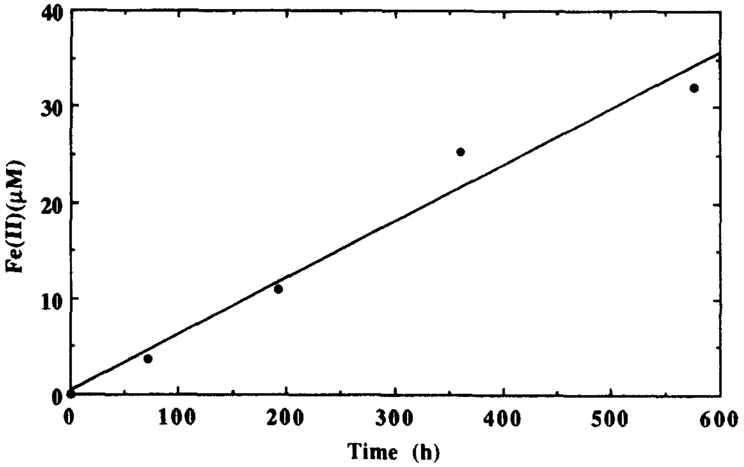

FIG. 9. Reductive conversion of iron(III) oxyhydroxide formed in the presence of TRIS by fulvic acid: formation of iron(III) oxyhydroxide: $Fe(II)_0$ 1.0 × 10^{-4} M, TRIS 0.5 M, PO_2 = 0.2 atm, $NaHCO_3$ 3.0 × 10^{-4} M, $NaClO_4$ 1.0 × 10^{-2} M, pH 7.5, 20°C; dissolution of the iron(III) oxyhydroxide in a closed system: $Fe(OH)_3(s)$ 0.01 g/l, fulvic acid 5 mg/l, pH 7.5, 20°C.

$$Fe(II) + 1/4O_2 + \text{org.} = Fe(III)\text{–org. complex} \quad (3)$$

$$Fe(III)\text{–org. complex} = Fe(II) + \text{oxidized org.} \quad (4)$$

$$Fe(II) + 1/4O_2 + \text{org.} = Fe(III)\text{–org. complex} \quad (5)$$

When the rate of oxygenation of Fe(II) is slow in comparison to iron(III) reduction by the organic substances, a relatively high steady-state concentration of iron(II) can be maintained in the system as long as the organic substance is not fully oxidized. Thus, the reaction rate obtained in Fig. 9 can be considered to be the net result of reduction and oxygenation of the $>Fe^{III}$–OH/Fe(II) "wheel" coupled with fulvic acid (DENG and STUMM, 1993).

Some environmental implications

Figure 10 schematically depicts some of the phenomena observed in this study and their implications in natural waters. The results obtained indicate that the formation of aquatic iron(III) oxyhydroxides is accompanied by binding or incorporating reactive inorganic species (such as $H_2PO_4^-$), organic substances (such as humic materials, fatty acid) and surfaces, such as bentonite and aluminum oxide. The solutes and surfaces can modify to a different extent the reactivity of aquatic iron(III) oxyhydroxides as reflected by their tendency to dissolve. The dissolution of aquatic iron(III) oxyhydroxides, on the other hand, is accompanied by release of the solutes which are incorporated into the structure of the iron(III) oxyhydroxides (such as phosphate) or adsorbed on their surfaces (such as silicic acid, DENG, 1992). Thus, it is reasonable to expect that in a real system the redox cycling of iron largely governs the fate of these reactive inorganic and organic species, and is coupled with the biogeochemical cycles of many other elements, such as trace metals and oxygen.

One of the interesting findings of this study is that iron(III) oxyhydroxides formed at the surface of hydrous oxides and aluminum silicate are more reactive than the iron(III) oxyhydroxide formed in the absence of these surfaces. The phenomenon observed may represent one of the important mechanisms in formation of active iron(III) oxyhydroxides since various surfaces are abundant in real aquatic systems. It appears that these surfaces not only enhance the oxygenation of iron(II) which is in accord with previous findings (TAMURA *et al.*, 1980), but also induce the formation of iron(III) oxyhydroxides which are more active toward the dissolution reactions.

It has been a matter of debate for several years whether the iron(II) profile found in the anoxic zone of natural waters can be generated from direct interactions between humic substances and iron(III) oxyhydroxides because no previous laboratory evidence supported this pathway. The experimental results in this study show that fulvic acid is able to reduce iron(III) oxyhydroxides at neutral pH under suitable conditions. In natural waters, iron-rich particles <120 nm in size are ubiquitous (WELLS and GOLDBERG, 1991) and reductants other than fulvic acid may be operative. Thus, the cycle given in Fig. 10 reflects the overall situation in the iron(III)–iron(II) transformations. Essentially O_2 oxidizes organic substrates and the iron(III)–iron(II) redox couple acts as an electron transfer mediator. In a real system, microorganisms could also influence various steps in the cycle of iron coupled with fulvic acid. This experimental evidence illustrates that the $>Fe^{III}$–OH/Fe(II) "wheel" can turn even in the ab-

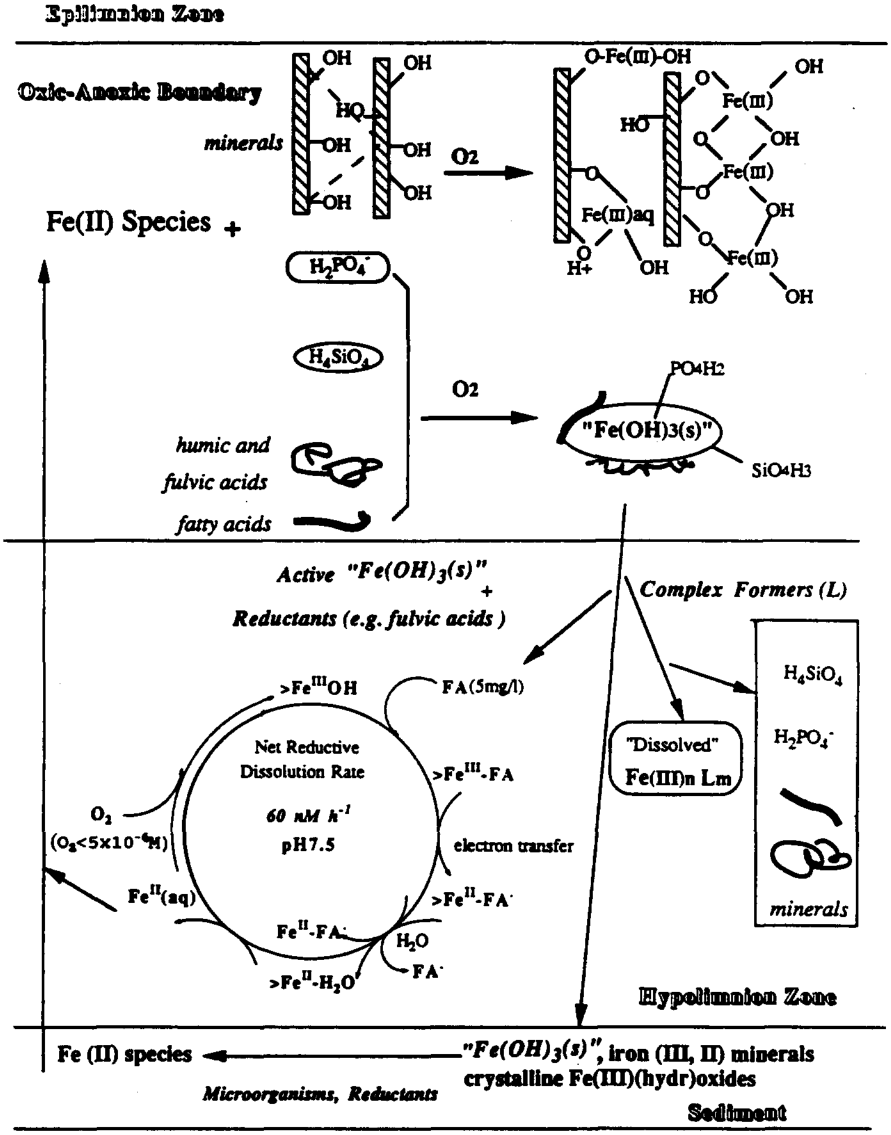

FIG. 10. Schematic diagram showing the environmental implications of the main results obtained in this study.

sence of light and microorganisms.

Different types of aquatic iron(III) oxyhydroxides are produced in this study in terms of their physical and chemical nature, such as form, size, color, composition, structure, dissolution rate, etc. Although the properties of various aquatic iron(III) oxyhydroxides (morphology, structure etc.) produced in this study are not well understood and may not be fully representative of the naturally occurring iron-rich particles, our observations may help in understanding the fact that a variety of iron-rich particles is found in aquatic systems.

CONCLUSIONS

1. The reactivity of iron(III) oxyhydroxides is dependent on the conditions of their formation. The kinetics of dissolution of iron(III) oxyhydroxides is most likely determined by the quantity of the active surface sites and the coordination arrangement of the functional groups at the surface of the iron(III) oxyhydroxides. The extent of endstanding -OH groups per iron(III) center on the surface appears to be particularly important.

2. Surfaces, such as clay and aluminum oxides, not only accelerate the oxygenation of iron(II), but also induce the formation of iron(III) oxyhydroxides which are more reactive toward the dissolution reactions. Polymerization of iron(III) oxyhydroxides on the surfaces occurs predominantly in two dimensions rather than in three dimensions.

3. Under suitable conditions, fulvic acid can reduce iron(III) oxyhydroxide to ferrous species at neutral pH values. Although reductants other than fulvic acid may be of importance in natural waters, the

results obtained in this study provide the laboratory evidence that the $>\mathrm{Fe}^{III}$–OH/Fe(II) redox couple is able to act as an electron-transfer mediator for the oxidation of natural organic substances, such as fulvic acid by molecular oxygen either in the absence of microorganisms or as a supplement to microbial activity.

Acknowledgements—We thank R. Giovanoli (University of Bern) for characterization of the solid phases. We are greatly indebted to I. Grenthe, S. Banwart (The Royal Institute of Technology, Sweden) and Y. Zuo (Florida International University) for many helpful discussions. We thank Dr D. Postma and one anonymous reviewer for their valuable comments. This work was supported by EAWAG and the Swiss National Science Foundation.

Editorial handling: Mike Edmunds

REFERENCES

Berner R. A. (1981) A new geochemical classification of sedimentary environments. *J. Sediment Petrol.* **51**, 359–365.

Buffle J., de Vitre R. R., Perret D. and Leppart G. G. (1988) Physico-chemical characteristics of a colloidal iron phosphate species formed at the oxic-anoxic interface of a eutrophic lake. *Geochim. Cosmochim. Acta* **53**, 399–408.

Canfield D. E. and Berner R. A. (1987) Dissolution and pyritization of magnetite in anoxic marine sediments. *Geochim. Cosmochim. Acta* **51**, 645–659.

Clesceri L. S., Greenberg A. E. and Trussell R. R. (1989) *Standard Methods—For the Examination of Water and Wastewater*, 17th Edn, pp. 4-177–4-181. Port City Press.

Davison W. (1985) Conceptual models for transport at a redox boundary. In *Chemical Processes in Lakes* (ed. W. Stumm), Chap. 2, pp. 31–53. Wiley-Interscience.

Davison W., Heaney S. I., Talling J. F. and Rigg E. (1980) Seasonal transformation and movements of iron in a productive English lake with deep-water anoxia. *Schweiz. Z. Hydrol.* **42**, 196–224.

Degussa Company (1977) Aluminiumoxid C, Schriftenreihe Pigments, 56.

Deng Y. (1992) Formation and dissolution of aquatic iron(III) (hydr) oxides—Implications for redox cycling of iron in natural waters. Ph.D. Thesis, ETH Zürich, No. 9724.

Deng Y. and Stumm W. (1993) Kinetics of redox cycling of iron coupled with fulvic acid. *Aquatic Sci.* **55**, 103–111.

Grenthe I., Stumm W., Laaksuharju M., Nilsson A.-C. and Wikberg P. (1992) Redox potentials and redox reactions in deep groundwater systems. *Chemical Geology* **98**, 131–150.

von Gunten U. and Schneider W. (1991) Primary products of the oxygenation of Fe(II) at an oxic-anoxic boundary: nucleation, aggregation and aging. *J. Colloid Interface Sci.* **145**, 127–139.

Hochella M. F., Jr. (1990) Atomic structure, microtopography, composition, and reactivity of mineral structures. In *Mineral–Water Interface Geochemistry*, *Review in Mineralogy* (eds, M. F. Hochella and A. F. White), Vol. 23, Chap. 3, pp. 87–132. The Mineralogical Society of America.

Laxen D. P. H. and Chandler I. M. (1983) Size distribution on iron and manganese species in freshwaters. *Geochim. Cosmochim. Acta* **47**, 731–741.

Luther III. G. W. (1990) The frontier-molecular orbital theory approach in geochemical processes. In *Aquatic Chemical Kinetics* (ed. W. Stumm), Chap. 6, pp. 173–198.

Martin J. H. and Gorden R. M. (1988) Northeast Pacific iron distributions in relation to phytoplankton productivity. *Deep-Sea Res.* **35**, 177–196.

Miller W. P., Zelazny L. W. and Martens D. C. (1986) Dissolution of synthetic crystalline and non-crystalline iron oxides by organic acids. *Geoderma.* **37**, 1–13.

Perret D., de Vitre R. R., Leppard G. G. and Buffle J. (1990) Characterizing authchthonous iron particles and colloids—the need for better particle analysis methods. In *Large Lakes* (eds M. M. Tilzer and C. Serruya), Chap. 12, pp. 224–244.

Rich H. W. and Morel F. M. M. (1990) Availability of well-defined iron colloids to the marine diatom *Thalassiosira weissfloggi*. *Limnol. Oceanogr.* **35**, 349–358.

Schneider W. and Schwyn B. (1987) The hydrolysis of iron in synthetic, biological, and aquatic media. In *Aquatic Surface Chemistry* (ed. W. Stumm), Chap. 7, pp. 167–194. Wiley-Interscience.

Sillen L. G. and Martell A. E. (1964) Stability constants of metal-ion complexes. Special publication No. 17, The Chemical Society, Burlington House.

Smith R. M. and Martell A. E. (1975) *Critical Stability Constants*. Vol. 2: Amines, Plenum Press.

Stumm W., Furrer G., Wieland E. and Zinder B. (1985) The effect of complex-forming ligands on the dissolution of oxides and aluminosilicates. In *The Chemistry of Weathering* (ed. J. I. Drever), NATO ASI Series C, Vol. 149, pp. 55–74. Dordrecht.

Stumm W. and Morgan J. J. (1981) *Aquatic Chemistry*, 2nd edn. Wiley-Interscience.

Sulzberger B., Schnoor J. L., Giovanoli R., Hering J. G. and Zobrist J. (1990) Biogeochemical of iron in an acidic lake. *Aquatic Sci.* **52**, 56–74.

Sulzberger B., Suter D., Siffert C., Banwart S. and Stumm W. (1989) Dissolution of Fe(III) (hydr) oxide in natural waters; Laboratory assessment on the kinetics controlled by surface coordination. *Marine Chem.* **28**, 127–144.

Suter D., Banwart S. and Stumm W. (1991) Dissolution of hydrous iron(III) oxides by reductive mechanisms. *Langmuir* **7**, 809–813.

Tamura H., Goto K., Yotsuyanagi T. and Nagayama M. (1974) Spectrophotometric determination of iron(III) with 1,10-phenanthroline in the presence of large amounts of iron(III). *Talanta* **21**, 318–321.

Tamura H., Kawamura S. and Nagayama M. (1980) Acceleration of the oxidation of Fe^{2+} ions by Fe(III)-oxyhydroxides. *Corros. Sci.* **20**, 963–971.

Thurman E. M. and Malcolm R. L. (1983) Structural study of humic substances: new approaches and methods. In *Aquatic and Terrestrial Humic Materials* (eds R. F. Christman and E. Gjessing), Chap. 1, pp. 1–23. Ann Arbor.

Tipping E., Woof C. and Cook D. (1981) Iron oxide from a seasonally anoxic lake. *Geochim. Cosmochim. Acta* **45**, 1411–1419.

Wehrli B. and Stumm W. (1988) Oxygenation of vanadyl (IV)—Effect of coordinated surface hydroxyl groups and OH^-. *Langmuir* **4**, 753–758.

Wehrli B., Wieland E. and Furrer G. (1990) Chemical mechanisms in the dissolution kinetics of minerals; the aspect of active sites. *Aquatic Sci.* **52**, 3–31.

Wells M. and Goldberg E. D. (1991) Occurrence of small colloids in sea water. *Nature* **353**, 342–344.

Wersin P. (1990) The Fe(II)–CO_2–H_2O system in anoxic natural waters: Equilibria and surface chemistry. Ph.D.Thesis, ETH Zürich, No. 9230.

Wersin P., Höhener P., Giovanoli R. and Stumm W. (1991) Early diagenetic influences on iron transformations in a freshwater lake sediment. *Chem. Geol.* **90**, 233–252.

White A. F. and Yee A. (1985) Aqueous oxidation-reduction kinetics associated with coupled electron cation transfer from iron-containing silicate at 25°C. *Geochim. Cosmochim. Acta* **49**, 1263–1267.

WIELAND E., WEHRLI B. and STUMM W. (1988) The coordination chemistry of weathering: III. Generalization on the dissolution rates of minerals. *Geochim. Cosmochim. Acta* **52**, 1969–1981.

APPENDIX

I. Calculation of the standard redox potential of the $Fe(OH)_3(s)/Fe^{2+}$ *redox couple for iron(III) oxyhydroxides formed in TRIS and imidazole*

A platinum electrode (saturated calomel electrode as reference) is used to measure the electrode potential for the $Fe(OH)_3(s)/Fe^{2+}$ redox couple in different iron(III) oxyhydroxide systems.

$$\text{Hg, HgCl}_2 \,|\, \text{KCl} \,||\, \text{Fe(OH)}_3\text{(s), Fe(II)/Pt}$$

$$E_{cell} = E_H - E_{ref} \qquad (1)$$

The electrode potentials (E_{cell}) are −0.147 V and −1.71 V at 25°C for the systems of TRIS and imidazole, respectively when $(Fe^{2+}) = 5.0 \times 10^{-5}$ M (experimental determined) and pH = 7.0.

E_{ref} is known as 0.244 V at 25°C (STUMM and MORGAN). Thus, the redox potential (E_H) of the redox couple ($Fe(OH)_3(s)$ /Fe^{2+}) can be calculated as follows:

for TRIS:

$$E_H = E_{cell} + E_{ref} = -0.147 + 0.244 = 0.097 \text{ (V)}$$

for imidazole:

$$E_H = E_{cell} + E_{ref} = -0.171 + 0.244 = 0.073 \text{ (V)}.$$

According to the Nernst equation, the half reaction for the reductive dissolution of an iron(III) oxyhydroxide ($Fe(OH)_3(s) + 3H^+ + e = Fe^{2+} + 3H_2O$) can be described as follows:

$$\begin{aligned} E_H &= E^0_{H,Fe(OH)_3(s)/Fe^{2+}} + 0.059 \log [H^+_{NBS}]^3/[Fe^{2+}] \\ &= E^0_{H,Fe(OH)_3(s)/Fe^{2+}} + 0.059 \log [H^+_{NBS}]^3/(Fe^{2+})\gamma_{Fe^{2+}} \end{aligned} \qquad (2)$$

where $E^0_{H,Fe(OH)_3(s)/Fe^{2+}}$ is the standard redox potential for the $Fe(OH)_3(s)/Fe^{2+}$ redox couple. $[H^+_{NBS}]$ denotes the activity of proton (pH electrode was calibrated by standard buffer solutions). $[Fe^{2+}]$ is the activity of Fe^{2+}; $\gamma_{Fe^{2+}}$ is the activity coefficient for Fe^{2+}; (Fe^{2+}) is the concentration of Fe^{2+} without ionic strength correction, i.e. $[Fe^{2+}] = (Fe^{2+})\gamma_{Fe^{2+}}$. The values of the standard redox potential for iron(III) oxyhydroxides formed in TRIS and imidazole can be calculated as follows:

$$E^0_{H,Fe(OH)_3(s)/Fe^{2+}} = E_H - 0.059 \log [H^+_{NBS}]^3/ (Fe^{2+})\gamma_{Fe^{2+}}. \qquad (3)$$

1. *Calculation for the activity coefficient of* Fe^{2+}. The Davies Approximation (STUMM and MORGAN, 1981) is used to calculate the activity coefficient of Fe^{2+}:

$$\log \gamma_{Fe^{2+}} = -Az^2\{[\sqrt{I}/(1+\sqrt{I})] - 0.3I\} \qquad (I < 0.5\,\text{M}) \quad (4)$$

where $A \approx 0.5$ for water at 25°C; z is the charge of ion; and I(M) is the ionic strength which can be calculated as below:

$$I = 1/2 \sum C_i z_i^2 \qquad (5)$$

where C_i is the concentration of ion and z_i is the charge of ion.

(1) *TRIS system.* The acid–base equilibrium of TRIS (pK_a = 8.0, SMITH and MARTELL, 1975) is:

$$HA^+ = H^+ + A.$$

The concentration of HA^+ species at pH 7 (total concentration of TRIS: C_T = 0.50 M) can be calculated as follows:

$$[HA^+] = C_T \times \alpha_0 = 0.50 \times 0.90 = 0.45 \text{ (M)}$$

$$\alpha_0 = [H^+]^2/G = (1.0 \times 10^{-14}/(1.1 \times 10^{-14}) = 0.90$$

$$\begin{aligned} G = [H^+]^2 + K_a[H^+] &= (1.0 \times 10^{-7})^2 \\ &+ (1.0 \times 10^{-8} \times 10^{-7}) = 1.1 \times 10^{-14}. \end{aligned}$$

HA^+, Na^+ (0.010 M) and ClO_4^- (0.010 M) are the main charged species in the system. Thus, the ionic strength (I) can be calculated as below:

$$I = 1/2(0.45 + 0.010 + 0.010) = 0.24 \text{ (M)}.$$

The activity coefficient of Fe^{2+} is then calculated:

$$\begin{aligned} \log \gamma_{Fe^{2+}} = &-0.5 \times (2)^2\{[\sqrt{0.24}/(1+\sqrt{0.24})] \\ &- 0.3 \times 0.24\} = -0.52. \end{aligned}$$

(2) *Imidazole system.* The acid–base equilibrium of imidazole (pK_a=7.0, SMITH and MARTELL, 1975) is:

$$HB^+ = H^+ + B.$$

The concentration of HB^+ species at pH 7 (total concentration of imidazole: C_T = 0.010 M) can be calculated as follows:

$$[HB^+] = C_T \times \alpha_0 = 0.010 \times 0.50 = 5.0 \times 10^{-3} \text{ (M)}$$

$$\alpha_0 = [H^+]^2/G = (1.0 \times 10^{-7})^2/2.0 \times 10^{-14} = 0.50$$

$$\begin{aligned} G = [H^+]^2 + K_a\,[H^+] &= (1.0 \times 10^{-7})^2 \\ &+ (1.0 \times 10^{-7} \times 1.0 \times 10^{-7}) = 2.0 \times 10^{-14}. \end{aligned}$$

HB^+, Na^+ (0.010 M) and ClO_4^- (0.010 M) are the main charged species in the system. Thus, the ionic strength (I) can be calculated as below:

$$I = 1/2\,(5.0 \times 10^{-3} + 0.010 + 0.010) = 1.3 \times 10^{-2} \text{ (M)}.$$

Then, the activity coefficient of Fe^{2+} is calculated:

$$\begin{aligned} \log \gamma_{Fe^{2+}} &= -0.5 \times (2)^2\{[\sqrt{1.3 \times 10^{-2}}/(1 + \sqrt{1.3 \times 10^{-2}})] \\ &- 0.3 \times 1.3 \times 10^{-2}\} = -0.19. \end{aligned}$$

2. *Calculation of the standard redox potential of the* $Fe(OH)_3(s)/Fe^{2+}$ *redox couple.* The standard redox potential of the $Fe(OH)_3(s)/Fe^{2+}$ redox couple for the iron(III) oxyhydroxides formed in TRIS and imidazole can be calculated using Eqn (3) ($[H^+_{NBS}] = 1.0 \times 10^{-7}$ M, $(Fe^{2+}) = 5.0 \times 10^{-5}$ M):

$$\begin{aligned} E^0_{H,Fe(OH)_3(s)/Fe^{2+}} &= E_H - 0.059 \log [H^+_{NBS}]^3 \\ &+ 0.059 \log (Fe^{2+})\gamma_{Fe^{2+}} \end{aligned}$$

TRIS system ($\log \gamma_{Fe^{2+}} = -0.52$):

$$\begin{aligned} E^0_{H,Fe(OH)_3(s)/Fe^{2+}} &= 0.097 + 1.2 - 0.25 \\ &- 3.0 \times 10^{-2} \approx 1.0 \text{ (V)} \end{aligned}$$

imidazole system ($\log \gamma_{Fe^{2+}} = -0.19$):

$$\begin{aligned} E^0_{H,Fe(OH)_3(s)/Fe^{2+}} &= 0.073 + 1.2 - 0.25 \\ &- 1.1 \times 10^{-2} \approx 1.0 \text{ (V)}. \end{aligned}$$

II. Calculation of the solubility product of the iron(III) oxyhydroxides formed in TRIS and imidazole

As shown in *Appendix I*, the half reaction for the reductive dissolution of an iron(III) oxyhydroxide can be expressed by Eqn (2) using the Nernst equation. In a similar way, the half reaction can also be expressed using the Nernst equation by considering the Fe^{3+}/Fe^{2+} redox couple and the solubility product (K_{s0}) of the iron(III) oxyhydroxide ($Fe^{3+} + 3OH^- = Fe(OH)_3(s)$, $K_{s0} = [Fe^{3+}][OH^-]^3$):

$$\begin{aligned} E_H &= E^0_{H,Fe^{3+}/Fe^{2+}} + 0.059 \log [Fe^{3+}]/[Fe^{2+}] \\ &= E^0_{H,Fe^{3+}/Fe^{2+}} + 0.059 \log K_{s0}/([OH^-]^3[Fe^{2+}]) \\ &= E^0_{H,Fe^{3+}/Fe^{2+}} + 0.059 \log K_{s0}/(K_W)^3 \\ &\qquad + 0.059 \log [H^+_{NBS}]^3/(Fe^{2+})\gamma_{Fe^{2+}} \end{aligned} \tag{6}$$

where $E^0_{H,Fe^{3+}/Fe^{2+}} = 0.77$ V (STUMM and MORGAN, 1981) is the standard redox potential for the Fe^{3+}/Fe^{2+} redox couple. K_W is the ion product of water ($K_W = 1.01 \times 10^{-14}$ at 25°C, STUMM and MORGAN, 1981).

Comparing Eqns (2) and (6), we have:

$$E^0_{H,Fe(OH)_3(s)/Fe^{2+}} = E^0_{H,Fe^{3+}/Fe^{2+}} + 0.059 \log K_{s0}/(K_W)^3 \tag{7}$$

Thus, we obtain:

$$\log K_{s0} = (E^0_{H,Fe(OH)_3(s)/Fe^{2+}} - E^0_{H,Fe^{3+}/Fe^{2+}})/0.059 + 3 \log K_W \tag{8}$$

The standard redox potential of the $Fe(OH)_3(s)/Fe^{2+}$ redox couple is 1.0 V for both systems of TRIS and imidazole (see Appendix I). Based on Eqn (8), the solubility product of the iron(III) oxyhydroxides formed in TRIS and imidazole can be estimated as follows:

TRIS system:

$$\log K_{s0} = [(1.0 - 0.77)/0.059 + 3 \times (-14.0)] \approx -38$$

imidazole system:

$$\log K_{s0} = (1.0 - 0.77)/0.059 + 3 \times (-14.0) \approx -38.$$