

Kinetics of iron oxide dissolution as enhanced by organic ligands

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Previous studies indicate that colloids may be released in the subsurface environment upon the dissolution of cementitious iron oxides (Ryan and Gschwend, 1992). Our field investigation showed that the concentrations of both total and ferrous iron increased during an injection of natural organic matter (NOM), implying an NOM-enhanced dissolution of iron oxide and mobilization of the oxide colloids *in situ* (Liang *et al.*, 1993). Because of the lack of quantitative data, predictions on the rates and the extent of iron-oxide dissolution in a natural system are hindered. The current laboratory studies are aimed at developing and testing conceptual and mathematical models for iron oxide dissolution. Here experimental work is undertaken to determine the rates of dissolution of ferrihydrite as influenced by organic ligands, such as oxalate, citrate and ascorbate ions. The type of organic ligands, ligand concentrations, and pH were varied in order to determine the effect of each variable on the kinetics of the dissolution reaction. An important application of this project is to assess iron oxide colloid mobilization corresponding to the dissolution of the oxide in groundwater, which is investigated in column flow-through systems.

Materials and methods

Ferrihydrite was prepared according to Cornell and Schwertmann (1979). The specific surface area of the oxide was 254.2 m²/g. Ligand solutions of the appropriate concentrations were made with one of the following reagents: potassium citrate (monohydrate, J.T. Baker, Inc.), potassium oxalate (monohydrate, J.T. Baker, Inc.), and ascorbic acid (EM Industries, Inc.). All solutions were made with Milli-Q water.

For batch studies, the organic-ligand solutions were made in 600 mL reactor at concentrations ranging from 0.1–5 mM. Ferrihydrite was introduced to the ligand solutions to reach a concentration of 0.4 g/l.

The reactor was wrapped in foil to keep out light. All experiments were conducted at ambient temperature and dissolved oxygen levels. A pH titrator (Metrohm's model 719 S Titrimo) was used to maintain a constant pH at 4 or 6.5. The solution in the reactor was stirred continuously during the experiment.

A 5 to 10 mL sample was taken periodically after iron oxide was placed in the organic solution to follow the dissolution kinetics. The sample was pre-filtered through 0.2 µm syringe filters, Acrodisc[®] CR PTFE filters, and then filtered through a 3000 MW DIAFLO[®] ultrafiltration membrane using an Amicon[®] ultrafiltration cell. Iron passing through the filter was defined as dissolved and was analysed by an atomic absorption spectrophotometer (Perkin-Elmer[®] 5000). The filtered samples were also analysed to determine the organic ligand concentration by using a total organic carbon analyser (Rosemount[®] Dohrmann[®] DC-190). In the presence of ascorbic acid, a significant amount of Fe(III) was reduced to Fe(II), which was determined by 1,10-phenanthroline method using a Hach DR/2000 Spectrophotometer.

Results and discussion

Data collected during the dissolution batch studies are plotted for the total dissolved iron *vs* reaction time. In general, these plots show two distinct regions: a steep initial increase in total dissolved iron concentration within the first 10 h of the reaction and then a gradual change in the dissolved iron (Fig. 1). For the second region, a small increase of dissolved iron is often observed for ligands at lower concentration, but a decrease for higher concentrations of ligands (Figs. 1,2).

At pH 4, the initial-rate constants show that the ligand concentration have a direct influence on the dissolution reaction of ferrihydrite: increasing the rate at higher ligand concentrations. The pH increase has an inverse effect on the dissolution rates, in

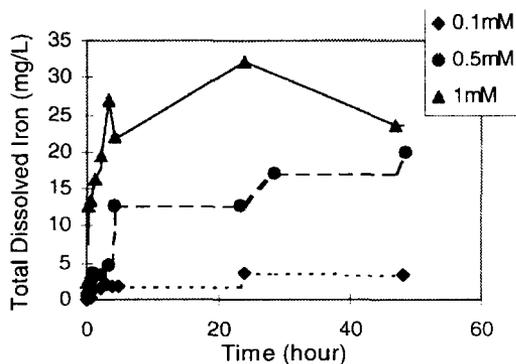


FIG. 1. Rates of dissolution of ferrihydrite by ascorbic acid at pH 4.

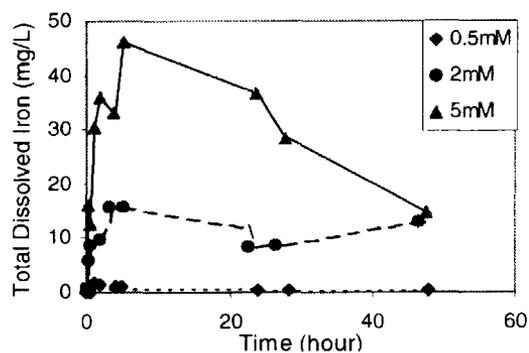


FIG. 2. Rates of dissolution of ferrihydrite by oxalate at pH 4.

agreement with the earlier observations on the other type of metal oxides (Zinder *et al.*, 1986). Of the three types of organic additives studied, ascorbic acid dissolves ferrihydrite most readily under the same pH conditions. Previous work with goethite showed similar trend, i.e. significant dissolution took place with ascorbic acid among a series of carboxylic acids (Chiarizia and Horwitz, 1991).

However, previous studies showed a linear increase of dissolved iron with time as opposed to the two reaction regions as observed here. Furthermore, in the ferrihydrite dissolution with 5 mM oxalate (Fig. 2) the decrease in the dissolved iron concentration at later reaction times is a phenomenon that was observed repeatedly. Previous studies exploring the dissolution of ferrihydrite in the presence of tripolyphosphate have reported decreases in the total soluble iron concentration after an initial increase (Lin and Benjamin, 1990). These decreases were attributed to the adsorption of dissolved iron-tripolyphosphate complexes to ferrihydrite.

A similar process may be occurring between ferrihydrite and iron-oxalate, iron-citrate, or iron-ascorbic acid complexes. It appears that the dissolution rate is determined by sorption of ligands, desorption of the surface species and re-sorption of iron-ligand complexes. At the initial stage of the reaction, sorption of the organic ligands drives the reaction toward dissolution. As the metal organic complexes in the solution increases following the dissolution, the equilibrium shifts to favour re-adsorption of the metal-organic complexes, thus removing the dissolved Fe from solution. Support of this hypothesis comes from the concentrations of dissolved ligands, showing the same trend as that of dissolved iron after the initial stage of dissolution. Immediately following the iron addition, the concen-

trations of dissolved organic ligands sharply decreased. The removal of the ligands from solution is expected because of the adsorption to ferrihydrite. As reaction proceeded dissolved ligand concentrations increased, corresponding to the increase in dissolved iron, indicating that the adsorbed organic ligand is released as iron is dissolved. At later reaction times, ligand concentrations decreased as seen in dissolved iron. Adsorption of the Fe-ligand complexes to ferrihydrite seems plausible.

Conclusion

The results of this study have shown that the dissolution kinetics of ferrihydrite varies with chemical conditions. The rate of ferrihydrite dissolution increases as the pH decreases and as the ligand concentration increases. Ascorbic acid appears to be the most effective among the organic ligands studied. Analyses of dissolved iron and ligand concentration during dissolution suggest that the reaction rate is determined by sorption of ligands, desorption of the surface species and re-sorption of iron-ligand complexes. The type of ligands and the concentration of the ligands have subtle effect on these processes. Observed dissolution rates show that the initial rates are not sustained for the three types of ligands studied under the experimental conditions. In light of batch dissolution kinetics, the occurrence of colloids as initiated by oxide dissolution in column tests will be discussed.

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