

THE INFLUENCE OF SURFACE SPECIATION ON THE RELEASE OF DISSOLVED FE AND FERRIHYDRITE COLLOIDS FROM POROUS MEDIA

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Background and Methodology

The transformation between Fe(II) and Fe(III) occurs when the redox conditions are significantly altered by chemical perturbations. For example, organic pollutants may transform iron oxide to soluble Fe(III) or Fe(II) via surface reduction and dissolution. Additionally, iron oxide colloids could be released into the environment. Because of the high affinities of many contaminant metals and radionuclides to the oxides (Zachara et al., 1994; Ledin, et al., 1994; Stumm, 1993), the release of Fe(III)-oxide colloids could ultimately shape the distribution and movement of these contaminants in the aquatic and subsurface environments (Stumm and Morgan, 1996).

An earlier field investigation (Liang et al., 1993) showed that both Fe(III) and Fe(II) increased in the groundwater following the injection of natural organic matter (NOM) into an aquifer. A large portion of this Fe(III) was colloidal Fe oxide. The observation of both Fe(II) and colloidal Fe(III) suggests that the NOM may have dissolved Fe(III) oxide, and simultaneously mobilized the oxide colloids in situ. To test our hypothesis on the relative importance of electrostatic repulsion versus chemical dissolution in releasing ferrihydrite particle from sand media, we conducted a detailed laboratory study with batch adsorption, dissolution, and column breakthrough experiments using citrate as a surrogate for a dissolution-promoting moiety of the NOM (Liang et al., 2000). The results of this work imply that in Fe-chemistry dominated aquifer, a chemical perturbation (e.g. a plume of organic ligands) is likely to induce colloid release initially. Over time, dissolution will take a controlling role, changing the ratio of dissolved and colloidal iron.

We propose that the surface speciation on iron oxide is fundamental to the observed ferrihydrite dissolution and particle release. To quantitatively predict the release of dissolved iron and colloidal oxide particles from a porous medium, we conducted the current work with changing citrate concentrations, in an attempt to model the surface speciation.

Experiments were conducted in a column flow-through system filled with ferrihydrite-coated quartz (Szecsody et al. 1994). Natural quartz sand with a diameter ranging from 180-220 μm was subjected to acid cleaning before use. The kinetics of ferrihydrite colloid release was investigated by eluting a citrate solution of respectively 1, 3 and 5 mM at pH 4 and 10 mM NaCl. Flow rate was set constant at 0.5 ml min^{-1} . Effluent samples were collected over time for citrate and iron analyses and pH was measured with time. Dissolved and colloidal iron was separated via ultra-filtration through 3000 Dalton DIAFLO membranes. Iron concentration in the bulk and filtrate was determined using ICP-MS.

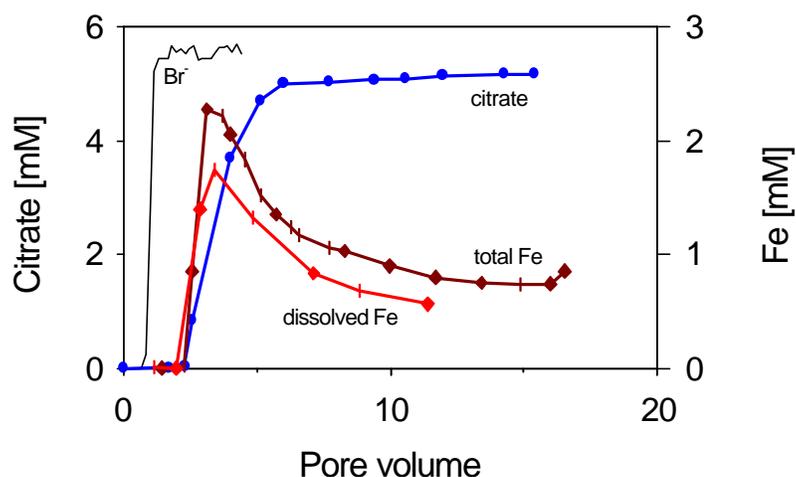


Figure 1: Break through curves of bromide, citrate, total and dissolved iron at 5 mM inflowing citrate concentration.

Ferrihydrite colloids were characterized by micro-electrophoretic mobility measurements. For model calculations, we used MINTEQA2 to determine surface species and PREEQC to simulate the flow through experiment.

Results and Discussion

The characteristics of Fe and citrate breakthrough are illustrated in figure 1. Both dissolved and total Fe breakthrough rapidly, with a peak value occurred at ~ 3 pore volumes. Stable concentrations reached at longer run times, after citrate breakthrough. For dissolved Fe, the initial peak values were considerably attenuated at lower concentrations of inflowing citrate (data not shown). Colloidal ferrihydrite particles, defined as the difference between total and dissolved Fe, varied correspondingly with total Fe, exhibiting a peak values before citrate breakthrough (Figure 2). Separate analysis by turbidity agreed with data derived from Fe measurements.

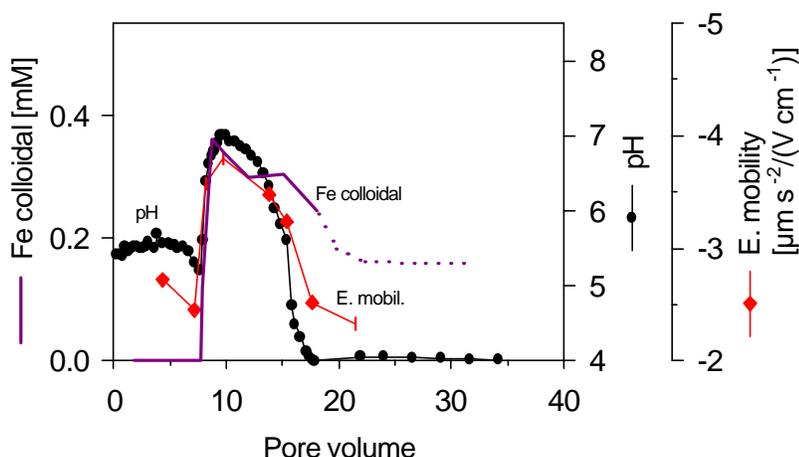


Figure 2: Break through curves of colloidal iron and pH. Measurement of electrophoretic mobility.

Citrate adsorption imparts negative charge to iron oxide particles. This was verified by electrophoretic mobility of the effluent particles, which showed negative values consistently. However, the magnitude of the electrophoretic mobility varied with the effluent citrate concentration and the peak values of -3.5 to $-4.0 \mu\text{m s}^{-1}/(\text{V cm}^{-1})$ occurred at peak concentrations of colloidal ferrihydrite. After citrate breakthrough, they stabilized at a value of $-2.5 \mu\text{m s}^{-1}/(\text{V cm}^{-1})$ (Figure 2). At this point, colloid concentrations reached a stable value. The adsorption of citrate

and the dissolution of Fe(III) both release OH^- into solution, which was detected in our experiments. Figure 2 shows that the effluent pH increased during the initial phase of adsorption-dissolution to pH 7-8, and subsequently it returned to the initial value of pH 4 following the citrate breakthrough (Figure 2).

The solution pH governs the extent of surface protonation and surface complexation, thus influencing the surface electric potential. We infer that the development of the mobility peak during citrate breakthrough is the result of the pH variation, shifting the surface protonation and complexation equilibrium. The corresponding trends among pH, electrophoretic mobility, and colloidal Fe clearly indicated electrostatic repulsion as a driving force for ferrihydrite colloid release during the initial phase of citrate adsorption.

For dissolved Fe, the amount increased with increasing citrate elution (Figure 1) at the initial breakthrough and peaked at ~ 3 pore volumes. Although influenced by pH variations, the rates indicated a first order dependence on adsorption density, as it would be expected from surface complexation theory (Stumm and Wieland, 1990). The rates compared satisfactorily with initial dissolution rates in batch system for similar surface adsorption densities and pH. The constant flow of fresh ligand through the column ensured that dissolution was maintained in the system. Under conditions of maximum surface adsorption, dissolution came to a stable value with a rate comparable for all experiments. This result was expected for surface complex promoted dissolution.

Conclusion

Experiments showed that the ferrihydrite colloids were dissolved and released from the oxide-coated quartz media during the elution of citrate. The initial colloid peak was caused by electrostatic repulsion between the quartz grains and the ferrihydrite particles as a result of surface speciation. This colloid peak was directly related to the increase of surface electric potential as demonstrated with electrophoretic mobility measurements. Ferrihydrite dissolution was characterized by an initially strong dependence on influent citrate concentrations. During the period from the initial to complete breakthrough of citrate, dissolution rates showed complex relation to the rate of adsorption, adsorption density, and pH variations. After complete breakthrough of citrate, dissolution rates stabilized. Models based on surface chemical equilibrium and dissolution kinetics provide valid tools for predicting the relevant amounts of dissolved and colloidal Fe as a result of aqueous chemistry change.

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