

Transformation of soil iron minerals under static batch and flow through conditions: application for soil remediation

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Abstract

Ferrihydrite is poorly crystallized mineral, commonly the most abundant iron mineral found in soils and sediments. The mineralogical transformation of ferrihydrite into Fe^{II} bearing minerals represents a potential way to improve the soil self-remediation capacity. Indeed, reduction by Fe^{II} may be a significant abiotic pathway in the natural attenuation of environmental contaminants including organic and inorganic pollutants. The aim of this laboratory study was to investigate the Fe^{II} induced mineralogical transformations of three matrixes: ferrihydrite, ferrihydrite-rich sand and a pristine soil under static batch and flow through conditions. Since Fe^{II} is more reactive than only Fe^{III} minerals to promote the remediation of various soil pollutants, generation of Fe^{II} bearing minerals in soil-packed column was optimized. The starting and resulting solids were characterized through X-ray diffraction (XRD), Mössbauer spectrometry, transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

Key Words

Ferrihydrite, mineralogical transformation, magnetite, green rust, soil reactivity

Introduction

Iron oxyhydroxides are abundant in the environment and influence the biogeochemical cycling and availability of Fe via the redox couple connecting solid phase ferric oxides and soluble Fe^{II} species. Iron oxides and oxyhydroxides are present in the soils as a wide range of minerals most commonly goethite, ferrihydrite, hematite and lepidocrocite with different characteristics such as stability, specific surface area and reactivity (Cornell and Schwertmann 1996). In reduced soil zone, they exist as mixed Fe^{II} and Fe^{III} compounds such as magnetite (Fe₃O₄) or fougérite, the mineral counterpart of the Fe^{II}Fe^{III} green rust (Trolard *et al.* 1997). Ferrihydrite is poorly crystallized mineral, the most abundant iron mineral commonly found in soils and sediments. It plays a substantial role in soil due to its high surface area and intrinsic reactivity.

The chemistry of Fe in aquatic and soil/sediment systems also strongly influences the transport and availability of various nutrients (e.g., C, N, and P) and contaminants (organic and inorganic) due to adsorption and surface precipitation processes (Elsner *et al.* 2004). The ubiquitous presence of iron suggests that reduction by iron may be a significant abiotic pathway in the natural attenuation of environmental contaminants. Fe^{II} is one of the most abundant reductants typically present in aquatic and terrestrial environments under suboxic and anoxic conditions (Rügge *et al.* 1998) but sorbed Fe^{II} and structural Fe^{II} are often more powerful reductants than dissolved Fe^{II}. Indeed, contaminants such as carbon tetrachloride, nitro benzenes, and U(VI) are readily reduced by sorbed or structural Fe^{II} but not by aqueous Fe^{II} complexes (Amonette *et al.* 2000). This Fe^{III}-Fe^{II} redox couple is implicated in the fate and mobility of various soil contaminants including organic and inorganic pollutants (Elsner *et al.* 2004). The stability and reactivity of iron oxyhydroxides are strongly affected by their interactions with aqueous Fe^{II} inducing their structural modification and bulk phase transformation which depend upon Fe^{II}/Fe^{III} molar ratio, pH, anionic media and structure of initial iron oxyhydroxide substrate (Pedersen *et al.* 2005). Therefore, *in situ* generation of Fe^{II} bearing minerals in soil could modify the soil capacity for natural remediation of environmental contaminants. The objective of this study is to monitor the mineralogical transformations in three matrixes: ferrihydrite, ferrihydrite-rich sand and a pristine soil under static batch and flow through conditions. The reactivity of Fe^{II} with endogenous iron mineral fraction in a pristine soil with low organic carbon was investigated.

Methods

Experiments were conducted with synthetic ferrihydrite (F) and ferrihydrite rich sand (FCS). The 2-line ferrihydrite (F) was synthesized according to the method of Schwertmann and Cornell (Schwertmann and Cornell 2000). The quartz sand (Fontainebleau, France) 150-300 µm was cleaned with 1 M HCl for 48 hours,

and then rinsed with pure water. The FCS was synthesized by heterogeneous suspension method. The final ferrihydrite rich sand was stored at ambient temperature for further use. Soil sample was collected from a pristine forest. The organic litter was removed to expose mineral soil. Particle size, carbon, nitrogen and soil moisture content analyses were performed. The soil is mainly composed of sand with a clay content of about 1 %, Fe-oxide content of 2.2 %, Al-oxide of 2.1 % and low OC (e.g., ~ 0.5 %). The Fe^{II} induced reaction test was conducted with the 2 mm size fraction of soil. The mineralogical transformation of substrates was conducted by reacting them against Fe^{II} and NaOH in appropriate amounts to synthesize either magnetite or green rust (GR). All experiments for preparation were conducted in a gas tight reactor with continuous N₂ bubbling in aqueous solution in order to ensure the evacuation of dissolved oxygen and to avoid the oxidation of Fe^{II}. Column studies were conducted to evaluate the Fe^{II} induced transformations of FCS under flow through conditions. In a glass chromatographic column of 40 cm length and 2.6 cm internal diameter (XK 26/20, GE Healthcare), the FCS particles were packed to a height of 9.5 cm, corresponding to a dry mass of 76 g. The dry porous bed had a uniform bulk density (ρ) of $1.23 \pm 0.01 \text{ g/cm}^3$. After packing, the column was cautiously wetted upward with the background electrolyte solution (NaCl, 10^{-2} mol/L). Throughout the experiments, the flow rate was hold constant at 0.5 ml/min, corresponding to a pore water velocity of 0.09 cm/min, the flow direction was from bottom to top of the column. Dissolved iron and aqueous silica concentrations in the outflow were measured by ICP-AES. The starting and resulting solids from both batch and column tests were characterized through X-ray diffraction (XRD), Mössbauer spectrometry and Transmission electron microscopy (TEM).

Results

Static batch conditions

In the presence of Fe^{II}, the poorly crystallized iron oxide, ferrihydrite, can be transformed either into green rust (Fe^{II}:Fe^{III}=2:1) or magnetite (Fe^{II}:Fe^{III}=1:2). The Mössbauer spectrums of end-products of these transformations are shown in Figure 1. Mössbauer spectroscopy is a powerful technique for determining accurately the relative proportion of Fe^{II} and Fe^{III} species. The Mössbauer spectrum (a) of first sample is essentially composed of two doublets with a ratio Fe^{II}:Fe^{III}=66:33, which could be attributed to green rust (Figure 1a). The spectrum (b) was fitted with two sextets assigned to magnetite, it is constituted by a superposition of two subspectra associated to the distribution of the iron in the octahedral and tetrahedral sites. The two valence states on octahedral sites are not distinguishable (valence Fe^{2.5+}) due to a fast electron hopping between Fe²⁺ and Fe³⁺ in octahedral sites (Figure 1b). This magnetite is non-stoichiometric and poorly crystallized.

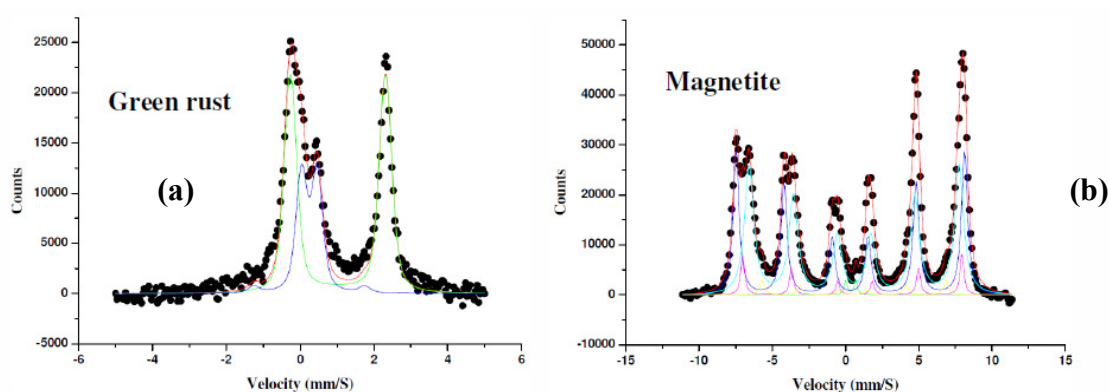


Figure 1. Mössbauer spectra of GR and magnetite generated through FeII reaction with Ferrihydrite.

The same spectrum was obtained when ferrihydrite was initially mixed with sand quartz (i.e. FCS). Five diffraction peaks at $2\theta = 21.2^\circ$, 35° , 41.2° , 50.4° and 62.8° are shown in the XRD diffractograms, which could be assigned to Fe₃O₄, magnetite (Figure 2). The d-space values of these main peaks were 2.53, 2.96, 2.09, 4.85 and 1.71 Å which may correspond to the more intense lines 311, 220, 400, 111 and 422, respectively of magnetite (Schwertmann and Cornell 2000). In addition to the diffraction peaks of magnetite, the transformation product of FCS showed the peaks of quartz represented by Q.

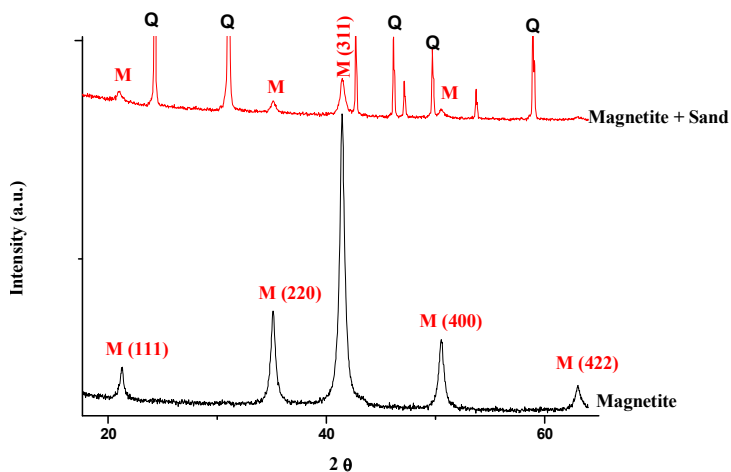


Figure 2. XRD for magnetite (From Ferrihydrite) and magnetite sand (from FCS).

Figure 3 shows the morphological features of initial ferrihydrite substrate (F) and final magnetite. It was indicated that particles of F are very small and strongly aggregated which makes it almost impossible to identify single crystals in TEM. TEM image for magnetite indicate that magnetite particles are poorly crystallized and size of particles is not uniform. The shape of crystals varied from round to octahedral.

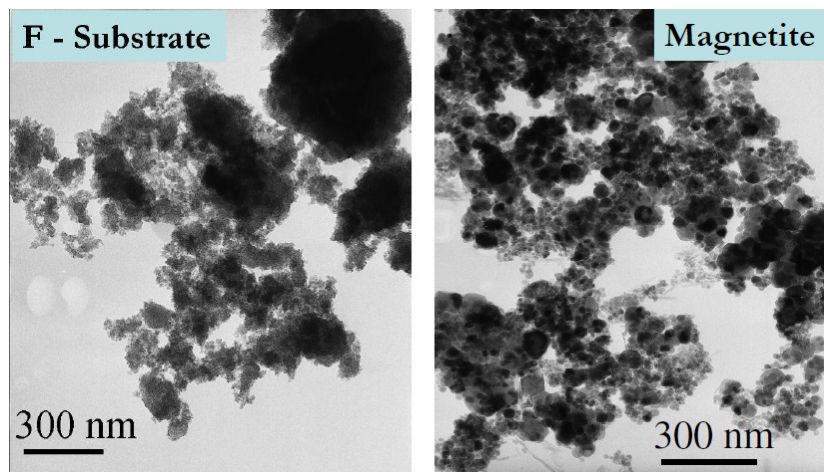


Figure 3. TEM of ferrihydrite and generated magnetite.

Saturated column test

In the column where Fe^{II} solution was injected in open system, the FCS color was darkened at the bottom of column, while it remains unchanged in the rest of column (i.e. red-brown) (See Figure 4. left). This color modification was noted after 2h corresponding to the injection of 4 PV of Fe^{II} (0.4mM) solution (pH~6.5) at flow rate of 0.5mL/min. Mössbauer and XRD analyses showed this black color was likely due to the formation of mixture of magnetite (Fe_3O_4) and goethite ($\alpha\text{-FeOOH}$) (Figure 4). A darkening was however observed in the whole column when Fe^{II} solution was injected in closed loop system (See Figure 4. right). No color stratification was noted. Mineralogical characterization showed that there are at least three mineral phases: untransformed ferrihydrite (proposed formula, $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), little of magnetite (Fe_3O_4) and hematite ($\alpha\text{-Fe}_2\text{O}_3$). Increases of crystallinity of Fe-oxide together with formation of Fe^{II} -mineral species were observed.

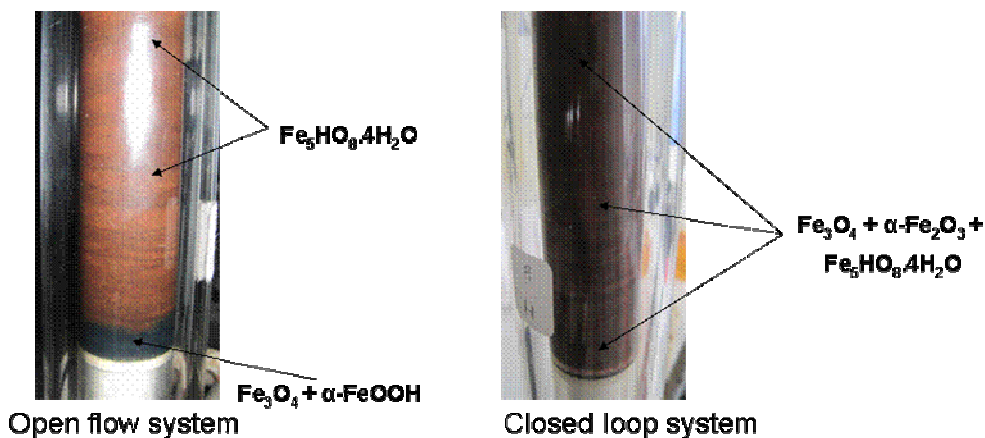


Figure 4. Pictures of soil bed in columns.

For soil column experiment, poor crystallinity and low concentrations of Fe oxides can be responsible for the difficulty in their identification and quantification by spectroscopic techniques. However chemical analyses showed an increase of the degree of crystallinity. This parameter was evaluated from the ratio of amounts of Fe extracted with oxalate-oxalic acid and with bicarbonate-citrate-dithionite mixtures. This step is crucial for the application of the above mentioned transformation processes in soil remediation. Further study is still needed in order to optimize the reaction of Fe^{II} with soil iron minerals under flow through conditions.

Conclusion

Fe^{II}-induced mineralogical transformation of ferrihydrite involved the generation of more reactive iron (II) bearing minerals under batch test. Formation of Fe^{II}-mineral species as well as increases of crystallinity of Fe-oxide were however observed under flow through conditions. Fe^{II}-induced mineralogical transformation test in a pristine soil did not provide desired results, probably due to the low Fe soil content and air oxidation of newly iron (II) formed. A current study is under progress to monitor *in situ* the mineral transformation using miniaturized Mössbauer spectroscopy implanted in the front of the column.

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