



Ferrihydrite interaction with silicate and competing oxyanions: Geometry and Hydrogen bonding of surface species

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Abstract

Silicic acid is omnipresent in nature and interacts with ferrihydrite (Fh) changing the environmental fate of elements. For freshly prepared ferrihydrite, pH and electrolyte dependency of the Si adsorption was measured and interpreted with the charge distribution (CD) model using reactive site densities derived with a surface structural analysis. Proton adsorption data disclose the surface area ($A \sim 610 \text{ m}^2 \text{ g}^{-1}$) and mean particle size ($d \sim 2.5 \text{ nm}$) of the Fh studied. Similarly, a range of $A \sim 530\text{--}710 \text{ g m}^{-2}$ and $d \sim 2.3\text{--}2.8 \text{ nm}$ Fh is found for Fh used in literature. Modeling of our Si adsorption data indicates the formation of Si-oligomers alongside with a Si-monomer. There is quantitative agreement with spectroscopy (ATR-IR, XPS, IR). Innersphere complexation of monomeric Si results in the formation of a mononuclear monodentate complex. However, one of the Si—OH ligands strongly interacts with an adjacent $\equiv\text{FeOH}$ group, forming an extraordinary hydrogen ($\text{O} \cdots \text{H} - \text{O}$) bond in which the H^+ ion is significantly shifted, transferring supplementary proton charge ($\Delta s_{\text{H}} = \sim 0.20 \text{ v.u.}$) towards the surface changing the interfacial charge distribution coefficients of the complex, in agreement with the adsorption data. The shift of charge inhibits the protonation of the $\equiv\text{FeOH}$ surface group, leading to a stable $\equiv\text{FeOH}-\text{FeOSi}(\text{OH})_3$ configuration. Depending on pH and Si-loading, oligomers are present as a Si trimer and some Si tetramer. These complexes have a double-monomer Fe_2Si_2 structure in which two Si tetrahedra are connected to two Fe octahedra each via a single $\text{Fe}-\text{O}-\text{Si}$ bond. The various MO/DFT (B3LYP and BP86) optimized geometries can reproduce the mean Fe-Si distances of 324 and 331 pm found with differential PDF analysis. The outer ligands of the Si-monomer remain protonated, whereas one of the outer ligands of the Si-oligomers is deprotonated, in line with the structural model derived. Competition experiments identified phosphate as a very good competitor for silicate, implying that in nature, siliceous Fh can only be formed in sub-neutral systems that are low in phosphate and rich in silicate, in agreement with reported chemical compositions. Nearly all Si can be removed from the surface by phosphate at sub neutral pH despite a 10–100 times lower phosphate equilibrium concentration in comparison to silicic acid (H_4SiO_4). Siliceous Fh particles in lab and field are smaller than two-line Fh synthesized in the absence of Si, and have a larger specific surface area. At oxidative removal of Fe(II) from groundwater with 0.3 mM Si at circum-neutral pH, small ($d = 2.0 \pm 0.2 \text{ nm}$) siliceous Fh particles ($\text{Si}/\text{Fe} = 0.18$, $\text{P}/\text{Fe} = 0.016$) are formed with a surface area near $\sim 900 \text{ m}^2 \text{ g}^{-1}$. The size is in good agreement with the length of the coherent scattering domain (CSD) reported in literature for synthetic Si-Fe(III) co-precipitates having a primary particle structure in excellent agreement with the surface depletion model for Fh. The competitive interaction of silicate (SiO_4) with phosphate (PO_4), arsenite ($\text{As}(\text{OH})_3$), and arsenate (AsO_4) can be predicted very well with the CD model using affinity constants ($\log K$) collected in monocomponent systems only.

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1. INTRODUCTION

Fe oxide nanoparticles are very important in nature. Even if present in small quantities, these particles can be a major reactive phase (Hiemstra et al., 2010). At the nanoscale, ferrihydrite (Fh) is chemically the most stable Fe (hydr) oxide (Hiemstra, 2015). It is omnipresent in nature and can be easily synthesized in the lab. It has been recognized as an important adsorbent for ions from the early days on (Kurbatow, 1931).

In natural systems, ferrihydrite materials can be rich in Si. Schwertmann and Fechter (1982) and Parfitt et al. (1992) reported molar Si/Fe ratios in the range between 0.1 and 0.4. Similar values were found by Cismasu et al. (2011). One of the reasons that Fh materials in nature are siliceous is the high Si surface loading ($\mu\text{mol m}^{-2}$) due to formation of Si-oligomers (Vempati et al., 1990), occurring at relatively high concentrations of dissolved H_4SiO_4 (Swedlund and Webster, 1999). Another reason may be the relatively small size of the primary particles of siliceous Fh as follows from low angle X-ray powder diffraction (Parfitt et al., 1992) and high energy total X-ray scattering (Cismasu et al., 2014).

Silicate ions may interfere in numerous geochemical processes related to the formation and preservation of Fh. For instance, silicate ions reduce the rate of heterogeneous Fe (II) oxidation by suppressing the formation of Fe(II) inner-sphere complexes (Kinsela et al., 2016). This leads to the preferential formation of Fh over lepidocrocite at the studied conditions in agreement with earlier work (Kaegi et al., 2010). The retardation of the Fe(II) oxidation by silicate ions has implication for the migration of contaminants in the environment.

Silicate ions may also have an important effect on the binding of arsenic in natural systems, as found for aquifer materials from Bangladesh (Stollenwerk et al., 2007) and Vietnam (Thi Hoa Mai et al., 2014). Adsorbed silicate may mobilize arsenite (Meng et al., 2000; Luxton et al., 2006) and reduce the binding of SeO_3^{2-} (Anderson and Benjamin, 1985). In engineered systems used in water treatment, silicate ions may interfere in the removal of arsenic (Holm, 2002). It may lower the binding capacity of bed-packed columns with Fe (hydr)oxide (Padungthon and SenGupta, 2013). Isotopic fractionation of Si is another process in which silicate adsorption acts (Delstanche et al., 2009). The above examples underline the importance of silicate in geochemical and environmental processes, and specifically, its role in surface complexation.

Traditionally, surface complexation by Fh is often modeled with the diffuse layer model (DLM) of Dzombak and Morel (1990). In this thermodynamic approach, the electrostatic contribution of ion adsorption is calculated in a highly simplified manner omitting the presence of a Stern layer. The model does not allow ion pair formation and outersphere complexation. Therefore, a structural interpretation of ion complexation with this model is very limited because all adsorbed complexes, including polymers, are reduced to single point charges located in the surface.

The DLM model is unable to describe the primary charge of Fh properly. This is problematic since it

determines the electrostatics, which dominantly rules ion adsorption. Moreover, the site density is made in this model to an adjustable parameter (Venema et al., 1996a) without relating it to the surface structure. In addition, the ΔpK value for the two-step protonation reaction is used as a fitting parameter. Despite this flexibility created in the DLM, description of the pH and electrolyte dependency of the primary charge remains rather poor (Pivovarov, 2009).

Swedlund et al. (2010a) has applied the DLM model to fit for Fh the Si adsorption using Si species of large size (oligomers). Monodentate and bidentate reactions were formulated. However, the software used (FITEQL) defines the surface activity of species in the same unit as used in solution chemistry (mol L^{-1}), allowing mathematically direct implementation of the species concentration in the mass balance of the system. This is justified when only monodentate reactions are used in the modeling, but for bidentate reactions, the outcome at a given value of $\log K$ will be sensitive to the specific surface area A used, the site density N_s applied, and the solid-to-solution ratio ρ_s present (Hiemstra and Van Riemsdijk, 1996a) as has been discussed and well-demonstrated recently by Lützenkirchen et al. (2015). Dependency on the solid-to-solution ratio is most problematic, since the solid-to-solution ratio often varies within one set of experiments. For instance, the solid-to-solution varied by a factor 40 in the Si experiments of Swedlund and Webster (1999). Moreover, in natural systems such as soils, sediments, surface and ground waters, the solid-to-solution ratio can be very different from the values used in lab experiments and this requires adaptation of the $\log K$ values for multi-dentate reactions (Lützenkirchen et al., 2015).

In the present contribution, a charge distribution (CD) approach will be used in which the surface activity is based on the mole fraction as defined in Hiemstra van Riemsdijk (1996a). Therefore, the CD model can correctly handle multi-dentate surface complex formation from the thermodynamic perspective. The present challenge is to improve for Fh our insights in the silicate adsorption and contribute in general to the implementation of ion adsorption modeling for this material giving it a sound surface structural basis.

Until recently, little was known about the surface structure of Fh and this has tremendously limited the development of a mechanistic model interpretation of adsorption data for this material. This has changed by new developments (Michel et al., 2007; Michel et al., 2010; Hiemstra, 2013) that allow the formulation of a mechanistic multisite ion complexation (MUSIC) model for this material as this has started recently (Hiemstra and Zhao, 2016).

Ten years ago, Michel et al. (2007) proposed a new crystal structure for Fh having sheets of regular Fe1-octahedra (60%) that are linked together by Fe in octahedral (Fe2) and tetrahedral (Fe3) coordination (20% each). The bulk composition is $\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$, in agreement with the earlier suggested formula of Towe et al. (1967). High energy total X-ray scattering (HEXS) shows that a significant number of these sheet-linking Fe polyhedra (Fe2, Fe3) are absent in freshly prepared Fh (Michel et al., 2010). This was attributed to the presence of a high number of defects in the initial precipitate that would gradually disappear upon aging of

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