

SYNTHESIS AND PRELIMINARY CHARACTERIZATION OF 2-LINE FERRIHYDRITE CONTAINING DIFFERENT AMOUNTS OF Si

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Ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$) is the reddish-brown, nearly amorphous hydrous ferric oxyhydroxide mineral with variable composition, widespread in various near-surface environments. Being thermodynamically unstable, it transforms with time into goethite ($\alpha\text{-FeOOH}$) or hematite ($\alpha\text{-Fe}_2\text{O}_3$). Due to its low crystallinity and high surface area, ferrihydrite is highly reactive and plays, through co-precipitation and adsorption reactions, an essential role in e.g. geochemical cycling of various trace elements and capturing of contaminants from streams and groundwater in such environments as iron-laden springs, mine wastes and acid mine drainage. The environmental importance is one of the main reasons for numerous studies on ferrihydrite properties which have been carried out recently. These studies have been dealing with, among others, solubility, thermodynamic features, surface chemistry, sorption and catalytic properties etc. However, in the majority of experimental works synthetic ferrihydrite analogues with chemical composition close to ideal have been applied. Such approach might cause oversimplification, because ferrihydrite always contain substantial amounts of admixtures, with Si, C, P, As, Ca, Al being probably most common. One of the most important and the most common impurity is Si, which in the form of silicate ion has strong affinity for a hydrous ferric oxyhydroxide surface. An association of ferrihydrite with Si not only retards the rate of its transformation to the stable phases (goethite or hematite), but also seriously affects e.g. surface chemistry. Although Si-ferrihydrite was successfully synthesized in several studies, relatively little is known about its properties. The aim of this work was to fill that gap.

Ferrihydrite samples having different Si/Fe molar ratios: 0.00, 0.05, 0.10, 0.20, 0.25, 0.50, 0.75, 1.00, and 1.50, were obtained by reaction of $\text{Fe}_2(\text{SO}_4)_3$ with NaOH in the presence of Na_2SiO_3 at pH 8.2. The precipitates were incubated for four days at room temperature, then the suspensions were dialyzed to remove an excess of salt, and finally freeze

dried. The products were characterized using a variety of analytical techniques, including X-ray powder diffraction (XRD), inductively coupled plasma atomic emission spectrometry (ICP-AES), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and Raman spectroscopy.

The X-ray pattern of pure ferrihydrite reveals two asymmetric broad bands with maxima at 2.55 Å and 1.50 Å, characteristic for 2-line ferrihydrite. With increasing Si/Fe molar ratio, shifting in position of the first (ca. 35°2 θ) peak towards lower angles (up to ca. 29°2 θ) was observed. Gradual broadening of the peak and declining its asymmetry were noticed as well. Both the position and the shape of the second band did not shift at the same time. These features indicate reducing crystallinity and lowering grain size of Si-ferrihydrite in comparison to those for the pure ferrihydrite.

Infrared spectrum of the pure (Si-free) ferrihydrite shows a broad band at ca. 400 cm⁻¹, with a shoulder at 600 cm⁻¹, attributable to Fe-O stretching vibrations. Distinct bands at 1635 cm⁻¹ and 3400 cm⁻¹, related to OH stretching, are apparent as well. The presence of small peaks at 975 cm⁻¹, 1055 cm⁻¹ and 1125 cm⁻¹ is probably an effect of sulfate complex formation on the ferrihydrite surface. Increasing Si concentration strongly affects infrared spectra of ferrihydrite: additional intensive band at ca. 990 cm⁻¹ (Si-O stretching) appears and is getting stronger with increasing Si/Fe ratio. The position of this band is shifted slightly towards higher wavenumbers (up to 1003 cm⁻¹) at higher-Si-ferrihydrite spectra. At the same time, ~ 600 cm⁻¹ shoulder and sulfate peaks disappear.

Results of Raman spectroscopy are in general consistent with those of FTIR and gave more specific information about the band at ca. 400 cm⁻¹, which is quite indistinct on infrared spectra and attributed to Fe-OH unsymmetrical-stretching vibrations. The band is getting broader and is slightly shifted to higher wavenumbers with increasing Si/Fe ratio but its intensity decreases drastically for the highest-Si samples (Si/Fe $\geq$ 0.75). At the same time, characteristic 720 cm⁻¹ peak and ca. 500 cm⁻¹ shoulder become hardly visible and the spectra are getting dominated by broad but intensive band of ca. 1500–1700 cm⁻¹, typical for amorphous silica. Additionally, sharp peak at 980 cm⁻¹ present on lower-Si spectra is probably an effect of relic sulfate ion adsorption onto ferrihydrite surface.

Preliminary results indicate that silicate ions not only cause decreasing crystallinity and retard ferrihydrite transformation but also strongly affect its surface properties. To verify this hypothesis and to enhance characteristics of Si-ferrihydrite, additional analyses are planned, including solubility, surface area and pH_{PZC} determinations, thermal analyses and electron microscopy. Sorption/desorption studies involving cations and anions binding are planned as well.

This work was financed by the AGH University of Science and Technology statutory grant.