Supplementary Information for

Impurity-Bearing Ferrihydrite Nanoparticle Precipitation/Deposition on Quartz and Corundum

Chong Dai¹, Juanjuan Liu¹,², and Yandi Hu¹*

¹Department of Civil & Environmental Engineering,
University of Houston, Houston, TX 77004
²College of Natural Resources and Environment,
Northwest A&F University, Yangling, Shanxi 712100, China

E-mail: yhu11@uh.edu
Phone: (713)743-4285
Fax: (713)743-4260
http://www.cive.uh.edu/faculty/hu

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Summary

Six pages including two figures, experimental details, and data analysis.
GISAXS Critical Angle

Our GISAXS measurements were conducted at water-substrate interfaces. Here, we have used Snell Equation (Eqn. (1)) to calculate the critical angle ($\alpha_1$) for total external X-ray reflection.\(^{1}\)

$$\alpha_1 = \cos \left( \frac{1 - \delta_{\text{substrate}}}{1 - \delta_{\text{water}}} \right) \left( \frac{180}{\pi} \right)$$  (1)

Where, $\delta_{\text{substrate}}$ and $\delta_{\text{water}}$ represent the refraction indices of the substrates and water, respectively. With density values of 2.68, 3.97, and 1.00 g/cm\(^3\) for SiO\(_2\), Al\(_2\)O\(_3\), and H\(_2\)O and an X-ray energy of 14 KeV, the indices of refraction ($\delta$) for SiO\(_2\), Al\(_2\)O\(_3\), and H\(_2\)O were calculated to be $2.85 \times 10^{-6}$, $4.14 \times 10^{-6}$, and $1.18 \times 10^{-6}$, respectively.\(^{1}\) Applying Eqn. (1), the critical angles for total external X-ray reflection at water-SiO\(_2\) and water-Al\(_2\)O\(_3\) interfaces were calculated to be 0.105° and 0.136°, respectively. Therefore, 0.10° was chosen as the incident angle for all sample measurements.

XPS Measurements

X-ray photoelectron spectroscopy (XPS) measurements were also conducted to determine the oxidation states of Mn in the precipitates formed from FeMn solution. To collect enough precipitates, 500 mL FeMn solution (Table 1) was freshly prepared and let to sit for 1 hr. Then, the particles were collected using centrifugal filter unit, and were transferred to a gold wafer. After drying the sample in a desiccator overnight, the photo-electrons, produced via a monochromatic Al-k X-ray source (1486.6 eV) operated at 350 W, were collected on a Physical Electronics Model 5700 X-ray photoelectron spectroscopy (XPS) instrument. The analyzed area, collection solid cone and take off angle were set at 800 m, 5° and 45°, respectively. All spectra
were acquired under vacuum condition (< \(5 \times 10^{-9}\) torr). Data processing was carried out using the Multipak\textsuperscript{TM} software package. A Shirley background subtraction was applied. Unfortunately, the amounts of Mn in Mn-bearing ferrihydrite nanoparticles on substrates were lower than the detection limits of XPS measurements (Figure S2).

**Mn\textsuperscript{2+} and Al\textsuperscript{3+} ion adsorption vs. Mn(OH)\textsubscript{2} and Al(OH)\textsubscript{3} precipitation on substrates**

The zeta potential changes of the substrates in Mn and Al solutions could be caused by either Mn\textsuperscript{2+} and Al\textsuperscript{3+} ion adsorption or heterogeneous precipitation of Mn(OH)\textsubscript{2} and Al(OH)\textsubscript{3} on substrates. In our previous study, GISAXS control experiment with 0.5 mM Al(NO\textsubscript{3})\textsubscript{3} solution in contact with quartz under similar experimental condition (0.5 mM Al(NO\textsubscript{3})\textsubscript{3} and pH = 3.7 ± 0.1) was conducted. No GISAXS scattering curves were measured after background subtraction, indicating no Al(OH)\textsubscript{3} particle formation on quartz.\textsuperscript{2} Accordingly, in this study, the formation of Al(OH)\textsubscript{3} particles on substrates was not expected as well. Meanwhile, at 25 °C, the solubility of Al(OH)\textsubscript{3} (\(K_{sp} = 1.3 \times 10^{-33}\)) is much lower than Mn(OH)\textsubscript{2} (\(K_{sp} = 1.9 \times 10^{-13}\)). Therefore, the solutions were slightly undersaturated with respect to Al(OH)\textsubscript{3} (saturation index = - 0.08) and highly undersaturated with respect to Mn(OH)\textsubscript{2} (saturation index = -10.8). That means, if the formation of Al(OH)\textsubscript{3} on substrates did not occur, the formation of Mn(OH)\textsubscript{2} on substrates should not be expected as well. Therefore, Mn\textsuperscript{2+} and Al\textsuperscript{3+} ion adsorption rather than heterogeneous precipitation of Mn(OH)\textsubscript{2} and Al(OH)\textsubscript{3} on substrates were likely to have occurred, which changed the zeta potential values of substrates.
Figure S1. Lorentz-corrected intensity curves of GISAXS scattering caused by ferrihydrite nanoparticles precipitated/deposited on quartz (Figures A1-A3) and corundum (Figures B1-B3)
Figure S2. XPS measurements of ferrihydrite particles formed in FeMn solution
References