

Fe(II) adsorption at the oxide-water interface: From macroscopic observations to spectroscopic measurements

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The remarkable reactivity of Fe oxides, and the discovery of microbial Fe respiration has led to intense speculation about the surface species that form when Fe(II) ions adsorb on mineral surfaces. Spectroscopic measurements of Fe(II) adsorbed at the Fe-mineral water interface, however, have been difficult to obtain because of the very small quantity of Fe at the interface and interference from the bulk structural Fe(III). We are using the isotope specificity of ^{57}Fe Mössbauer spectroscopy to characterize Fe(II) adsorbed on commonly occurring Fe minerals, such as hematite ($\alpha\text{-Fe}_2\text{O}_3$), as well non-Fe containing oxides, such as aluminum oxide (Al_2O_3).

Using this technique, we have previously observed that electron transfer occurs between adsorbed Fe(II) and structural Fe(III) in ferrihydrite [1]. These experiments, however, were somewhat limited in that only a narrow range of geochemical conditions was explored (pH 7.4, KBr electrolyte, and low Fe(II) concentrations). Here, we expand on these experiments to spectroscopically characterize adsorbed Fe(II) over an environmentally relevant range of Fe(II) concentrations and pH values (i.e., adsorption isotherms and pH edges).

Initial results suggest that electron transfer between adsorbed Fe(II) and structural Fe(III) in hematite occurs in the presence of high aqueous Fe(II) concentrations (up to 1 mM) and over a pH range of 6.8 to 8.2. At a pH value of 8.2, however, an Fe(II) doublet is observed in the room temperature Mossbauer spectra, suggesting that at least some portion of the Fe(II) is not oxidized. The spectral parameters of the Fe(II) doublet are not consistent with a ferrous hydroxide precipitate and may represent an adsorbed Fe(II) species.

Reference

Williams A. G. B. and Scherer M. M. (2004). *Environ. Sci. & Technol* **38**(18), 4782-4790.

Does surface acidity of ferric (oxy)hydroxides affect reactivity towards H_2S ?

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Material and Methods

The reactivity of hematite (Hem), goethite (Gt), 2-line (2LFh) and 6-line ferrihydrite (6LFh) with respect to H_2S has been studied at steady-state conditions in a pH range between 2 and 5 using a fluidized-bed reactor which is supplied with a constant flow of electrochemically generated H_2S .

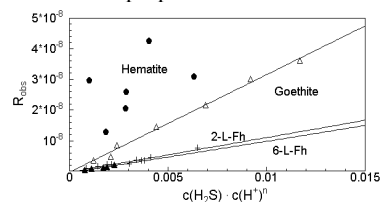
Results and Discussion

Except for Hem, the experimental reaction rates R_{obs} showed a strong pH dependency and also varied between minerals. The pH dependency can be explained by a surface speciation model according to which the rate is proportional to the concentration of a surface complex $>\text{FeHS}$ that forms upon reaction with $>\text{FeOH}$.

Considering this model an empirical rate law can be derived

$$R_{\text{obs}} = k^* c(\text{H}_2\text{S})_{\text{tot}} c(\text{H}^+)^{-n}$$

where the empirical rate coefficient k^* accounts for surface and solution chemical properties..



k^* significantly varies between minerals and increases in the order 6LFh, 2LFh, Gt, Hem. Assuming that the different mineral phases also have different surface acidities, the pH pattern of the reaction rate could be satisfactorily fitted by an intrinsic pK_{a} of 4.9 for hematite and 6.9 for goethite.

Conclusion

There are two major implications from this study: 1) A low intrinsic $\text{pK}_{\text{a}1}$ provides a higher concentration of the reactive surface species $>\text{FeOH}$ under acidic conditions and therefore the rate will be higher for this mineral; 2) the higher the intrinsic $\text{pK}_{\text{a}1}$, the more the rate will depend on pH.

References

Dos Santos Afonso M & Stumm W. *Langmuir*, 8, 1671-1675
Peiffer S et al, *Environ. Sci. Technol.*, 26, 2408-2413