

Electron transfer at Fe clay mineral surfaces: Reversibility and consequences for contaminant reduction

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Structural Fe in clay minerals is an important source of renewable redox equivalents in subsurface environments. We recently demonstrated that structural Fe(III) can be reduced by interfacial electron transfer from Fe(II) sorbed to clay mineral surfaces [1]. In the redox reaction, sorbed Fe(II) is oxidized and a solid Fe(III) phase forms [2]. It is unknown whether the observed interfacial electron transfer and secondary Fe(III) oxide formation are reversible and how the presence of an *in situ*-formed solid Fe(III) oxidation product might affect the reactivity of Fe(II)-containing clay minerals.

To test for the (ir)reversibility of interfacial electron transfer, we combined sequential extractions and pH titration with ⁵⁷Fe-Mössbauer spectroscopy to monitor changes in the speciation of structural and sorbed/oxidized Fe. Our results suggest that changes in aqueous solution chemistry, particularly the presence of phosphate anions and low pH, lead to oxidation of structural Fe(II) and concomitant reduction of the Fe(III) precipitate, suggesting that electron transfer is reversible.

To determine whether the observed solid Fe(III) oxidation product affects the overall redox reactivity of Fe(II)-reduced clay minerals, we used nitroaromatic compounds as reactive probes. We compared the reduction kinetics in reactors containing Fe(II)-reduced clay mineral to reactors with dithionite-reduced clay mineral with the same Fe(II)/Fe(III) ratio and found differences in reaction order and rate constant. We are currently investigating the (trans)formation of iron oxidation products and the clay mineral Fe(II)/Fe(III) ratio during probe molecule reduction to explain the observed differences in reactivity.

[1] Neumann, Olson & Scherer (2013), *Environ Sci Technol*, **47**, 6969-6977. [2] Schaefer, Gorski & Scherer (2011), *Environ Sci Technol*, **45**, 540-545.