Effect of stoichiometry on magnetite redox potentials and chlorinated ethene reduction rates.

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Magnetite stoichiometry (x = Fe(II)/Fe(III)) has been shown to significantly influence rates of contaminant reduction in soils and sediments [e.g., 1]. It remains unclear, however, how magnetite stoichiometry effects magnetite redox potentials and whether magnetite redox potentials could be predictive of contaminant reduction rates. Here, we measured open-circuit potentials of magnetite as well as chlorinated ethene (CE) reduction rates over a range of magnetite stoichiometries, pH values, and dissolved Fe(II) concentrations. As expected, our preliminary results indicate that redox potentials decrease as stoichiometry increases from x = 0.09 to 0.50 (Figure 1). Specifically, we observed a linear relationship between redox potential and stoichiometry at pH 7.1. The slope of the redox potential vs. x at pH 7.1 was -543 \pm 87 mV (*n* = 6 and *R*² = 0.91). Consistent with our previous work with stoichiometric magnetite (x = 0.5), we found electron transfer mediators were not necessary to measure equilibrium potentials [2].

We also explored the effect of magnetite stoichiometry on CE reduction rates. We observed negligible cis-1,2-dichloroethene (cis-DCE) reduction by magnetite regardless of stoichiometry similar to what we previously observed for perchloroethylene (PCE) and trichloroethylene (TCE) [3]. We did, however, observe slow reduction of PCE, TCE, and cis-DCE by stoichiometric magnetite when Fe(II) was added under conditions where ferrous hydroxide was expected to precipitate. Additional work is underway to evaluate whether magnetite stoichiometry influences rates of CE reduction by magnetite with added Fe(II) and whether redox potentials measured under these conditions correlate with rates of CE reduction. We aim to assess whether abiotic reduction of CEs by magnetite under anoxic conditions where Fe(II) is present contributes to natural attenuation of CE plumes and whether measured redox potentials may be useful for predicting abiotic natural attenuation rates for CEs.

[1] Abiotic reduction of uranium by Fe(II) in soil, Latta, D.E., et al. (2012), *Applied Geochemistry* 27(8), 1512-1524.

[2] Redox potentials of magnetite suspensions under reducing conditions, Robinson, T.C., et al. (2022), *Environmental Science & Technology* 56(23), 17454-17461.

[3] Reduction of PCE and TCE by magnetite revisited, Culpepper, J.D., et al. (2018), *Environmental Science: Processes* & *Impacts* 20(10), 1340-1349.

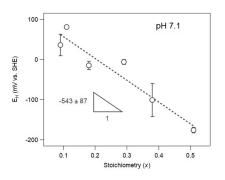


Figure 1. Open circuit potentials measured for magnetite suspensions as a function of pH in the absence of added Fe(II). Experimental conditions: 1 g L⁻¹ magnetite, 50 mM MOPS Buffer, 25 mM KCl.