

Reduction of halogenated groundwater contaminants by nano-sized magnetite

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Introduction

Permeable reactive barriers have been shown to be a viable technology for remediation of halogenated solvent contaminated groundwaters. When the zero-valent iron used in these barriers corrodes under anoxic conditions, the corrosion film that forms at the iron-water interface is often composed of nanocrystalline corrosion products such as magnetite (Fe_3O_4). This magnetite has the potential to participate in the reduction of halogenated contaminants. The ubiquity and small size of nanoscale magnetite makes this a potentially important reactive phase in granular iron systems. Many nanosized materials exhibit reactivities that differ significantly from larger sized bulk particles. The objective of this study was to quantify the reactivity of nanoscale magnetite particles under anoxic conditions towards halogenated solvents and to determine if a relationship exists between reactivity and particle size.

Experimental

Monodisperse suspensions of Fe_3O_4 were synthesized under anoxic conditions. Several batches of magnetite were synthesized under different solution conditions (pH, ionic strength, co-solutes) such that precise control of particle size was possible. Batch reactors of buffered magnetite (both nanosized as well as bulk magnetite) were spiked with halogenated solvents (carbon tetrachloride, trichloroethene) and monitored over periods of one week.

Results and Discussion

The reduction of halogenated solvents occurred more rapidly when exposed to nanoparticulate (10-20 nm diameter) magnetite as compared to "bulk" magnetite particles (>100 nm). In addition, daughter products were more fully reduced by nanoparticulate magnetite than by bulk magnetite.

This presentation will address the relationship between magnetite particle size and halogenated contaminant reduction capability. Additionally, this presentation will discuss the effects of oxidation on particle aggregation in nano-sized magnetite suspensions.

Thermochemistry of bulk and nano akaganeite

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Enthalpy of formation of akaganeite, $\beta\text{-FeOOH}$, as a function of particle size is reported for the first time. Fourteen samples with the particle size range of 5-100 nm and surface area 30-280 m^2/g were prepared. Characterisation was performed using XRD, FTIR, BET, TEM, SEM and TGA. Solution enthalpy in hydrochloric acid at room temperature and in sodium molybdate at 700 °C was measured. Refinement of XRD data showed that at higher surface areas akaganeite has a monoclinic polymorph. Calorimetric data were corrected for excess water assuming this loosely adsorbed water has the same energetics as bulk liquid water. The plot of enthalpy of solution for monoclinic akaganeite vs surface area (see figure) gives a surface enthalpy of $0.33 \pm 0.05 \text{ J/m}^2$ and enthalpy of formation of bulk akaganeite of $-557.3 \pm 1.2 \text{ kJ/mol}$. Although surface energy of akaganeite is found to be lower than for lepidocrocite $\gamma\text{-FeOOH}$ and goethite $\alpha\text{-FeOOH}$, the amount of adsorbed water is higher

especially for lower surface areas (see figure). The reason is probably the tunnel structure of akaganeite, with excess water accumulating in the tunnels. Preliminary calorimetric data showed that the surface energy of akaganeites with lower surface areas (and probably a different polymorph) is higher, but additional work is required. The energetics of adsorbed water on the akaganeite surface is also under investigation.

