

Biostimulation of nitrate, iron and chromate reduction at hyperalkaline conditions

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Worldwide production of chromium via the 'high lime' process has resulted in large volumes of highly alkaline chromite ore processing residue (COPR). Alkaline leachates (pH>11) from such wastes can have elevated Cr(VI) concentrations (as chromate) and are locally hazardous to the environment. This study investigates the biogeochemical and geomicrobiological factors that influence the fate of aqueous chromate in soil-water systems exposed to COPR leachate. In microcosm experiments, soil taken from beneath a COPR site in England was incubated anaerobically with site leachate with an initial pH of 11.38 and chromate concentration of 293 μM. Four microcosms systems were established including sterile controls: 1. unamended; 2. acetate amended; 3. bicarbonate amended, and; 4. acetate and bicarbonate amended. A time series of redox active species behaviour and samples for genetic fingerprinting were collected over 175 days. Complete nitrate reduction was observed in all active systems by 15 days, with little to no reduction observed in all sterile controls. 100% Cr(VI) reduction was observed in both systems amended with bicarbonate at pH ~9.5 by 68 days, compared with just 64% in acetate stimulated system at 175 days, and none in the unamended system. Amended sterile controls show small amounts of Cr(VI) removal at later timepoints. Iron reduction was observed after 68 days in all but the unamended system. Sulfate concentrations were unchanged showing that no sulfate reduction occurred in any system. rRNA intergenic spacer analysis (RISA) indicates changes in fragment length over the course of the experiment for all systems that were also different for all systems. Reducing the pH to ~9.5 and/or stimulation with acetate appears to have aided the development of a microbial community capable of inducing nitrate, chromate and iron reduction. Rate expressions indicate that Cr(VI) reduction is likely to be via reaction with Fe(II) produced as a result of active microbial Fe(III)-reduction. The varying RISA signatures over time suggest the population is changing to reflect the dominant terminal electron acceptor present.

Reduction of Hg(II) to Hg(0) by magnetite

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Background

Mercury is a highly toxic element, and its contamination of groundwater is a significant threat to terrestrial ecosystems. Understanding the geochemical processes that mediate mercury transformations in the subsurface is necessary to predict its fate and transport. In this study, we present macroscopic and spectroscopic evidence that the iron oxide mineral magnetite (Fe₃O₄) can reduce Hg(II) to Hg(0).

Methods

Laboratory experiments were conducted to quantify Hg(II) reduction rates as a function of magnetite suspension density, pH, and chloride concentration. The production of volatile Hg(0) was measured by purging the reaction vessel with N₂ into a trapping solution of acidified potassium permanganate. Mercury was analyzed by cold vapor atomic absorbance spectroscopy. ⁵⁷Fe-specific Mössbauer spectroscopy and X-ray photoelectron spectroscopy were conducted to examine the solid-phases changes in Fe speciation and the Hg surface state.

Results and Discussion

The experimental data demonstrated that reaction of Hg(II) with magnetite results in the loss of Hg(II) and the formation of volatile Hg(0). Kinetic experiments showed that Hg(II) reduction occurred within minutes, with reaction rates increasing with increasing magnetite suspension density (0.05 to 0.2 g/L) and pH (4.8 to 6.7), and decreasing with increasing chloride concentration (10⁻⁶ to 10⁻² mol/L). Mössbauer analysis of reacted magnetite samples revealed a decrease in Fe(II) content, corresponding the oxidation of Fe(II) to Fe(III) in the magnetite structure. X-ray photoelectron spectroscopy detected the presence of Hg(II) on magnetite surfaces, suggesting that adsorption is involved in the electron transfer process. These results suggest that Hg(II) reaction with solid-phase Fe(II) is a kinetically favorable pathway for Hg(II) reduction in magnetite-bearing soils and sediments.