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Reduction and Immobilization of Radionuclides and Toxic Metal Ions Using Combined Zero Valent Iron and Anaerobic Bacteria

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Research Objective

Previous research findings indicate that both zero valent iron and sulfate reducing bacteria (SRB) can yield significant decreases in Cr(VI) or U(VI) concentrations due to abiotic and microbial reduction, respectively. The major hypothesis associated with this research project is that a combined abiotic-biological system can synergistically combine both processes to maximize metal ion reduction in an engineered permeable reactive barrier. The overall goal of this project is to design a combined abiotic/microbial, reactive, permeable, in-situ barrier with sufficient reductive potential to prevent downgradient migration of toxic metal ions. The field-scale application of this technology would utilize anaerobic digester sludge, Fe(0) particles for supporting anaerobic biofilms, and suitable aquifer material for construction of the barrier. Successful completion of this goal requires testing of the two hypotheses listed above by evaluating: (1) the rates of abiotic metal ion reduction, and (2) the rates of microbial metal ion reduction in microbial and combined abiotic/microbial reduction systems under a range of environmental conditions.

Research Progress and Implications

This report summarizes work after one and one-half years of a three year project.

Abiotic studies: The thrust of the abiotic research conducted to date has been to determine the rates of Cr(VI) reduction in batch reactors and to evaluate the role of aquifer materials on those rates. Experiments have been conducted to determine the rates of reduction by Fe(II) and Fe(0). The parameters that have been evaluated are the effect of pH and the presence of sulfide and aquifer material.

All reactions were conducted in a 1.5-L jacketed reaction vessel. Degassed water was used in all experiments and was prepared by bubbling 99.999% Ar through boiled Nanopure water. Dissolved oxygen levels could be reduced to below 5 ppb in this manner. The experiments were conducted in a glove bag under Ar. The water jacket was used to maintain a temperature of 23° C. The mixing rate was maintained at 400 rpm.

It has been proposed that the diphenylcarbazide (DPC) spectrophotometric method for measuring Cr(VI) could lead to incorrect measurements in the presence of Fe(II) (1). At the low pH of the DPC reagent, the Fe(II) reaction with Cr(VI) is extremely rapid and may continue simultaneously causing errors in the Cr(VI) measured. A spectral-fitting method has been used to measure Cr(VI) without the addition of any colorimetric reagents (1). In this method the molar extinction coefficients of CrO_4^{2-} , HCrO_4^{1-} , Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^{1+}$ are determined over a range of wavelengths. This spectral data is then manipulated in order to solve for the Cr(VI) concentration when the absorbance spectra of a sample are measured. In our research, both the spectral fitting method and the DPC method were examined. Both methods yielded reproducible results under the conditions examined. In addition, experiments conducted to examine the reduction of Cr(VI) by Fe(II) using the DPC method yielded rate constants that were similar to those reported by Buerge and Hug (1).

Preliminary experiments investigating the reduction of Cr(VI) by Fe(II) have been conducted for the purpose of establishing the kinetics in our system over a range of pH. The kinetic data fits the second-order rate law proposed by Buerge and Hug (1).

Experiments have been conducted to evaluate the reduction of Cr(VI) by zero-valent iron (Fe(0)). The reaction of Cr(VI) with Fe(0) alone was examined over a range from pH=5.5 to pH=7. In each case 20 grams of commercial grade iron filings were used in 1500 ml of buffered degassed water

and allowed to equilibrate for 1 hour prior to Cr(VI) addition. After this hour, high initial Fe(II) concentrations were measured. However, shortly after Cr(VI) addition, Fe(II) was rapidly depleted to below detection limits. To initiate the experiments Cr(VI) was added to yield an initial Cr(VI) concentration of 500 μ M. In each experimental run an initial rapid decrease in Cr(VI) was observed followed by a region of much slower reduction. The rapid initial Cr(VI) reduction is presumably due to sorption and the presence of Fe(II) in solution. Addition of excess Fe(II) to the system led to a concomitant increase in the initial reduction of Cr(VI). As pH increases the initial drop in Cr(VI) concentration also decreases.

Chromate reduction was also evaluated for Fe(0) in the presence of other constituents (at pH=7). These include sulfide, Fe(II) and aquifer material. As in the case of Fe(0) alone, a rapid initial decrease in Cr(VI) concentration was observed followed by a region of much slower loss. The rapid initial decrease in Cr(VI) concentration was greater for those systems containing either excess Fe(II) or sulfide compared to systems containing Fe(0) alone or those with Fe(0) or the aquifer material tested to date. After the initial drop in Cr(VI) concentration the rate of Cr(VI) loss was similar for all systems tested containing Fe(0). The reduction of Cr(VI) was decreased by the addition of Ottawa sand which is in contrast to the enhanced reduction measured in the presence of aluminosilicates (2).

Combined abiotic-biological studies: Studies using continuous flow columns are being conducted to investigate the effect of SRB and zero valent iron on the reduction of Cr(VI). Four columns, each with a total volume of 72 mL, were constructed. Columns A, B, and C were packed with fine steel wool (5 gm), producing a porosity of 98.6%. Columns B and C were inoculated with mixed liquor from a chemostat enriched for SRB. Lactate was also added to column C influent. Column CL served as an unpacked and unseeded control. Each column was feed 10 mL/day of basal media spiked with Cr(VI) and sulfate.

The columns were first spiked with 192 μ M (10 ppm) of Cr(VI). After 1.5 pore volumes the Cr(VI) concentration was increased to 384 μ M (20 ppm). At these concentrations, the effluent concentrations of total chromium have been near non-detectable for each of the columns A, B and C. The pH in the effluent during both experiments ranged between 8 and 9, possibly as a result of iron corrosion.

Sulfate loss was greatest in column C, possibly due to lactate consumption. An electron balance indicates the loss of sulfate and lactate in column C is not stoichiometric.

1. Buerge, I.J.; Hug, S.J. 1997. Environ. Sci. Technol., 31, 1426-1432.
2. Powell, R.M.; Puls, R.W. 1997. Environ. Sci. Technol., 31, 2244-2251.

Planned Activities

Studies will be conducted in then next 1-1/2 years to examine and quantify Cr(VI) reduction by amorphous iron sulfide alone and in the presence of Fe(0). Also the effect of competing adsorbates and various aquifer materials on Cr(VI) reduction will be evaluated. Additional combined abiotic-biological column experiments will be conducted to examine Cr(VI) reduction at higher Cr(VI) concentrations and to quantify the stoichiometry between sulfate reduction and electron donor oxidation in the presence of elevated levels of Cr(VI).