Project 1025340

Reduction and Reoxidation of Soils During & After Uranium Bioremediation; Implications for Long-Term Uraninite Stability & Bioremediation Scheme Implementation

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RESULTS TO DATE: This research focuses on the conditions and rates under which uranium will be remobilized after it has been precipitated biologically, and what alterations can be implemented to increase its long-term stability in groundwater after the injection of an electron donor has been discontinued. Furthermore, this research addresses short-term iron reoxidation as a mechanism to enhance/extend uranium bioremediation under iron reduction, without its remobilization. The research to date has focused on long term column experiments involving the biological removal of uranium from groundwater under iron and sulfate reducing conditions. Aquifer sediment was collected from the background area of the Old Rifle UMTRA site and dried and sieved (<2 mm) before being packed into four 15 cm long x 5 cm diameter glass columns. The initial porosity of each column ranged from 0.33 to 0.40. Prior to biostimulation of the columns, 30 mM bicarbonate (purged with CO2/N2 gas, 20:80 ratio) was pumped through the columns to flush out the natural uranium present in the sediment. After the natural uranium was flushed out of the system, 20 uM of uranyl acetate was added to the 30 mM bicarbonate influent media. The column was operated for 11 days to ensure that the effluent U(VI) concentration was equal to the influent U(VI) concentration (no removal of U(VI) occurred before biostimulation). The start of the biostimulation experiment was facilitated by the addition of one pore volume of a growth culture containing the Fe(III) and U(VI) reducing microorganism, Geobacter metallireducens. Flow to the columns was suspended for 24 hours, after which pumping was resumed with acetate (2.8-3.0 mM), as well as trace vitamins and minerals, supplied to the feed media. The columns were operated at 22 +/- 1 degrees C, upright and under up-flow conditions at a rate of 0.2 ml/min (equivalent to a linear groundwater travel time of approximately 135 m/yr). Water samples from column inlets and outlets were collected and analyzed for acetate, U(VI), Fe(II), Br-, NO3- and SO42-. Iron reduction and U(VI) removal was detected in all four columns after three days of column operation with acetate in the inflow. The Fe(II) concentration at the effluent of the columns increased at a rate of 16.6 (+/-1.9) uM/d until leveling off after 10 days of column operation. The pseudo steady-state Fe(II) concentration at the effluent for each column ranged 130 uM to 170 uM. Uranium removal reached steady-state conditions after approximately 23 days of column operation with removal of between 58% to 77% of the initial 20 uM U(VI) added at the influent of the column. Bromide was added as a tracer after 1 month of column operation in order to document hydraulic retention times and diffusion limitations. The hydraulic retention time for each column ranged from 3.6 h to 8.8 h. Trends were observed regarding column hydrodynamics, Fe(II) production and U(VI) removal from each column. The longer retention time resulted in higher Fe(II) concentrations at the effluent of the column and more uranium removal. Sulfate was present in the influent media as part of the trace vitamin and mineral solution added with the 30mm bicarbonate. Sulfate reduction was also measured in the columns resulting in ~ 50% - 70% of the initial 0.7 mg/L sulfate removed in each column. Most of the phosphate, present in the influent media at a concentration of 1.2 mg/L, was also removed from the system. One of the four columns was taken offline after 104 days of column operation and destructively sampled to analyze geochemical parameters such as Fe(II), total HCl extractable iron, U(VI), total uranium, and acid extractable sulfide. The analysis of these samples is not complete, but preliminary results indicate that all or most of the Fe present in the sediment (after 1h extraction in 0.5N HCl) is in the form of Fe(II) with the Fe(II) concentration on the surface of the sediment throughout the column measured to be 9.4 (+/-3.9) umol/g dry sediment. In addition to the analysis performed in Dr. Jaffe?s laboratory, samples were packed anaerobically, frozen and provided to Dr. Myneni and Dr. Zachara for additional analysis. Dr. Myneni is currently analyzing the samples using X-ray absorption spectroscopy to determine the uranium speciation throughout the column and Dr. Zachara is using Mossbauer spectroscopy to determine the Fe phases throughout the column. Both Dr. Myneni and Dr. Zachara will compare their analysis of the reduced samples to the pristine sediment and the reoxidized sediment (when available). Very preliminary results of Dr. Myneni?s analyses indicate significant amounts of immobilized U(VI) in the reduced sediments. This is surprising and is still being verified. Extractions with bicarbonate are also being conducted on the reduced sediments in order to determine directly the amount of sorbed U(VI). A series of initial experiments were performed to determine the potential extent of iron reduction in the Old Rifle sediment. The bioavailable Fe(III) concentration has been estimated through extraction in 0.5N HCl for 1h. The Fe(II) and total Fe concentration of the pristine Old Rifle sediment after 1h extraction in 0.5N HCl was measured to be 2.3 (+/-0.04) umol/g and 8.0 (+/-0.4) umol/g dry sediment, respectively, thus yielding an estimate of the bioavailable Fe(III) concentration to be 5.7 umol/g dry sediment. Analyses of the manganese present in the sediments found that all of the manganese (2.2 +/- 0.2 umol/g dry sediment) present in the sediment was in the form of Mn(II), indicating that the presence of manganese oxide should not delay the onset of iron and uranium reduction. A series of batch experiments using G. metalireducens, 10 mM acetate and 50uM AQDS (added to facilitate Fe(III) reduction) determined that the amount of Fe(II) produced using different buffer solution (D.I water, 30mM bicarbonate, 30mM bicarbonate with vitamin and minerals) was 10.7 umol/g dry sediment. In addition, a uranium sorption experiment measured the Kd for uranium sorption to initial Old rifle sediment to be 0.36 ml/g, resulting in a retardation factor of 2.5.

DELIVERABLES: Komlos, J., R. Kukkadapu, J.M. Zachara, and P.R. Jaffe, ?Quantification of Iron Oxidation in Microbially Reduced Subsurface Sediments in a Continuous Flow Porous Media Reactor,? submitted. Komlos, P.R. Jaffe, J., R. Kukkadapu, and J.M. Zachara, ?Quantification of Iron Reoxidation in Microbially Reduced Sediments,? to be presented at the 2005 AGU Fall meeting in San Francisco.

COLLABORATIONS: John Zachara (PNNL) will be a co-PI on this project and will be responsible for mineralogical analyses using Mossbauer.