

Microcosm Study of the Effects of pH, Reductant and Sediment Type on Uranium Immobilization

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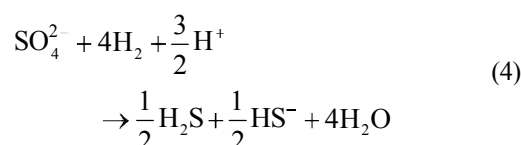
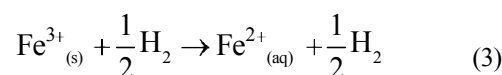
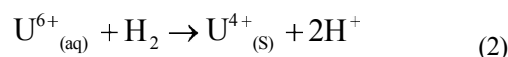
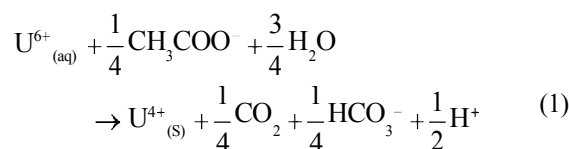
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Abstract: Uranium mining by in-situ recovery (ISR) involves injecting dissolved oxygen (DO) into the subsurface to oxidize and solubilize uranium minerals (e.g., uraninite), and then pumping the groundwater to the surface and removing the uranium by ion exchange. After ISR mining operations are completed, the groundwater must be restored to baseline conditions. One promising new technology for restoring groundwater at ISR sites is to inject chemical reductants that can stimulate growth of indigenous iron- and sulfate-reducing bacteria that can also reduce and immobilize uranium. Although numerous studies have validated the general feasibility of this approach, significant uncertainty remains about the effects of groundwater pH, reductant type (particularly organic versus inorganic), and sediment type (particularly pre-leaching versus post-leaching). In this study, a 2³ experimental factorial design was used to assess the effects of pH, reductant type, and sediment type on uranium immobilization in 160-mL serum-bottle sediment microcosms. The experimental results showed that both reductant type and sediment type have statistically significant effects on uranium immobilization.

Keywords: uranium immobilization

I. INTRODUCTION

The average concentration of uranium in the Earth's crust is about 1.7 mg/kg (Wedepohl, 1995). Most natural waters have low concentrations of dissolved uranium; however, there are regions with higher uranium concentrations in surface water and groundwater due to the geological conditions. In addition, activities associated with mining and processing of uranium for nuclear fuel and weapons, and also processing of spent fuel, have generated substantial quantities of waste materials that are contaminated with uranium. In particular, nearly 70% of U.S. Department of Energy (DOE) facilities report groundwater contamination by radionuclides, including uranium. Consequently, there is significant interest in cost-effective approaches for immobilizing uranium in contaminated groundwater (Finneran et al. 2002).



In this study, microcosm experiments were used to investigate factors that could impact the effectiveness of bioremediation to immobilize uranium *in situ* following procedures similar to those described by Nyman *et al.* (2006). In particular, the experiments compared the effectiveness of hydrogen and acetate as electron donors for stimulating microbial reduction and immobilization of uranium. Equations 1-2 present simplified stoichiometric equations for U(VI) reduction by acetate and hydrogen respectively, while Equations 3-4 present simplified stoichiometric equations for competing hydrogen consumption by iron and sulfate reduction (similar equations would apply for acetate).

II. RESEARCH OBJECTIVE

The purpose of this experiment was to quantify how changing three conditions affected the removal of soluble uranium in aquifer sediment microcosms. A factorial experimental design was used to compare soluble uranium removal in microcosm bottles with different aquifer sediment types (oxidized versus reduced), amended with different electron donor substrates (hydrogen versus acetate), and adjusted to different initial pH (6.5 versus 8.5). It was initially hypothesized that hydrogen would be more effective than acetate as a reductant for stimulating microbial reduction and immobilization of uranium.

III. MATERIALS AND METHODOLOGY

The 2³ factorial experimental design was set-up as shown in Table 1 (Clapp, 2010). Triplicate microcosm bottles were set up for each combination of the three factors. The Mesteña sediment cores were collected from depths of 428 to 447 feet bgs and characterized as “reduced” based on their grey color.

Table 1: 2³ factorial experimental design

Bottle	Sediment	Donor	Initial pH
1	Mesteña	H ₂	6.5
2	Mesteña	H ₂	6.5
3	Mesteña	H ₂	6.5
4	Mesteña	H ₂	8.5
5	Mesteña	H ₂	8.5
6	Mesteña	H ₂	8.5
7	Mesteña	Acetate	6.5
8	Mesteña	Acetate	6.5
9	Mesteña	Acetate	6.5
10	Mesteña	Acetate	8.5
11	Mesteña	Acetate	8.5
12	Mesteña	Acetate	8.5
13	URI	H ₂	6.5
14	URI	H ₂	6.5
15	URI	H ₂	6.5
16	URI	H ₂	8.5
17	URI	H ₂	8.5
18	URI	H ₂	8.5
19	URI	Acetate	6.5
20	URI	Acetate	6.5
21	URI	Acetate	6.5
22	URI	Acetate	8.5
23	URI	Acetate	8.5
24	URI	Acetate	8.5
25	None	None	7.4
26	None	None	7.4

The Kingsville Dome sediment cuttings were collected from depths of 570-590 feet bgs during and were considered “oxidized” based on their rust color. The sediments were stored in an anaerobic chamber (with an atmosphere of approximately 99:1 N₂:H₂) within one day after collection. The microcosms were initially set up in the anaerobic chamber. Each serum bottle was prepared with 25 g of sediment and then filled to 60 mL with post-restoration

groundwater. Twelve bottles contained Mesteña sediments and twelve contained Kingsville Dome sediments. Two additional bottles contained 60 mL of groundwater only. The pH of each microcosm was adjusted to either 6.5 by adding HCl or 8.5 by adding NaOH. The 100-mL headspaces of twelve microcosm bottles were flushed with pure hydrogen gas (industrial grade) at atmospheric pressure and capped tightly with Teflon-lined rubber septa. Similarly, twelve microcosm bottles were amended with 85 mg of sodium acetate (CH_3COONa), flushed with pure nitrogen gas at atmospheric pressure, and capped tightly with Teflon-lined rubber septa. The total electron donor potential added to all the bottles was 8.31 milli-equivalents (meq). The microcosm bottles were then placed on a platform shaker (set at 150 rpm) and incubated within the anaerobic chamber (Figure 1). Dissolved total uranium (U), molybdenum (Mo), iron (Fe), manganese (Mn), calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) were measured using a Thermo Electron inductively coupled plasma mass spectrometer (ICP-MS). Chloride (Cl^-), bromide (Br^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), and acetate (CH_3COO^-) were measured using Dionex ion chromatograph (IC) (Figure 2).



Figure 1: (top) anaerobic chamber; (bottom) sediment bottles on platform shaker



Figure 2: Photographs (a) measuring pH, and (b-d) centrifuging microcosm samples.

IV. RESULTS

Physical Appearance - The Mesteña microcosms were initially light brown, whereas the URI sediments were initially light grey. For both the Mesteña and URI sediments, the H₂-amended microcosms turned darker within one week, whereas the acetate-amended microcosms did not start turning noticeably darker until after about three weeks (Figure 3).



Figure 3: Photograph of microcosm bottles after 2 months of incubation (1st row: Mesteña sediments amended with H₂; 2nd row: Mesteña sediments amended with acetate; 3rd row: URI sediments amended with H₂; 4th row: URI sediments amended with acetate; control bottles with only groundwater are at back).

Change in Soluble U Concentration - The effects of initial pH, reductant type, and sediment type on the final soluble U concentration are summarized in Figure 4. All the H₂-amended microcosms and the acetate-amended URI microcosms had significant decreases in soluble U; however, the acetate-amended Mesteña microcosms had significant increases in soluble U. Under equivalent reductant and initial pH conditions, the URI sediments consistently had greater soluble U removal than the Mesteña sediments. Similarly, under equivalent sediment and initial pH conditions, the H₂-amended microcosms consistently had significantly greater soluble U removal than the acetate-amended microcosms. Initial pH had only a minor effect on soluble U removal, with slightly greater removals consistently observed in microcosms with an initial pH of 8.5.

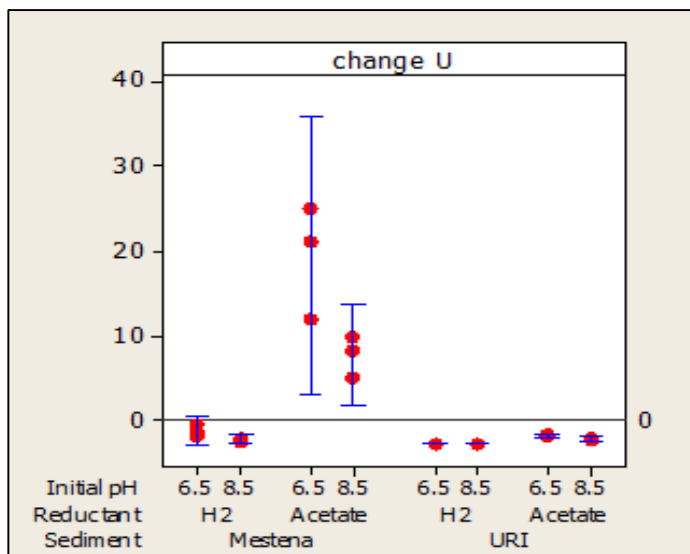


Figure 4: Change in U concentrations (ppm) under different conditions of pH, reductant type, and sediment type. Error bars show 95% confidence intervals for the mean.

Change in ORP - The effects of initial pH, reductant type, and sediment type on the final ORP are summarized in Figure 5a. All the microcosms had significant decreases in ORP. However, the microcosms amended with hydrogen consistently had significantly greater reduction in ORP than those amended with acetate (averages of -345 mV versus -119 mV, respectively). In contrast, the overall effect of initial pH on ORP reduction was not statistically significant. The effect of sediment type was significant for the H₂-amended microcosms (average of -381 mV for Mesteña sediments versus -310 mV for URI sediments), but negligible for acetate-amended microcosms (Figure 5).

Change in pH - The effects of initial pH, reductant type, and sediment type on the final pH are summarized in Figure 5b. The microcosms adjusted to an initial pH of 6.5 consistently increased to 7.4±0.2 (H₂-amended) or 6.9±0.2 (acetate-amended), whereas the microcosms adjusted to an initial pH of 8.5 consistently decreased to 8.2±0.2 (H₂-amended) or 7.4±0.4 (acetate-amended). Under the same initial pH and sediment type conditions, the final pH for the H₂-amended microcosms was consistently 0.5 to 1.0 greater than for the acetate-amended microcosms. Sediment type (Mesteña or URI) had only a very minor effect on pH change (Figure 5).

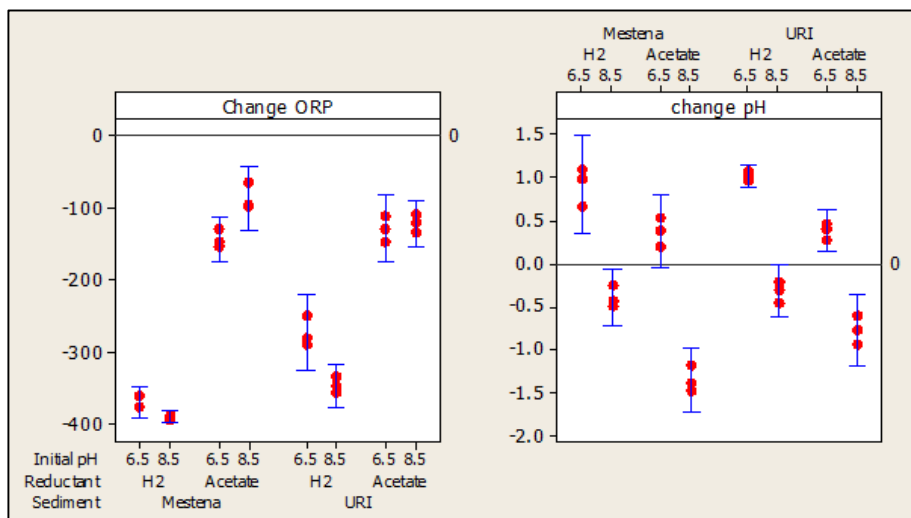


Figure 5: Change in ORP and pH under different conditions of initial pH, reductant type, and sediment type. Error bars show 95% confidence intervals for the mean.

V. CONCLUSION

Figure 5 shows a Pareto chart of the standardized effects of initial pH (6.5 versus 8.5), reactant type (H_2 versus acetate) and sediment type (reduced versus oxidized). Both sediment type and reductant type had very strong effects on U removal, whereas initial pH had a minor, but nonetheless statistically significant, effect. H_2 was significantly more effective than acetate for stimulating immobilization of U, and significantly greater U immobilization was observed with reduced URI sediments than with oxidized Mesteña sediments. Slightly greater U removals were consistently observed in microcosms with an initial pH of 8.5. Finally, no significant two-way interactions between the effects of pH, reductant type, or sediment type were observed.

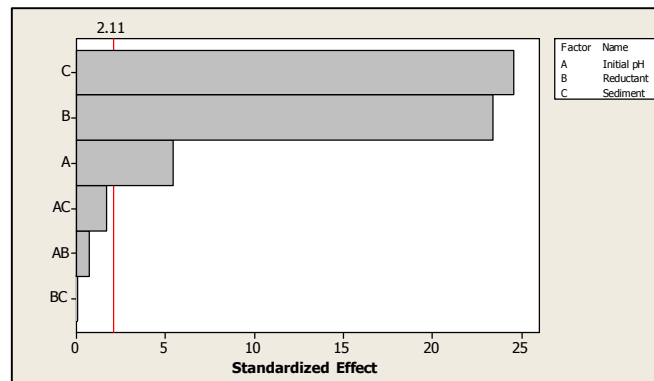


Figure 6: Pareto chart of standardized effects of initial pH, reductant type, and sediment type on U removal from solution.

ACKNOWLEDGEMENTS

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