Treatment of Uranium in Subsurface Water – 11616

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ABSTRACT

Treatability studies were conducted to evaluate in-situ treatment of pond and subsurface water contaminated with uranium (U). This presentation is applicable for U in-situ treatment at multiple Department of Energy and U mine/mill sites.

At one location, the water contained dissolved U and high total dissolved solids, which is typical of hard rock U mine sites. Constituents of concern included U and sulfate. The groundwater contamination at the other site was a result of an in-situ leaching process to extract U from natural porous sandstone deposits. At the conclusion of this mining process, U and selenium were present at elevated concentrations in the oxidized groundwater.

Chemical treatments to remove soluble hexavalent uranium (U[VI]) included pH adjustment, flocculation, phosphate addition, and adsorption on activated red mud (a waste product from bauxite ore processing). Geochemical modeling predicted that U[VI] should be removed by phosphate precipitation and by adsorption on the iron and aluminum oxides present in the activated red mud. Geochemical modeling also indicated that the addition of lime (CaO) to precipitate dissolved sulfate as calcium sulfate ($CaSO_4$) would be hindered by the formation of soluble magnesium sulfate complexes that kept the sulfate in solution. Laboratory tests confirmed the model results.

Under reducing conditions, bacteria can utilize an organic or inorganic substrate to reduce soluble U[VI] to U[IV], which subsequently precipitates as one of several insoluble minerals, such as uraninite or coffinite. These organisms gain energy from this process. In some instances, the reduction of U[VI] can also occur indirectly as a result of biological processes. Under reducing conditions, bacteria will reduce ferric iron (Fe[III]) to ferrous iron (Fe[II]) and sulfate to sulfide (S^{2-}), and these reduced species can subsequently reduce U[VI] through a direct chemical process. In either case (i.e., the direct or indirect process), the biological reduction of U[VI] results in the formation of stable and insoluble U[IV] minerals.

The laboratory tests have successfully demonstrated that application of either adsorption on activated red mud, precipitation following phosphate addition, or biological treatment can lower U concentrations to acceptable levels.

INTRODUCTION

Three studies concerning the treatment of U in water and sediment are discussed in this paper. The results demonstrate that, at sites where there are issues with U in groundwater or pond water, site conditions dramatically influence the efficacy of treatment and site-specific studies are indicated to understand transient changes in dissolved U concentrations and to determine long-term compliance. The first of these sites is a surface mine that has a pond which has been impacted by mining operations. The pond water has high total dissolved solids and contains elevated levels of dissolved U. This water is typical of many hard rock mine sites. The other sites used an oxidative in-situ leaching process to extract U from natural deposits. At the conclusion of this in-situ leaching process, U and selenium (Se) were present at elevated concentrations in the oxidized groundwater. All three site investigations were performed for confidential clients, and as such, this paper only provides enough detail to show important trends.

Shaw used its prior experiences treating metals using conventional water treatment technologies, in-situ and ex-situ biological-based metals treatment, and thermodynamic modeling to design these treatability studies.

Thermodynamic Modeling and Uranium Chemistry

Chemical and biological approaches were considered to treat U in pond waters at the first site, while only biological treatments were considered for the other two sites. All waters (3 locations) were aerobic and had elevated dissolved oxygen (DO) concentrations. Thermodynamic solubility model calculations were performed using the surface mine pond water characterization data for the evaluation of potential treatment alternatives to decrease the soluble U concentration. For this analysis, the pond water was analyzed for the filtered and unfiltered U concentrations, filtered the United States Environmental Protection Agency (USEPA) Target Analyte Lists (TAL) analytes and major anions. In addition pH, density, total organic and inorganic carbon, total dissolved and suspended solids (TDS/TSS), and DO were measured. Under reducing conditions, U is in the tetravalent (U[IV]) form and precipitates as fairly insoluble oxides. As noted, all three waters had elevated DO, so the majority of the dissolved U was assumed to be the more soluble hexavalent (U[VI]) form. Based on the thermodynamic model results, the U[VI] solubility is expected to be a function of pH, carbonate concentrations, reactions of calcium and magnesium with carbonate, precipitation of U[VI] as a calcium or sodium salt, and adsorption onto clays and/or iron/manganese oxides in the soil or sediment.

Dissolved hexavalent uranium U[VI] reacts with dissolved anions such as phosphate, carbonate, nitrate, hydroxide, fluoride and chloride under specific conditions to form a wide variety of aqueous complexes (species). U[VI] can react with o-phosphate to form various low solubility precipitates. Carbonate is a very good complexing agent for U[VI], but only the carbonate ion (CO_3^{2-}), not bicarbonate or carbonic acid, forms the U complexes. Carbonate speciation is controlled by pH. At higher pH, most of the total carbonate is present as CO_3^{2-} so the solubility of U[VI] increases with increasing pH due to the formation of uranyl di- and tri-carbonate anions. At pH values from 7 to 9, and in the presence of dissolved carbonate, the model predicts that most of the dissolved U is present as the $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ anions. Increasing the total carbonate concentration also expands the hexavalent stability field, so U can remain soluble under moderately reducing conditions if the total carbonate concentration and pH are high. The specific assemblage of aqueous U species that forms is a function of the composition, redox state, and pH of the water.

For hard-rock mine sites with elevated levels of calcium, magnesium, sulfate and carbonate, increasing the pH via lime (CaO), hydrated lime ($Ca[OH]_2$) or magnesium oxide (MgO) addition causes the dissolved carbonate to precipitate as magnesite ($MgCO_3$) or calcite ($CaCO_3$). Removal of the dissolved carbonate via calcite or magnesite precipitation causes the re-speciation of U to the uranyl ion (UO_2^{2+}) which is then available to precipitate as the minerals such as $CaUO_4$ or $Na_2U_2O_7$. Removal of U via precipitation reactions may be achieved by increasing the pH using CaO, $Ca(OH)_2$ or MgO addition to precipitate the carbonate, and is predicted to be effective for the pond water treatment.

The addition of ferrous or ferric sulfate is predicted to be effective for U removal by providing a reactive negatively charged iron oxide surface that can aid in adsorbing uranyl anions and acting as a flocculent. However, ferrous sulfate alone will lower the pH, so it must be combined with an alkaline reagent so that the pH increases. A pH increase is required to precipitate most of the carbonate to form UO_2^{2+} before U can precipitate.

Modeling results also predict that under reducing conditions and the correct pH, soluble U[VI] can be reduced to insoluble U[IV]. More reducing conditions are needed as the pH increased. Bacteria can utilize an organic or inorganic substrate to reduce soluble U[VI] to U[IV], which subsequently precipitates as one of several insoluble minerals, such as uraninite or coffinite. These organisms gain energy from this process while being directly involved in the reduction of U[VI]. In some instances, the reduction of U[VI] can also occur as an indirect result of biological processes. Under reducing conditions, bacteria will reduce ferric iron (Fe[III]) to ferrous iron (Fe[II]) and sulfate to sulfide (S^{2-}). These reaction products act as reducing agents that can subsequently reduce U[VI] to U[IV] through a direct chemical process. In either case (i.e., the direct or indirect process), the biological reduction of U[VI] results in the formation of stable and insoluble U[IV] minerals. Although the organisms differ from those that reduce U, microbiological processes can also lead to the rapid reduction and precipitation of Se.

Based on the chemistry described above, a program was devised for the treatment of mine-impacted water and sediment which included evaluations of pH adjustment, calcium precipitation of sulfate, U adsorption on iron, adsorption and subsequent reactions of U with the iron/aluminum minerals in GeoBind™, precipitation of U with phosphate, and biologically assisted change in the redox condition using the naturally present microorganisms in the sediment/soil and site waters.

Hard Rock Mine Site

The pond waters evaluated in this study are similar to those found at many hard rock mine sites which have oxic conditions. The pH of the water was alkaline (8 to 10), and the water contained elevated concentrations of calcium, magnesium, sodium, and sulfate. The total dissolved solids were greater than 30,000 mg/L. The U concentrations ranged from ~6 to 8 mg/L. Most of the U was dissolved based upon concentrations detected in filtered and unfiltered samples. The site groundwater had lower concentrations of the elements of interest than the pond water. The groundwater concentrations of U were elevated due to natural processes occurring in the surrounding area. The pond contained sediment and plant growth. Because the plants have died over time, a thin reductive biological mat has formed and covers part of the sediment and is believed to have created anaerobic zones near the sediment surface. This paper focuses on the pond water and sediments that are covered by the biological mat. The site groundwater and area surrounding to the pond are not discussed in this paper.

A series of isotherm tests were conducted to evaluate the treatment of U in the pond water. Pond water was added to various blends of reagents used for the treatment of U and sulfate in water. Reagents included various combinations of GeoBind™, inactivated red mud, ferrous sulfate, ferric sulfate, sodium hydroxide, calcium carbonate, calcium hydroxide (hydrated lime), triple superphosphate and phosphate rock. The solid reagents and water were mixed on a platform shaker at 180 rpm for 7 days. After 7 days, the solids were allowed to settle, the extraction pH was measured, and the supernate was filtered through a 0.45 µm filter prior to analysis for metals by inductively coupled plasma spectroscopy (ICP).

GeoBind™ and unactivated red mud are by-products of aluminum manufacturing. GeoBind™ is red mud that is amended to improve its characteristics for removing certain metals from water and immobilizing certain metals in solids. The basic component of GeoBind™ is chemically treated alumina-depleted bauxite (“red mud”), which is created in the process of extracting aluminum metal from bauxite ore. According to the vendor, GeoBind™ comprises approximately 15 low solubility iron and aluminum minerals. Some of the basic minerals in GeoBind™ include:

- Hematite (α-Fe_2O_3); Boehmite (γ-AlOOH); Gibbsite ($Al(OH)_3$); Sodalite ($Na_4Al_3Si_3O_{12}Cl$); Quartz (SiO_2); Cancrinite $(Na,Ca,K)_8(Al,Si)_{12}O_{24}(SO_4,CO_3) \cdot 3H_2O$.)

This mixture of minerals provides more effective broad-spectrum treatment of certain metals than either iron or aluminum based treatments alone by providing a wide range of different kinds of sorption sites on the mineral surfaces. Some metals that are initially bound by adsorption convert to a more tightly bound state over time. Adsorption alone can be reversible to various extents given changes in water chemistry. GeoBind™ used in this project was a fine-grained reddish material that is delivered as a solid reagent in powder form.

Calcium carbonate and calcium hydroxide additions were used to increase the pH, precipitate U, and reduce the sulfate concentration by precipitation of calcium sulfate. Sodium hydroxide additions were used for pH adjustment. Ferrous and ferric irons were added in the form of sulfate salts. The added iron hydrolyzed as $Fe(OH)_3$ which acted as an adsorbent and flocculant. The added phosphate reacted with dissolved U[VI] to form low solubility U minerals.

Pond Water: GeoBind™ and Phosphate Adsorption/Precipitation Isotherms Results

Selected adsorption/precipitation isotherm results are found on Tables I and II. In these isotherms, treatment additives were shaken in closed plastic containers with pond water for seven days to determine the efficacy of each treatment.

Due to the vendor’s request and the proprietary nature of the GeoBind™ reagents mixtures, the various specific formulation of the GeoBind™ admixtures are not provided. The dose rate of the GeoBind™ admixture is provided in the table. Multiple GeoBind™ admixtures decreased the U concentration from about 6 to <0.056 mg/L. The composition of GeoBind™ admixtures and the dose rate of the admixtures were important factors in the effectiveness of the treatment.

Table I. Screening Chemical/Physical Treatment – 7 Day Isotherm Results.

Formulation Number	GeoBind™ Blend Dose Rate (g/L)	Ferrous Sulfate Heptahydrate as Iron (mg/L)	Ferric Sulfate as Iron (mg/L)	Sodium Hydroxide	Calcium Hydroxide Slurry (15%)	Calcium Hydroxide	Calcium Carbonate	pH (s.u.)	Sulfur (mg/L)	Uranium (mg/L)
14	2	-	-	-	-	-	-	9.63	10,400	0.250
17	2	-	-	-	-	-	-	9.70	10,800	0.943
16	2	-	-	-	-	-	-	9.80	10,400	0.966
13	2	-	-	-	-	-	-	8.55	10,400	1.18
15	2	-	-	-	-	-	-	9.78	10,200	1.43
4	1	-	-	-	-	-	-	8.68	10,700	1.97
7	1	-	-	-	-	-	-	9.73	10,500	2.33
19	2	-	-	-	-	-	-	8.63	10,400	2.44
12	2	-	-	-	-	-	-	7.27	10,400	5.32
28	-	-	-	-	-	60% Stoic SO_4	40% Stoic SO_4	12.5	6,010	<0.056
31	-	-	-	-	-	1.4 Stoic. SO_4	-	12.6	5,990	0.159
26	-	-	100	to pH 10	-	-	-	5.97	10,300	1.06
25	-	-	100	-	to pH 10	-	-	7.52	10,300	4.07
21	-	100	-	-	-	-	-	5.72	10,300	4.42
23	-	100	-	-	to pH 10	-	-	8.48	10,400	5.30
24	-	100	-	to pH 10	-	-	-	7.57	10,300	5.53
22	-	-	100	-	-	-	-	3.43	10,500	5.83

Table II. GeoBind™ and Phosphate Treatments – 7 Day Isotherm Results

Formulation Numbers	Triple Superphosphate (g/100 mL)	Rock Phosphate (g/100 mL)	GeoBind™ Blends (g/100 mL)	pH (s.u.)	Sulfur (mg/L)	Uranium (mg/L)
34	0.10	-	-	6.21	13,000	<0.056
35	-	0.10	-	8.04	12,700	7.15
36	0.05	0.05	-	6.64	15,900	<0.056
37	0.20	-	-	5.78	13,300	<0.056
38	-	0.20	-	7.91	11,300	6.98
39	0.10	0.10	-	6.2	13,200	<0.056
40	-	-	0.20	9.61	9,670	0.674
42	-	-	0.20	9.98	14,200	0.464
44	-	-	0.30	9.93	11,600	0.200
45	-	-	0.30	9.83	10,900	<0.056
46	-	-	0.30	9.82	11,300	<0.056
47	-	-	0.30	9.95	10,900	<0.056
48	-	-	0.2	9.92	11,700	0.492
52	-	-	0.3	9.75	13,700	<0.056

A long-term study was conducted using five of the GeoBind™ amended isotherms formulations listed in Table I to determine if the U would be released from the adsorption sites in GeoBind™ or the U removal would improve over time (Table III). The repeated formulations used ~500 cc pond water instead of 100 cc in the screening tests. Formulations 4 and 7 used 1 g GeoBind™ admixture per liter pond water and Formulations 14, 16 and 17 used 2 g GeoBind™ admixture per liter water. These 5 isotherms were continuously shaken for 4 months and allowed to sit without agitation for 7 months before analysis. In the screening tests (Table I), these treatments decreased the soluble U concentrations to 0.25 to 2.3 mg/L U. In contrast, all 5 long-term treatments decreased the dissolved U concentrations to <0.055 mg/L. The pH remained high (8.3 to 9.75) throughout the test, the liquid was clear and there was no sulfide/sulfur dioxide smell for the approximate 11-month test. This is in contrast to the month long isotherms containing sediment and pond water in which all samples had a sulfide/sulfur dioxide smell at the end of the test. DO was not measured in these long-term tests. Based on the appearance of these 5 samples, their lack of odor and no significant pH decrease, it appears that there was little biological activity in the absence of sediment. This is consistent with other water-sediment systems where much of the microbial activity occurs on or near the solid phase.

Table III. Long-Term GeoBind™ Study Result

Formulation Numbers	GeoBind™ Blend Dose Rate (g/L)	pH (s.u.)	Uranium (mg/L)
4	1	8.31	<0.055
7	1	9.75	<0.055
14	2	8.35	<0.055
16	2	9.76	<0.055
17	2	9.72	<0.055

Additions of moderately soluble triple superphosphate successfully lowered U concentrations to less than 0.7 mg/L. Less soluble rock phosphate formulations had minimal impact on dissolved U concentrations over the duration of the tests (see Table II).

Pond Water: Alkaline Calcium Reagent Precipitation Isotherms Results

Alkaline calcium reagent was added as mixtures of hydrated lime and calcium carbonate. The total calcium dose rate was based on multiples of the stoichiometric quantity required to precipitate gypsum from solution. When enough hydrated lime was added, the pH increased to ~12.5 and lowered the soluble U concentrations to <0.056 and 0.3 mg/L. At these high pH values, the U-carbonate complexes would have been converted to insoluble hydroxide/oxide compounds including sodium diuranate ($Na_2U_2O_7{\cdot}6H_2O$) and much of the precipitated U could resolubilize at the lower pH values.

It is expected under natural process, it would take a considerable length of time for the high pH resulting from lime addition to decrease to acceptable pH in the range of 7 to 9.5. Also, it is expected that when the pH decreased to 9.5 or less, much of the insoluble U[VI] species would be converted back to the water soluble U[VI]-carbonate complex.

Even when a 40% stoichiometric excess of calcium to sulfate was added, only about 40% of the total sulfate was removed from the solutions. This result agrees with the geochemical model results, which predicted that the majority of added sulfate will speciate as soluble $MgSO_4^o$, $CaSO_4^o$, and $NaSO_4^-$ complexes which are unavailable to precipitate as calcium sulfate (gypsum).

Pond Water: Iron Reagent Precipitation/Flocculation Isotherms Results

In the iron addition tests, none of the formulations had a significant impact on U removal except Formulation 26 (100 mg/L Fe(III)) with subsequent NaOH pH adjustment. Formulation 26 decreased the soluble U concentration from ~6 to 8 to ~1 mg/L and had little impact on the sulfate concentration. In these iron addition tests, iron was added and slowly mixed. The pH was slowly adjusted; the sample container capped and gently agitated. The container was then allowed to sit for 7 days. Allowing the container to set for 7 days was to simulate treatment in the pond and letting the pond react for 7 days. With most of the tests, the treated pond water pH decreased from 10 to below 7 over a 7-day period.

Sediment/Pond Water: GeoBind™ Treatment and Biological Reaction

Additional 500 cc isotherms were conducted in which sediment and pond water were used. The pond sediment was commingled with an organic mat, had a rotten egg smell and was assumed to be reductive due to organic content. Total analyses of the pond sediment showed that it contained a significant quantity of U. The pond water was alkaline (pH ~8.5) and had elevated carbonate/bicarbonate concentrations. Samples were set with and without GeoBind™ added. The containers were tightly capped and shaken at 180 rpm. After 2, 7, 14, 21 and 28 days, the liquid was analyzed for dissolved U concentration. Over time, the DO content in the water was consumed, presumably by a biological respiration. For the samples without GeoBind™ added, the pH decreased to 7 while the sample with GeoBind™ added maintain a pH from about 8 to 9. Samples with and without GeoBind™ added had a transient increase in soluble U concentrations. The maximum U concentration was observed after 2 days. The transient U spike concentrations were greater than in the original pond water added to the isotherms. The U transient increase in concentration was less in the sample amended with GeoBind™. The dissolved U concentration deceased rapidly after the transient and the final U concentrations were much less than the initial pond water concentration. This transient increase and subsequent decrease could have been caused by the reductive dissolution, via microbial metal reduction, of Fe(III) and/or manganese[IV] oxides/hydroxides in the sediment that were serving as reservoirs of U through adsorption. As the closed system continued to become more reductive, the dissolved U was reduced to U[IV] and removed from solution. Additionally, reduced iron(II) and manganese(II) formed during the transient process could chemically reduce U[VI] to U[IV], having the same effect as direct microbial U reduction.

This process may have been further complicated by the production of CO_2 and the lowering of the pH by biological degradation of the high TOC in the sediment. The system went from containing aerobic pond water/anaerobic sediment to one which contained anaerobic pond water/sediment where U[VI] could be reduced. The high dissolved CO_2 concentration reacted with the U and expanded the U[VI] Eh-pH field; then some of the precipitated U-oxides dissolved to form uranyl-carbonate complexes. This latter carbonate complexation effect may be more pronounced in a higher pH environment (e.g., where GeoBind™ was added) as compared to lower pH conditions which eventually existed in the sample without GeoBind™ added. Competing with this dissolution reaction is the adsorption reaction of U[VI] on the GeoBind™ thus limiting the peak U concentration.

An approximately 2-month long column study was conducted to further evaluate U release from the sediment/organic mat material. The column was initially loaded with sediment and pond water. Low DO content (~2 mg/L) groundwater was passed through a column of high TOC sediment to determine if U would be released from the sediment in a flowing system as was observed in the closed isotherm tests. The effluent DO concentration decreased to 0.7 to 1.5 mg/L due to reactions within the column. There was a transient U spike in the effluent that was similar to the isotherm tests; however, the U spike concentration was much less than in the isotherm test that had no GeoBind™ added (see Table IV).

Table IV. Column Study Results

Sample ID	pH (s.u.)	Dissolved Oxygen in (mg/L)	Dissolved Oxygen out (mg/L)	Sulfur (mg/L)	Uranium (mg/L)
Pond Water – Filtered	-	-	-	NA	6.94
Groundwater – Filtered	-	-	-	130	<0.056
Column Effluent: 1 Pore Volume	8.09	2.4	1.3	3,560	21.3
Column Effluent : 2 Pore Volume	7.94	2.01	0.78	3,440	33.1
Column Effluent: 4 Pore Volume	8.09	2.98	1.54	4,080	6.27
Column Effluent: 6 Pore Volume	7.92	2.2	1.1	2,500	1.81
Column Effluent: 7 Pore Volume	7.99	1.9	1.3	1,020	0.546

Hard Rock Mine Site Discussion

These results for the hard rock mining site show that site conditions affect the results and may limit the applicability of the treatment. Conventional water treatment technologies, modified to account for planned in-situ treatment and for extended time for reactions to take place in the pond, were used. Lime addition effectively lowered U[VI] concentrations to the detection limit; however, the resulting high pH was not acceptable for long-term treatment of the pond. The standard approach of adding a form of soluble calcium to precipitate sulfate from solution was not effective here because of the high concentrations of magnesium and sodium which are common at many hard rock mine sites. Fe(II) and Fe(III) additions have successfully been applied in conventional water treatment to remove metals and improve U removal. However, for this site where the pond water is to be left in place, iron addition was assumed to not be effective due to the expected changes in pH which will affect dissolved U concentrations and the expected need for additional iron treatments to maintain the dissolved U concentration.

GeoBind™ and soluble phosphate additions effectively removed U[VI] from the pond water. The long-term GeoBind™ isotherm study showed that U removal improved with time. Longer term studies are suggested for phosphate treatment to show permanence.

Redox conditions can affect long-term U solubility. As expected, when an oxic system was changed to anaerobic conditions, the soluble U[VI] concentration decreased. However, when oxic waters containing U[VI] are contacted with solid (e.g., soil, mine tailings, and sediment) that also contain U, there may be transient U spikes that occur during equilibration of redox conditions.

Uranium In-Situ Leaching Sites

With the application of In Situ Leach (ISL) mining process, an oxidizing solution is pumped through an initially reducing and porous sedimentary ore body to leach U, which is then pumped to the surface where the dissolved U is extracted. The leaching solution at most sites contains an oxidant such as hydrogen peroxide to oxidize the U[IV] to U[VI], and sodium carbonate to raise the pH to 9 or 10 and provide a carbonate complexing agent to maximize the solubility and mobility of the U[VI] species. After the U is extracted, attempts are made to return the leached zone to its initial (pre-mining) reducing condition so that residual U and other elements such as Se, molybdenum (Mo) and vanadium (V) are immobilized. Biologically mediated U immobilization studies were conducted for two sites that had used ISL. Tests were focused on identifying the "best" organic substrate to rapidly and permanently immobilize U[VI] as a U[IV] species and determine if biological reduction is feasible under simulated site conditions.

Small-scale laboratory microcosms were utilized to evaluate the reduction of U[VI] and Se by microorganisms indigenous to the sites. Cores of site materials were collected, shipped on ice and thoroughly homogenized prior to testing. The microcosms were prepared in 160-ml serum bottles. Each bottle received 50 g of core sediment and 125 ml of well-field groundwater. Sediment and water were added first, followed by amendments. The amendments for the two sites are as follows: the amendments used in Location B study were based on an earlier study (Location A results). Phosphate-amended bottles were prepared to evaluate the potential for chemical precipitation of U and Se as phosphate salts.

Location A

- No Addition (control)
- Phosphate only (170 mg/L; no carbon source)
- Emulsified vegetable oil (EOS: 2,000 mg/L)
- Acetate (1,000 mg/L)
- Acetate (1,000 mg/L) + yeast extract (250 mg/L)
- Molasses (sugar-beet; 2,000 mg/L)
- Methanol (1,000 mg/L) + molasses (2,000 mg/L)
- Methanol (1,000 mg/L) + molasses (2,000 mg/L) + yeast extract (250 mg/L).
- Safflower oil (2,000 mg/L) + ethanol (1,000 mg/L)
- Cheese whey (2,000 mg/L)
- Sugar Processing Waste (2,000 mg/L)
- Crude soybean oil (2,000 mg/L)

Location B

- No Addition
- Phosphate only (500 mg/L)
- Ethanol (2,000 mg/L)
- Safflower oil (2,000 mg/L) + Ethanol (1,000 mg/L)
- Safflower oil (2,000 mg/L)
- Molasses (2,000 mg/L)
- Molasses (2,000 mg/L) + Yeast Extract (250 mg/L)
- Cheese whey (2,000 mg/L)
- EOS (2,000 mg/L)

All amendments were added on a weight/volume basis to achieve final amounts approximately between 0.1 to 0.2%. After amendments were added, all bottles were sealed with Teflon-lined septa, flushed with nitrogen gas to remove oxygen in the bottle headspace, and then placed on a rotary shaker at 15°C for 24 hours. This period was used to allow the microcosms to reach chemical equilibrium. All microcosms were then incubated at 15°C to approximate *in situ* temperatures. At the selected collection times, 20-ml subsamples were removed from one of the bottles in each treatment by syringe. Sample collections were performed under a nitrogen headspace to avoid oxygen intrusion into the microcosms. All samples were passed through sterile 0.22-mM cellulose-acetate filters upon collection.

Location A

The experimental data for this study are presented in Figure 1. The soluble U in the untreated samples increased gradually during the study, reaching 10.85 mg/L at Day 35. The addition of 170 mg/L phosphate to the samples resulted in a decrease in the concentration of the soluble U to 4.09 mg/L. This decline most likely represents the chemical formation and precipitation of uranyl phosphates [e.g., autinite: $Ca(UO_2)_2(PO_4)_2$] within the sample microcosms. This hypothesis is supported by the fact that the soluble U in these samples did not decline further during the 35-day study. Selenium levels increased slightly in the phosphate-amended samples.

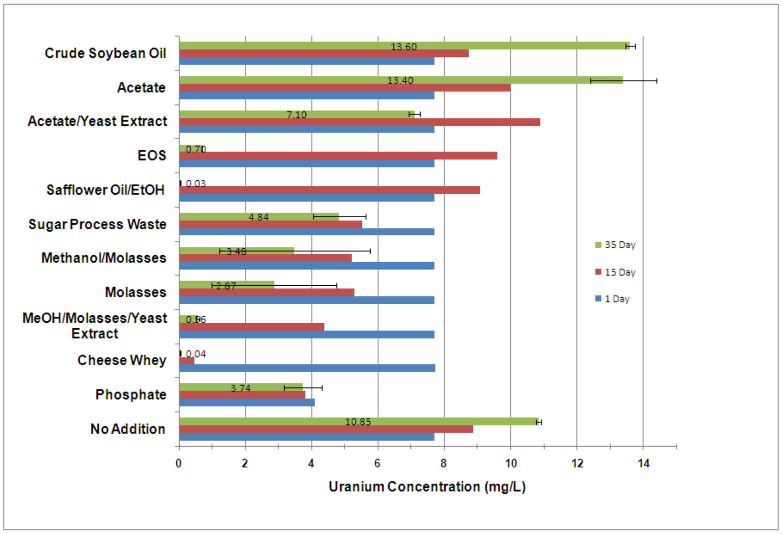

Fig. 1. Location A Levels of Soluble Uranium in Microcosm Bottles Treated with Different Amendments after 1, 15, and 35 Days of Incubation.

Amending the samples with substrate caused the dissolved U to either decrease over time, to spike to a higher level then decrease, or to continuously increase with longer incubation times. The most rapid and extensive reduction of soluble U occurred in the samples receiving cheese whey. Within 15 days, U concentrations declined from 7.72 mg/L to 0.47 mg/L. The U levels fell further to 0.04 mg/L in these samples after 35 days of incubation. Microcosms receiving a mixture of safflower oil/ethanol or EOS (emulsified vegetable oil) showed a U spike then good biological reduction of U, with levels reaching 0.03 and 0.7 mg/L, respectively, after 35 days. Samples receiving a mixture of molasses/methanol/yeast extract showed U levels at 0.56 mg/L after 35 days. Interestingly, the U levels in samples receiving molasses/methanol without yeast extract declined to only 3.48 mg/L during the same period, suggesting that the yeast extract enhanced U bioreduction when applied with these other substrates. Each of these treatments displayed a black precipitate after 35 days suggesting the presence of FeS generated from biological sulfate reduction. Some of the other amendments, including acetate/yeast extract, soybean oil, and sugar processing waste did not promote a biological reduction in soluble U. These samples also did not display a black FeS precipitate.

With the exception of sugar processing waste, each of the substrates resulted in a reduction in soluble Se from 0.69 mg/L to < 0.02 mg/L during the 35-day study. Moreover, 6 of the substrates (cheese whey, EOS, safflower oil/ethanol, soybean oil, acetate, and acetate/yeast extract) yielded this level of reduction within only 15 days. Thus, based on these data, microbial reduction and precipitation of Se is likely to be successful with most of the organic amendments tested.

Based on this study, a column study was conducted to confirm the finding in a "model aquifer" setting. Four columns were prepared using site sediments: (1) a control column which received no carbon source; (2) cheese whey at 200 mg/L; (3) safflower oil (crude, undiluted in batch) and ethanol at 67 mg/L; and (4) EOS at 200 mg/L. In the column receiving safflower oil and ethanol, approximately 5 mL of the safflower oil was added to the column via syringe pump during the first few days; then the substrate was replaced with ethanol, which was added continuously. The columns are approximately 1-inch in diameter and 6 inches long, and constructed using PVC pipe with fitted end-caps. Approximately 120 g of homogenized aquifer solids was packed into each of the columns, which were then set-up in a walk-in cooler set at 15°C to approximate groundwater temperature. Flow of site groundwater was then started into each column at a rate of approximately 1 mL/hour using a syringe pump. After 33 days of operation, amendments were continuously added to each column by syringe pump.

Effluent from each column was collected in a sterile 50-mL conical tube for a period of approximately 24 hours. After this time, the sample was filtered through a 0.45-um pore size filter and preserved with nitric acid and analyzed. Oxidation-reduction potential (ORP) and pH were measured periodically in column influent and effluent using laboratory probes.

The U results from the column study are presented in Figure 2. During the initial period before substrate addition, the effluent levels of U from each column quickly approached the influent value of ~9 mg/L, suggesting that equilibrium was established prior to adding the various substrates. After substrate addition, there was a lag period of approximately 30 days, during which time there was little decrease in U in any of the columns. However, after this period, a significant and extensive reduction of soluble U was observed in the column receiving cheese whey and in that receiving the safflower oil/ethanol treatment. After 36 days, U concentrations declined to 6.58 mg/L in the column receiving cheese whey and to 5.82 mg/L in the column receiving the safflower oil/ethanol mixture. Within 64 days, soluble U levels in both the cheese whey and safflower oil/ethanol amended columns were below 0.5 mg/L and by 80 days, effluent U levels from both columns were < 0.2 mg/L. From approximately 100 to 120 days, there was a slight increase in U levels, but this increase was transient. With the exception of one time point in which 0.6 mg/L U was detected in the safflower oil/ethanol column, the effluent U levels from both columns remained at or below 0.2 mg/L for the remainder of the study. A decline in soluble U was also observed in the column receiving EOS, but the lag period was appreciably longer than for the other substrates, (~100 days), and the rate and extent of decline were much less than for the other substrates. There was no appreciable decrease in soluble U in the control column during the study.

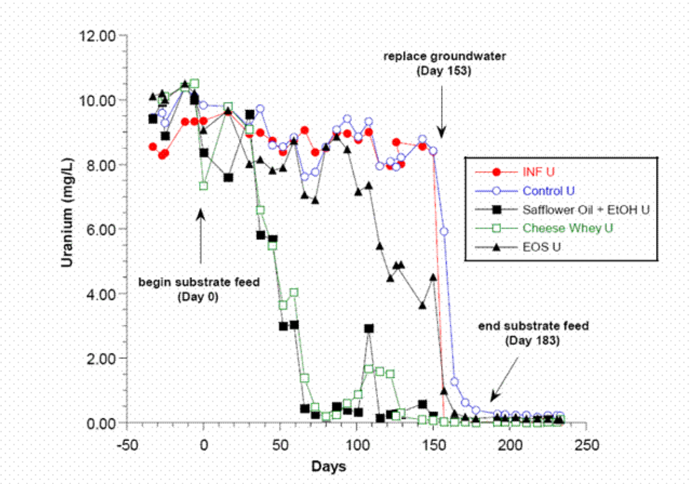

Fig. 2. Location A: Levels of Soluble Uranium in Aquifer Columns as a Function of Time.

On Day 153, the groundwater feed to the columns was switched to upgradient water from the site that contained only background levels of U and Se. On Day 183, the substrate feed to all columns was shut off. These changes (upgradient water and elimination of substrate feed) were performed to assess the potential for U remobilization from the columns. Remobilization was not observed in the cheese whey or the safflower oil/ethanol-treated columns for the remainder of the 233-day study. Uranium levels in the effluent of these columns remained below 0.1 mg/L from Day 157 to the end of the study.

Routine pH and ORP monitoring was added to the experimental protocol 55 days after the start of amendment addition. The ORP in all of the substrate-amended columns dropped into the negative range, showing that the reducing conditions necessary for biological degradation were achieved. In general, among the three substrate-amended columns, the most negative ORP values (indicative of more reducing conditions) were consistently seen in the column amended with safflower oil and ethanol, and the least negative in the column receiving cheese whey. In contrast, the ORP in the control column never went below +140, indicating that oxidizing conditions were maintained without the addition of substrate. The groundwater pH in the effluent of each substrate-amended column increased slightly over the course of the study; this increase being most noticeable in the EOS-amended column. However, pH remained in an optimal range for biological activity (i.e., 6 - 8) in all columns over the 233-day experiment.

The microcosms and column tests showed that bacteria capable of reducing U and Se are indigenous to the aquifer and these bacteria can be stimulated to reduce and precipitate soluble U and Se using several different substrates. The column study confirms the efficacy of the biological treatment shown in the microcosm studies. Cheese whey and a mixture of safflower oil and ethanol promoted the most extensive and rapid reduction of soluble U under continuous flow conditions. Precipitation of U was less rapid and complete when EOS was used as a substrate. All three substrates in the column study promoted rapid reduction and precipitation of Se.

Location B

At Location B, the initial concentration of soluble U in the prepared microcosms was 19.5 mg/L. The dissolved U concentration in the control increased slightly over time. Phosphate addition initially decreased dissolved U concentration to about 1.5 mg/L as insoluble U phosphate minerals were precipitated. After 14 days in bottles receiving phosphate, the soluble U in these samples increased gradually with time, reaching 4.4 mg/L by Day 63.

After 14 days of incubation, significant decreases in soluble U were observed in microcosms receiving cheese whey, molasses, molasses/yeast extract, and EOS (Figure 3). As with Location A, the most extensive decline was observed in samples receiving cheese whey. The average U concentration declined to 0.12 mg/L in these bottles after 14 days. After 29 days of incubation, appreciable decreases were observed in microcosms receiving each of the carbon substrates except for safflower oil. As observed at day 14, the lowest U levels after 29 days were in the samples receiving cheese whey (0.32 mg/L). After 63 days of incubation, U levels continued to decrease in microcosms amended with ethanol, safflower oil/ethanol, and EOS, and remained lowest in the microcosms amended with cheese whey. Samples receiving safflower oil had U spike similar to results from the Location A study. Uranium reduction was also observed in the microcosms amended with safflower oil after 63 days. There was, however, a significant increase in U levels in the microcosms amended with molasses and molasses/yeast extract between 29 and 63 days of incubation.

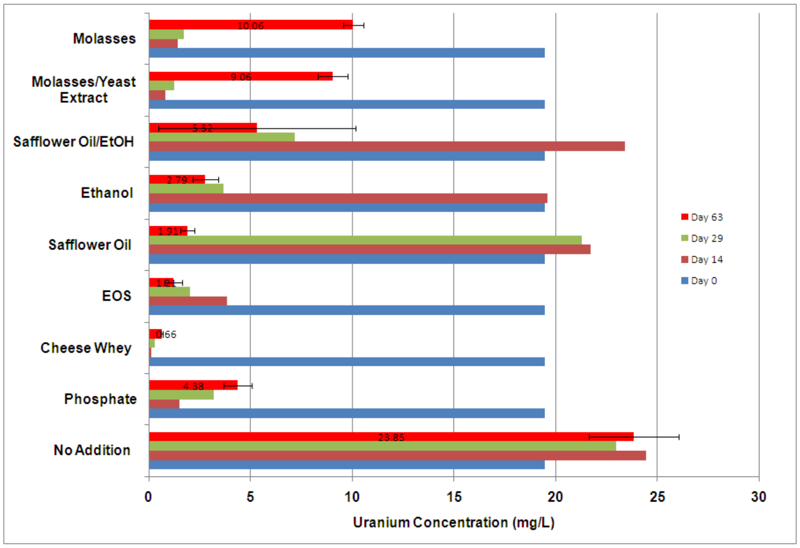

Fig. 3. Location B: Soluble Uranium in Microcosm Bottles Treated with Different Amendments

Over the 63-day study, a significant reduction in the target metals (U and Se) was observed in aquifer samples receiving several carbon amendments, including cheese whey, ethanol, safflower oil, ethanol, blended safflower oil and ethanol, and EOS. Molasses and molasses/yeast extract also led to rapid reductions in the target metals, but both U and V levels increased significantly between 29 and 63 days of incubation. The reason for this increase is unclear, but it probably reflects a geochemical change resulting in the release of reduced U and V from the sediments (i.e., U[IV] and V[IV]), rather than reoxidation of these metals.

Cheese whey led to the most rapid and extensive reduction in soluble U. This substrate was also very effective for reducing both Se and V levels. The primary carbon source in cheese whey is lactose, but this material also contains a variety of amino acids and vitamins, which may serve as important nutrients to stimulate the growth of metal-reducing organisms. Besides cheese whey, results for the three target metals were also reasonably good with safflower oil, ethanol, and EOS over the 63-day period.

These study data suggest that bacteria capable of reducing U, Se, and V occur naturally at the site and that several different substrates are capable of promoting reduction and precipitation of the target metals by these organisms. Cheese whey led to the most rapid and extensive reduction of U and should be considered for a field trial. However, based on cost and application conditions, various other materials, including EOS, safflower oil, and ethanol, could also be effective in the field based on the laboratory data.

Conclusions

Treatability studies show that dissolved U from three sites can be successfully treated to immobilize the U in laboratory studies. These studies used mining-impacted water and solid materials containing U. The pH of the waters ranged from neutral to alkaline values and the TDS ranged from moderate to high.

Based on modeling results, the dissolved U was an U(VI) ion complexed to varying degrees with carbonate, while U(IV) typically is sparingly soluble. The successful treatments in this study used chemical/physical reactions with U(VI) ion or reduced U(VI) to the less soluble U(IV) species, causing it to precipitate. Non-redox reaction included pH adjustment, adsorption with possible long-term respeciation on the adsorbent, and chemical precipitation to form less soluble U(VI) minerals. The redox reactions were all biologically mediated. The most effective treatment is a strong function of the site-specific conditions and future use of the site.

Due to variable nature of U contaminated subsurface water, it is recommended that laboratory tests be conducted for each site to better select promising treatments. As an example of site to site variability, this report has shown cases where different biological carbon source or substrates provide variable results for the extent and rate of U reduction and removal. In addition, when there are transient redox conditions, pH variations, and/or variations carbonate concentrations, the U concentration may decrease smoothly, spike to a high concentration, or cycle up and down during treatment. Laboratory testing can be used to effectively select conditions and reagents/amendments that produce effective results under site-specific conditions. Computer simulations using geochemical solubility-speciation-reaction models are useful in defining the reactions that are taking place, identifying important variables that need to be controlled, and quickly evaluating the effectiveness of different approaches.

It is also suggested that pilot-studies be conducted. There are several reasons for this suggestion: U(VI) can be removed from subsurface groundwater by adsorption, chemical precipitation, or respeciation resulting from redox changes. These reactions are impacted by site-specific conditions such as groundwater flow, presence of other ions, presence of reactive mineral surfaces, pH, native microbial populations, naturally occurring organic materials, and site-specific kinetic reaction rates. It is not possible to recreate all of these parameters in the laboratory. During a field scale study, the water and reagents may contact other mineral surfaces and groundwater compositions than tested in the laboratory study, which may yield divergent results. An additional issue is subsurface mixing of the added reagents. Perfect mixing is easy to achieve in the laboratory, but can be a challenge in the field, especially in lower permeability media. Furthermore, characterizing the in-situ redox conditions and reproducing them in the laboratory can be difficult.

The combination of laboratory scale testing with site-specific materials and computer simulations, followed by pilot-scale testing of the remedies that show favorable results, is strongly recommended for in situ treatment of U and associated elements.