Investigation of in situ leach (ISL) mining of uranium in New Mexico and post-mining reclamation

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Abstract

The purpose of this study was to consider the effectiveness of two methods of restoring groundwater quality in a subsurface uranium-bearing formation following in situ leach (ISL) mining. To accomplish this it was necessary to develop an understanding of the geochemical characteristics of an aqueous solution that might be produced by an ISL mine. Samples of material from three different uranium (U) mines were collected and their acid leachable elemental concentration determined. Additional samples were then leached with aerated sodium bicarbonate ($NaHCO_3$) solutions at concentrations ranging from 1 mM to 500 mM. The fraction of the acid-leachable U and other trace elements released by this leaching process depended on $NaHCO_3$ concentration, U mineralogy, and the amount of solid organic matter in the samples. Less than 5% U was leached from samples with high organic matter using the $NaHCO_3$ leach solution. Groundwater restoration methods were then investigated using column experiments. Two methods were evaluated, a chemical stabilization method based on addition of phosphate (PO_4) and a microbial method in which lactate was added to stimulate growth of dissimilatory sulfate and metal reducing organisms. Neither method was effective. This was believed to be due to sweeping of the leach solution from the columns by the phosphate- or lactate-amended solutions. This hypothesis is consistent with limited mixing in an aquifer as a result of plug flow through the formation.

Introduction

New Mexico has played a major role in the production of uranium (U) for the nuclear power industry and the nation's weapons programs, producing more than 340 M lbs of yellowcake (U_3O_8) (McLemore et al., 2013). Though the U mining and milling industry in New Mexico is inactive at present, increased interest in nuclear energy as a CO_2-free power source has led to renewed interest in development of U resources. Recently, projects have been proposed using both conventional underground mining and in situ leach (ISL) mining.

Currently, nearly all United States U production is from ISL mines. In 2015, total U.S. production was 3.3 M lbs of U_3O_8 from one underground mine and six ISL mines (U.S. Energy Information Administration 2016). The ISL mines are located in Nebraska, Texas, and Wyoming. Note that the domestic U industry continues to struggle as reflected by the fact that total production in 2015 was 32% less than in 2014 (U.S. Energy Information Administration, 2016).

ISL mining, also referred to as in situ recovery (ISR) mining, is accomplished by using a system of injection and extraction wells to circulate a solution or "lixiviant," through the subsurface ore formation (U.S. Nuclear Regulatory Commission, 2009). The lixiviant typically consists of an oxidant (oxygen or hydrogen peroxide) and a carbonate-complexing agent. It is injected into the aquifer to solubilize U by oxidizing it to more soluble phases, which then dissolve through a series of complexation reactions. The soluble U complexes are transported by groundwater flow to the extraction wells where they are pumped to the surface and are recovered in a mill. The barren lixiviant is then pumped back into the aquifer through injection wells and the process is repeated.

The major advantages of ISL mining are that (U.S. Nuclear Regulatory Commission, 2009): 1) it produces little disturbance of the land surface, 2) construction costs are much less than conventional underground mining, 3) it is much safer for workers than underground mining, 4) very little solid waste is generated because there is virtually no excavation, and 5) there is little impact on groundwater resources due to mine dewatering. Often these advantages result in significant cost savings.

However, there are also notable limitations of ISL mining. The ore deposit must be below the water table; the hydrogeology of the host formation must be amenable to circulation of lixiviant solutions through it; and the U minerals must be reactive with the leach solutions. Though ISL mining has been extensively practiced in other states, there is little experience with it in New Mexico.

A major challenge facing the ISL mining industry is that groundwater must be returned to acceptable quality at the conclusion of mining. ISL mining alters the geochemistry of the ore body resulting in release of other constituents at concentrations that may exceed state groundwater standards and federal drinking water standards. In New Mexico, aquifer restoration is especially important because groundwater may be the sole water supply for drinking and other uses, such as in the Grants Mining District.

The principal objective of this research was to evaluate two methods of stabilizing aqueous geochemistry and of restoring groundwater quality following ISL mining. A two-phase laboratory investigation was conducted in which different leach solutions were used to evaluate extraction of U from several low-grade ore samples. In contrast to other studies, which were done in batch systems, this investigation was performed using columns filled with U ore to better simulate ISL conditions. The purpose was to generate information regarding the chemistry of fluids that would be produced by ISL mining of NM U ores. The second phase of the investigation consisted of a series of column studies to evaluate two strategies for restoring groundwater quality. One method was based on chemical addition to stabilize minerals that release U and other constituents. This involved circulation of a phosphate (PO_4) solution. The second method was based on re-establishing reducing conditions in the aquifer by stimulating growth of anaerobic microorganisms.

Background and theoretical considerations

This section provides a brief summary of the theoretical considerations associated with ISL U mining in order to establish a fundamental basis for the research described in this paper. This summary also includes a brief overview of ISL mining and previous groundwater restoration studies.

Geochemistry of uranium and co-constituents

In the natural environment, U most commonly occurs in two oxidation states, U(IV) and U(VI). Uranium geochemistry strongly depends on its oxidation state and the presence of inorganic complexants, especially carbonate (CO_3). Its geochemistry can be conveniently summarized in a pe-pH diagram (also referred to as an Eh-pH diagram) in which the oxidation-reduction (redox) conditions of the solution are plotted on the vertical axis and acid-base conditions are plotted on the horizontal axis (Langmuir, 1997). A pe-pH diagram for U is presented in Figure 1. This diagram represents U-equilibrium chemistry in a solution containing 10^{-6} M U and 10^{-3} M dissolved CO_2 at 25°C. The diagram shows that under oxidizing conditions, U(VI) is thermodynamically stable, and its speciation depends on the pH of the solution. Below pH 5, the cationic uranyl ion (UO_2^{2+}) is present, while at higher pH the uranyl ion forms soluble mono-, di-, and tri-carbonate complexes. These complexes are soluble. Ternary complexes of uranyl with calcium (Ca^{2+}) and carbonate (CO_3^{2-}) near neutral pH have also been reported (Dong and Brooks 2006), but for the sake of simplicity are not shown on this diagram. Because most soil minerals have net negative surface charges above pH ~ 5, uranyl-carbonate complexes do not interact with soil mineral surfaces and therefore are readily transported by groundwater through aquifer materials. In contrast, U(IV) forms insoluble precipitates; uraninite ($UO_{2(s)}$) and coffinite ($USiO_{4(s)}$) are shown in this diagram. Deep ore deposits often are dominated by reduced U phases of which nearly 100 different minerals are known (De Voto, 1978; Burns and Finch, 1999).

Extracting insoluble U from ore generally involves oxidation followed by dissolution whether in a conventional mill or in an ISL mine (Thomson and Heggen, 1983). In a conventional mill, ore is pulverized then leached with an oxygenated strong acid such as sulfuric acid or a strong basic carbonate solution. The dissolved U is then recovered from solution by ion exchange (IX) or solvent extraction. In an ISL mine an oxygenated carbonate solution is circulated through the formation to oxidize, complex and dissolve the U, which is then recovered at the surface by IX. The geochemical reactions in the ISL process have been presented elsewhere (Davis and Curtis, 2007).

Several other metals and metalloids have redox chemistry similar to U, including arsenic (As), molybdenum (Mo), selenium (Se), and vanadium (V). Accordingly, it is common to find one or more of these elements present

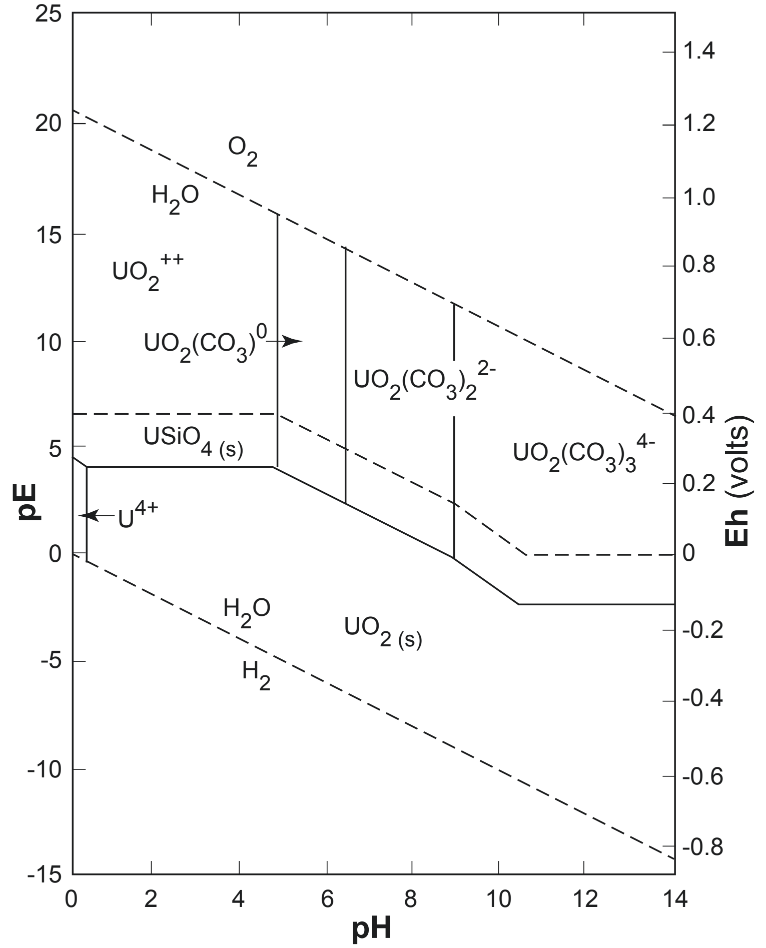

Figure 1. pe-pH diagram for U for a closed system where the total U concentration is 10^{-6} M and the total dissolved CO_2 and H_4SiO_4 concentrations are 10^{-3} M (diagram prepared by Thomson after Langmuir, 1997).

in U-bearing formations or as mixed U minerals such as carnotite ($K_2(UO_2)_2(VO_4)_2 \cdot 1\text{-}3H_2O$ or tyuyamunite ($Ca(UO_2)_2(VO_4)_2 \cdot 5\text{-}8H_2O$). This is why very high concentrations of these constituents are frequently found in U mill-tailing solutions (Thomson and Heggen, 1983).

ISL mining of uranium

It is necessary to understand the ISL process and aquifer geochemistry prior to considering groundwater restoration methods. Conditions that are required for successful ISL mining include (U.S. Nuclear Regulatory Commission, 2009; Maerten, 2013): 1) the ore body must be located below the water table, 2) the deposit geometry must be of sufficient size and shape to allow circulation of lixiviant through injection and extraction wells, 3) the host rock must be sufficiently permeable to allow the lixiviant to pass through the formation, and 4) the formation must be confined so that lixiviant flow can be contained and directed by injection and extraction wells, and, perhaps most importantly, 5) the mineralogy must be such that the U can be extracted from the ore material by the relatively benign oxidants and complexants used in ISL mining.

A conceptual diagram of the ISL process is presented in Figure 2. Barren lixiviant (i.e., a solution containing no dissolved U) is injected, passes through the ore formation causing oxidation and dissolution of U minerals, and soluble U is recovered in an extraction well. Uranium is removed from the lixiviant by IX, and the U-depleted solution is recirculated back through the formation.

The U.S. Energy Information Agency (2016) lists seven ISL U mines that were operating at the end of 2015, one U mine in standby status, eight in the permitting and licensing process, and three in the restoration/reclamation process. These mines are located in Nebraska (1), New Mexico (2), South Dakota (1), Texas (7), and Wyoming (8). The two proposed New Mexico mines are the Church Rock and Crownpoint mines proposed by HydroResources Inc., both with a planned capacity of 1 M lbs/yr of U_3O_8.

Though commercial U production by ISL mining has not been done in NM, a field-scale pilot study was performed beginning in 1979 near Crownpoint, NM. The project was conducted by Mobil Oil and consisted of four, five-spot well clusters drilled to approximately 2,000 ft with 100 ft spacing (Uranium Producers of America, 1995). The purpose of the pilot test was to evaluate the ability to extract U by ISL mining and then to evaluate groundwater restoration methods following mining. The latter was especially important because of the excellent background groundwater quality that met drinking water standards. Further, the aquifer is the sole source of water supply for the community of Crownpoint located approximately 5 miles from the proposed mine site.

The Crownpoint pilot test consisted of leaching for 10 months followed by restoration activities over a period of 12 months (Uranium Producers of America, 1995). Leaching was performed with a solution of hydrogen peroxide (H_2O_2) and sodium bicarbonate ($NaHCO_3$) at a total dissolved CO_2 concentration of 1,500 to 2,000 mg/L and pH 8.3. The pilot test produced maximum U concentrations of approximately 1,000 mg/L but also Mo concentrations of 100 to 200 mg/L. Due to the short duration of the pilot test, Vogt et al. (1982) estimated that only 15% of the U in the ore body was recovered; however, this was not confirmed. Aquifer restoration methods were investigated after completing testing of ISL mining. The restoration method involved flushing the ore body with formation water that had been treated by softening, IX and then reverse osmosis (RO) to remove contaminants. An estimated 11.3 pore volumes of water were passed through the ore body. By the end of the restoration test all of the regulated constituents were below New Mexico groundwater standards and most were near background levels except for pH, Mo, U, and $^{226}Ra/^{228}Ra$.

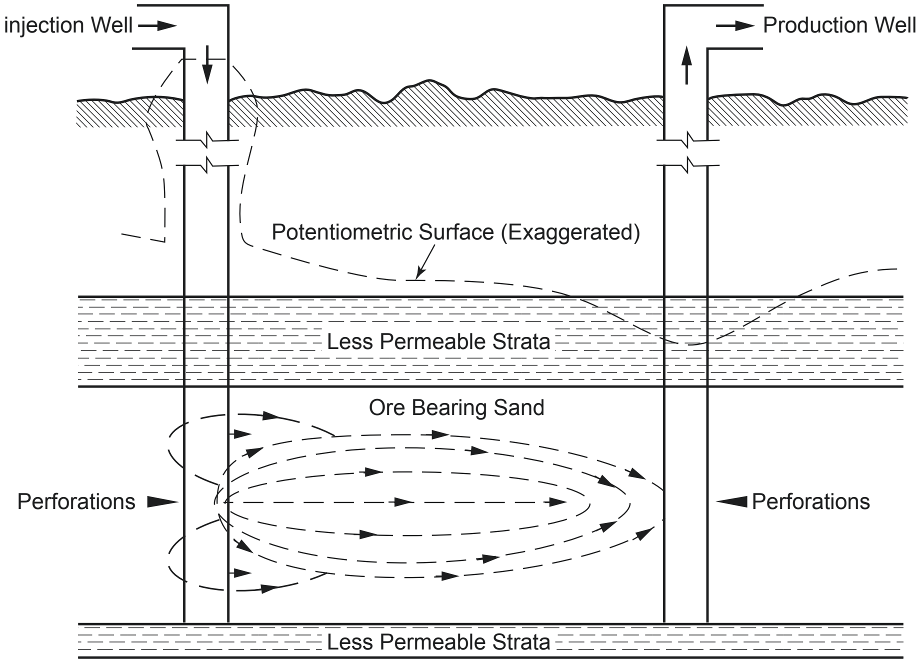

Figure 2. Conceptual diagram of the in situ leach (ISL) mining process (U.S. Nuclear Regulatory Commission, 2009).

Groundwater restoration following ISL mining

Four methods of groundwater restoration following ISL mining have been identified by the U.S. Nuclear Regulatory Commission (2009): groundwater transfer, groundwater sweep, RO permeate recirculation, and in situ stabilization. The International Atomic Energy Agency (IAEA) also includes natural attenuation as an alternative; however, this approach is unlikely to be acceptable in New Mexico where U-bearing aquifers are the sole source of water supply, so this strategy is not discussed here (IAEA, 2001). Groundwater transfer involves moving groundwater from a depleted ore body to a nearby formation undergoing mining so that uncontaminated water dilutes and transports contaminants through the depleted formation. Groundwater sweep consists of pumping water from all ISL wells, both injection and extraction, without injection. Uncontaminated native groundwater then sweeps through the depleted formation. Recirculation of RO treated groundwater involves pumping contaminated water from the mine, treating by RO at the surface to remove contaminants, then reinjecting and recirculating the water back through the mine. The recirculation pattern can be in either a forward or a reverse circulation pattern (Charbeneau, 1984). In situ stabilization consists of altering subsurface geochemical conditions to achieve immobilization of constituents released by the ISL process. Methods involving both chemical addition and stimulation of microbial growth to achieve biological reduction have been proposed (Davis and Curtis, 2007; Gallegos et al., 2015).

Investigations of chemical methods to restore groundwater quality have focused on addition of phosphate (PO_4) (Arey et al., 1999) and sulfide (S^{2-}) (Borch et al., 2012). Phosphate addition as a restoration method is based on the formation of insoluble U(VI)-PO_4 phases. Arey et al. (1999) investigated the addition of hydroxylapatite ($Ca_5(PO_4)_3OH$) as a restoration method by performing batch tests followed by sequential extraction. Apatite addition reduced U solubility, presumably by precipitation of secondary PO_4 phases. The presence of aluminum (Al) and iron (Fe) in the phosphate phases was noted. Residual U concentrations were higher in groundwater samples with higher dissolved organic carbon, presumably due to complexation reactions. Sulfide was considered for aquifer stabilization because it is both a strong reducing agent and will form insoluble precipitates with many transition metals. However, addition of a sulfide to a depleted ISL mine following groundwater sweep resulted in little attenuation of U, Fe, or Mn (Borch et al., 2012). It was thought that formation of strong U-carbonate complexes was responsible for poor U stabilization.

Use of microbial reduction to stabilize a depleted U formation is based on the premise that U and its frequent co-constituents of Mo, Se, and V are insoluble under reducing conditions. Microbial reduction can be achieved through stimulation of growth of dissimilatory sulfate and metal reducing organisms under anaerobic conditions. Two recent reviews of the microbiology and geochemistry have been provided by Williams et al. (2013) and Gallegos et al. (2015). The study by Gallegos et al. (2015) was of particular relevance as it involved collection of core samples from a mined U sandstone deposit in Wyoming and analysis of the mineralogy and microbial population. The study found residual U(IV) associated with organic-rich deposits that was resistant to oxidation and dissolution by ISL lixiviants. Much of the residual U(VI) was associated with Fe(III) minerals. This finding suggests that microbial reduction may present a short-term restoration challenge because adsorbed U(VI) species would become soluble if Fe(III) phases were reduced to more soluble Fe(II) species. In the long term residual reductants such as pyrite and organic carbon may provide long-term immobilization of contaminants from ISL mining.

Methods

The objective of this study was to investigate chemical and microbial stabilization of U and co-constituents following ISL mining. The investigation consisted of two phases. The first phase involved sample collection and leaching experiments to determine leachability of U and to develop an estimate of ISL lixiviant chemistry. The second phase consisted of scoping experiments to simulate in situ restoration by chemical and microbial methods. In contrast to other studies, which were done in batch systems, this investigation was performed using columns filled with U ore to better simulate ISL conditions.

Sample collection and characterization

Core samples of undisturbed underground ore weren't available, hence U-containing rock samples from three different sources were used: 1) stockpiled low-grade ore and waste rock from the Section 11/12 mine near Ambrosia Lake, 2) exposed beds from a mineralized zone at the Jackpile open pit mine on the Laguna Pueblo, and 3) stockpiled ore samples from the Mt. Taylor mine near San Mateo, NM. Several kilograms of samples were collected at each site. The Jackpile samples consisted of three samples from a mineralized zone with distinctive black, gray and yellow colors. The samples were broken using a stainless steel weight and then sieved. They were not pulverized in order to avoid fracturing the fine-grained minerals and unnecessarily exposing internal surfaces to leaching solutions. Particles between 0.425 mm and 0.075 mm were used in batch experiments. Particles between 2.00 mm and 0.425 mm were used in subsequent column experiments. The mineralogy of the samples was not determined.

The acid-extractable elemental composition was determined by leaching samples with aqua regia (three parts HCl and one part HNO_3) for 12 hours, heating at 90°C for 3 hours, then analyzing the extract for major and trace elements. A PerkinElmer Optima 5300 DV inductively coupled plasma-optical emission spectrometer (ICP-OES) was used for general metal analyses and a PerkinElmer Optima NexION 300D inductively coupled plasma-mass spectrometer (ICP-MS) was used to measure U and other trace constituents. Anions were measured by ion chromatography using a dionex ICS-1100 ion chromatograph equipped with a Dionex Ion Pac AS9-HC column. The organic fraction of the samples was determined by Loss on Ignition (LOI) analysis. This procedure involves drying the samples at 105°C, weighing to determine moisture content, then ashing the samples at 550°C and re-weighing. The difference in weight is assumed to be the loss of the organic solids, which are oxidized to $CO_{2(g)}$.

Leaching experiments

Batch leaching experiments were conducted before running the column tests to select an appropriate bicarbonate lixiviant for subsequent column tests and to anticipate the concentrations of constituents in the leachate. The column tests were performed to simulate the ISL leach process and to collect information about the water quality produced by ISL mining. These columns were subsequently subjected to stabilization methods; one set of columns was treated with PO_4 solution, and a second set of columns received addition of lactic acid in order to simulate microbial reduction.

Batch leaching experiments were conducted using sodium bicarbonate ($NaHCO_3$) solutions of varying concentrations to determine the U leachability of the different ore samples. Deionized water was used to prepare $NaHCO_3$ solutions of 1, 10, and 500 mM concentrations for these tests. Samples were leached in loosely capped plastic bottles to allow for oxygenation for 120 hours. Aliquots were collected periodically during the leach experiments to determine leaching kinetics. Samples were filtered through 0.45 µm membrane filters and preserved with HNO_3 to pH < 2 prior to elemental analysis.

Column leach experiments were performed in 5 cm x 25 cm Plexiglas® columns packed with ore samples from the Mt. Taylor mine with particle sizes between #10 (2.0 mm) and #40 (0.425 mm) sieve sizes. The columns had 1 cm of inert glass wool at each end to contain the crushed ore and to distribute flow transversely. Five columns were used; one to serve as a control, and two each to provide duplicates for chemical and microbial stabilization experiments. All columns were operated in an upflow direction and were sealed to prevent introduction of air. The columns were first fed a simulated groundwater solution (see Table 1) with major ion chemistry similar to that reported at the Crownpoint, NM, ISL pilot test (Uranium Producers of America, 1995). Other major ions commonly found in water were present at low concentrations, hence were not included in this recipe. The pH of the synthetic groundwater was 8.3. It was aerated by shaking each time solution was added to the columns to assure a well-oxidized solution.

Groundwater-flow velocities in an ISL mine are very low such that one pore volume of fluid might be replaced every few weeks or longer. It was not feasible to pump water continuously through the columns at such a slow velocity so instead they were fed discontinuously by feeding one pore volume of leach solution every two days for the chemical restoration experiments, and one pore volume every seven days for the microbial restoration experiments. The column studies began by passing one pore volume of the leach solution through each column and then allowing them to equilibrate for 11 days. Restoration experiments began after this equilibration period.

TABLE 1. Chemistry of synthetic groundwater used in column experiments.

Constituent	Concentration (mM)
Ca^{2+}	0.3
Na^+	4.8
HCO_3^-	2.6
SO_4^{2-}	0.4
Cl^-	0.7

Two types of restoration methods were simulated: chemical restoration using a PO_4 solution and biological stabilization achieved by stimulation of reducing microorganisms. The feed water solution consisted of synthetic groundwater (Table 1) with addition of PO_4 or lactate. Phosphate was added in the form of mono-basic phosphate (NaH_2PO_4) at a concentration of 100 µM (10 mg/L) of PO_4, a concentration similar to that used in previous studies (Arey et al., 1999; Mehta et al., 2016). Sodium lactate ($NaC_3H_5O_3$) at a concentration of 3 mM (270 mg/L) was used to stimulate growth of naturally occurring, anaerobic, sulfate- and metal-reducing organisms.

During the ISL restoration experiments, synthetic groundwater containing PO_4 was fed discontinuously to the columns at the rate of one pore volume every two days, as stated above. Because microbial growth is much slower than the precipitation reactions expected with PO_4 addition, the feed rate for the synthetic groundwater amended with lactate was one pore volume every seven days. A control column containing U ore was leached with synthetic groundwater to serve as a reference for comparison of results.

Samples of effluent from each column were collected each time the columns were fed. The samples were filtered and split, with half of the sample preserved with HNO_3 for metals analysis and the other refrigerated with no preservation for analysis of non-metals.

Results and Discussion

Concentrations of elements of interest extracted from the ore samples used in this study are summarized in Table 2. These elements were extracted from crushed ore by acid digestion. The concentration of U, other trace elements, and organic matter varied widely in the five samples. The highest U concentration was in the samples from the Mt. Taylor mine which is consistent with the fact that they were collected by mine staff from high U content ore exposed in the underground mine. Organic material in the samples was not characterized by any method other than LOI.

A simple aerobic batch leaching experiment was conducted to determine the leachability of the elements of interest using $NaHCO_3$ concentrations ranging from 1 mM

TABLE 2. Concentration of acid extractable elements of interest and organic matter as measured by loss on ignition in samples used in this study.

Sample	Mo (mg/kg)	Se (mg/kg)	U (mg/kg)	V (mg/kg)	LOI* (%)
Grants (Section 11/12 Mine)	2.54	12.3	1281	42.5	1.95
Mt. Taylor Mine	90.5	8.44	10767	512	3.99
Laguna Mine–Black	0.70	0.00	7602	24.0	21.8
Laguna Mine–Grey	0.00	0.00	1050	50.7	0.56
Laguna Mine–Yellow	1.20	0.00	38.4	0.00	1.74

*LOI = Loss on ignition

to 500 mM, concentrations typical of those that might be used in an ISL mine. The percentage of the total acid-extractable U leached by each $NaHCO_3$ solution depended in part on the U concentration and the presence of organic matter in the sample. This is illustrated in Figure 3 in which very little of the total U was leached from the Laguna Mine–Black sample which had very high organic carbon content. Because of this poor leachability, all subsequent testing was performed with the ore sample from the Mt. Taylor Mine.

The leachability of U and other constituents also depends on the $NaHCO_3$ concentration of the lixiviant as shown in Figure 4 for the Section 11/12 sample. It is notable that less than 30% of the total acid extractable U was leached. Leach kinetic data not presented in this paper showed that leaching by the bicarbonate solutions occurred rapidly and typically reached >90% of the final value within 24 hours (Ruiz Lopez, 2016). This suggests that the bicarbonate leaching only removed readily soluble forms of U and other elements and that little or no mineral oxidation occurred over the five-day batch leach process. It is also notable that a high fraction of Mo was released in the leaching experiments with comparatively small fractions of the other elements. This suggests that recovery of Mo may be feasible for some ISL U mines. It also indicates that Mo may present a challenge for groundwater restoration following ISL mining as was found during the Crownpoint pilot test (Uranium Producers of America, 1995).

The batch leach tests were performed to determine the appropriate $NaHCO_3$ concentration for the subsequent column tests and to anticipate the solute concentrations in the column tests. Based on the batch tests, 50 mM $NaHCO_3$

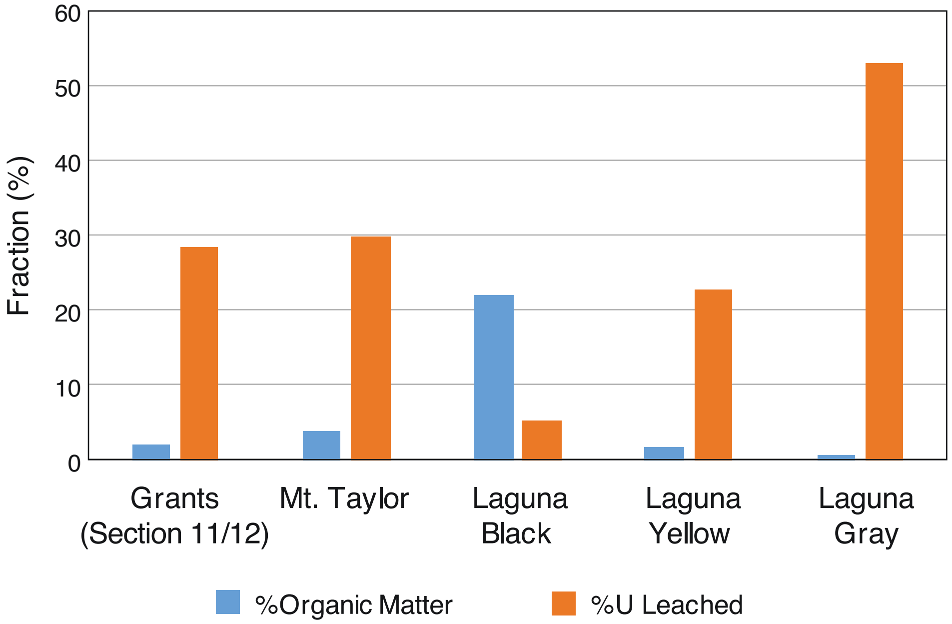

Figure 3. Fraction (%) of total U released by a 500 mM $NaHCO_3$ solution and fraction (%) of organic matter measured as LOI in different samples

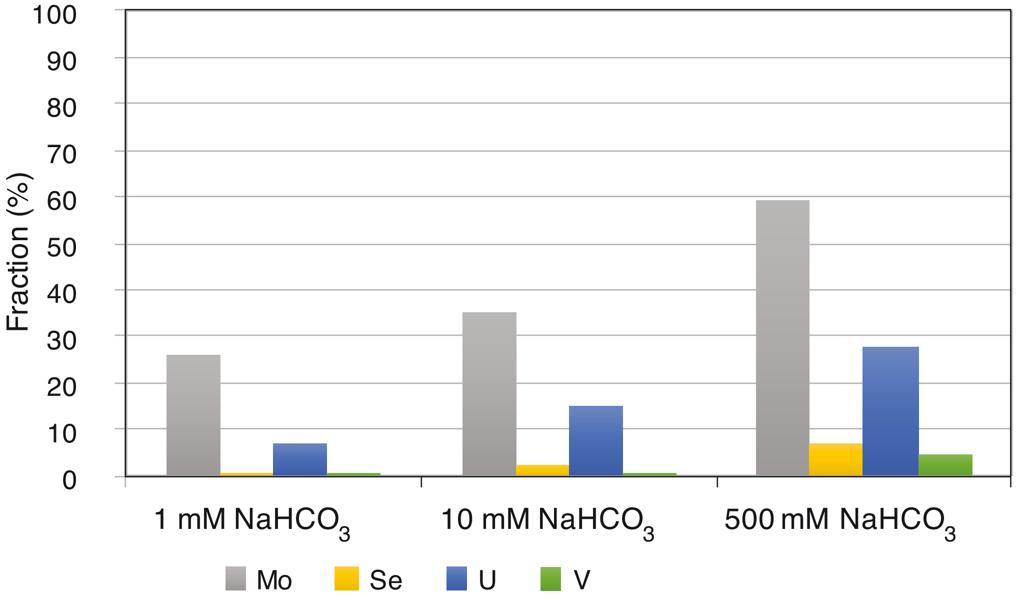

Figure 4. Fraction (%) of metals leached from the Grants (Section 11/12) mine sample after five days of leaching with different concentrations of $NaHCO_3$

was added to the synthetic groundwater (Table 1) to serve as a leachate. This concentration was chosen based on the results of the batch tests and is similar to that used in practice. The columns all contained Mt. Taylor ore samples, which were allowed to equilibrate with the leach solution for 11 days. The average quality of the leachate at the end of the equilibration period is shown in Table 3. The extremely high U concentration is almost certainly due to the high concentration of U in the Mt. Taylor samples, approximately 1% (Table 2). Although 50 mM of $NaHCO_3$ was added to the leach solution corresponding to an alkalinity of 52.6 meq/L, the measured alkalinity of the leachate from the columns was roughly half that. The decrease in alkalinity and the relatively low initial pH are believed to be due to acid produced by partial oxidation of sulfide minerals, such as pyrite (FeS_2), resulting from weathering reactions that occurred in the stockpiled ore.

Aquifer restoration experiments began in the sealed columns after the 11-day equilibration period. The results of the restoration process using the PO_4 addition are summarized in Figure 5, which plots U concentration and pH in the column effluent versus pore volumes of PO_4-amended synthetic groundwater fed to each column. The figure presents data for the two replicate columns (C1 and C2) and for the control column (CC) which was fed only with synthetic groundwater to simulate restoration by groundwater sweeping. The U concentration decayed asymptotically to below 20 mg/L while the pH climbed from an initial pH of 6.4 to about 7.5.

The results of the microbial restoration process in which lactate was used to stimulate growth of anaerobic microbial populations are summarized in Figure 6. The figure presents data for two replicate columns (C3 and C4) and a control column (CC) leached only with synthetic groundwater to simulate restoration by groundwater sweeping. The U concentration decayed asymptotically to below 20 mg/L while the pH climbed from an initial pH of 6.4 to about 7.5. For all of the columns it is suggested

TABLE 3. Average concentration of cations, anions, and metals in column leachate prior to starting stabilization tests. Solution pH = 6.4.

Constituent		**Constituent**		**Constituent**	
Major Cations	Conc (mg/L)	Major Anions	Conc (mg/L)	Trace Metals	Conc (mg/L)
Ca^{2+}	198	Cl^-	17.3	Mo	8.87
K^+	9.9	SO_4^{2-}	257	Se	.03
Mg^{2+}	12.8	Total Alkalinity[1]	1085	U	1627
Na^+	376			V	0.69

[1] Units of mg/L $CaCO_3$

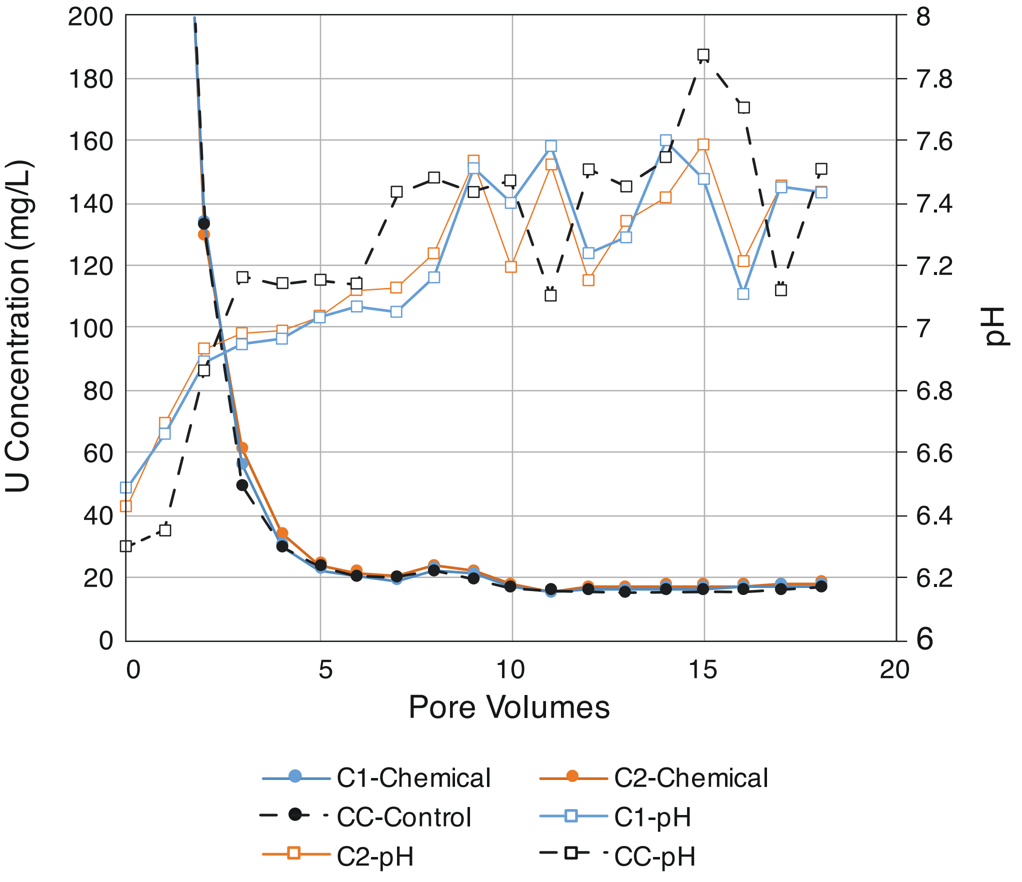

Figure 5. Uranium concentration (represented by solid dots) and pH (represented by open squares) plotted against pore volumes of feed solution for columns fed a 100 μM PO4 solution. Columns C1 and C2 are replicates and column CC is a control column.

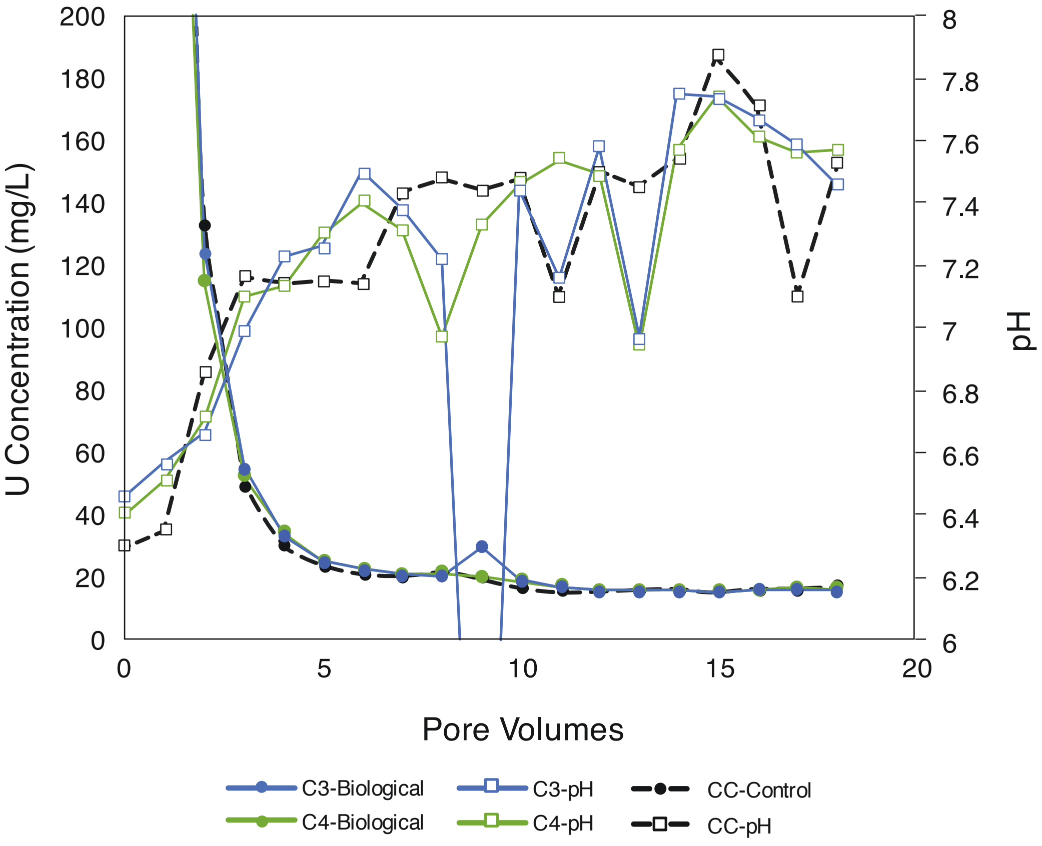

Figure 6. Uranium concentration (represented by solid dots) and pH (represented by open squares) plotted against pore volumes of feed solution for columns fed a 3 mM lactate solution to stimulate biological growth. Columns C3 and C4 are replicates while column CC is a control column.

that the residual U concentration was the result of continuing dissolution reactions from the ore material. Continued leaching of U from the Mt. Taylor ore samples in the columns may also be associated with slow diffusive transport of soluble U species from the interior of rock materials to the bulk fluid flow.

The most important conclusion drawn from these results is that neither chemical addition nor microbial reduction provided any beneficial effect in terms of decreasing U concentrations in synthetic groundwater passing through ore samples that had leached by high concentration of $NaHCO_3$ as used in the ISL uranium mining process. The U elution curves in columns leached by groundwater amended with PO_4 and lactate were essentially identical to a column leached by groundwater alone. It is not apparent that any chemical or biological reactions took place that would immobilize U in these experiments.

In comparing the results presented here with those reported by others it is important to recognize that this study used 1-dimensional packed columns whereas previous studies were done in batch systems. Chemical stabilization through PO_4 addition in batch systems was investigated by Arey et al. (1999) and Mehta et al. (2016). In these studies the principal objective was to identify the chemical and geochemical reactions occurring, not simulate groundwater restoration methods. Similarly, microbial reduction studies such as those described in the review paper by Williams et al. (2013) were done in batch systems for the purpose of understanding the microbial and geochemical processes associated with microbial reduction. These studies all found good immobilization of U in contrast to the findings of the present study. In comparing the results reported here with those reported by others it is important to recognize that this study utilized 1-dimensional packed columns to simulate ISL mining and subsequent aquifer stabilization methods, not batch studies in non-flowing systems.

The lack of U stabilization observed in this study is likely due to the hydrodynamics of the system. Specifically, under steady-state conditions, flow through a porous media occurs with little longitudinal or transverse mixing. To a large extent groundwater flow along a streamline can therefore be described as 1-dimensional plug flow. In the experimental system used in this study there was little interaction between the restoration fluids amended with PO_4 or lactate and the ISL lixiviant in the column at the start of the test. In short, water amended with soluble reactants experiences little mixing with the contaminated solution. Thus, U and other solutes were swept from the column ahead of the restoration fluids. Calculations based on the Ogata and Banks analytical solution of the transport equation presented by Charbeneau (2000) were performed to show this limited mixing (Ruiz Lopez, 2016). This may in part explain the poor performance of a field test at an ISL mine in Wyoming in which H_2S, a strong precipitating and reducing agent, was added with little beneficial effect on groundwater quality (Borch et al., 2012).

The findings of this experimental study have important implications when considering groundwater restoration options following ISL U mining. While chemical or microbial stabilization may be possible restoration method, it is clear that there are hydrodynamic considerations that must be recognized that are every bit as important as the geochemistry, mineralogy, and microbiology.

Conclusions

There are two notable conclusions that can be drawn from this study. The first is that bicarbonate leaching of U from an ore sample as used in ISL mining strongly depends on the mineralogy and geochemical environment of the U ore. Between 20% and 50% of the total acid extractable U could be leached by a 500 mM $NaHCO_3$ solution for most samples in five day leach tests. However, less than 5% of the total acid extractable U was leached from an ore sample containing 21.8% organic material. This result confirms that careful consideration of U ore characteristics and mineralogy are important to the success of an ISL-mining project.

Column studies were performed to simulate ISL mining followed by in situ groundwater restoration methods, also referred to as aquifer stabilization methods. Two approaches were considered: addition of PO_4 to achieve chemical stabilization through precipitation of U-PO_4 and related phases, and addition of lactate to stimulate growth of anaerobic organisms capable of reducing sulfate and sulfide. Neither remediation method reduced the concentration of U or other constituents any more effectively than groundwater sweep conducted in a control column. This was believed to be due to limited mixing between the contaminated groundwater and the amended restoration fluid. Instead of achieving chemical or biological reactions to immobilize soluble U in the columns, the restoration fluid simply forced the contaminated leachate from the column. This finding emphasizes the importance of groundwater hydrodynamics in addition to geochemistry and mineralogy when developing in situ restoration strategies.

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