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GROUNDWATER RESTORATION FOLLOWING IN-SITU LEACH MINING OF URANIUM

by

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Dedication and Acknowledgments

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Groundwater Restoration Following In-Situ Leach Mining of Uranium

by

Omar A. Ruiz Lopez

Bachelor of Science in Civil Engineering

Master of Science in Civil Engineering

Abstract

From 1950 to the early 1980's New Mexico played an important role in the production of uranium (U) for the nuclear power industry and the nation's weapon programs. 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 proposals for renewed development of U resources. In particular, U mining projects have been proposed using both underground mining and in situ leach (ISL) mining. When feasible, ISL mining minimizes waste by eliminating; mine waste, mine dewatering, radiation exposure and the recovered U does not require milling with consequent production of milling wastes. However, ISL does not completely avoid environmental impacts and it does produce some wastes which must be managed at the surface. A much greater concern is restoration of groundwater quality following completion of mining operations. This research consisted of 4 phases. Phase 1 involved collection of samples representative of ore materials that might be mined by ISL processes and characterization of their composition and characteristics. Phase 2 consisted of leach studies to determine the leachability of U from the ore materials and to generate an understanding of the expected chemistry after reaction with bicarbonate and dissolved oxygen which are used in ISL lixiviants. Phases 3 and 4 column experiments for the investigation of aquifer stabilization methods that might be used to restore groundwater following the completion of ISL mining. Phase 3 investigated the use of chemical methods while Phase 4 considered application of biological processes. Results from batch experiments suggest that U and co-constituents are released after reaction of ore solids with bicarbonate and dissolved oxygen showing the potential impacts of ISL U mining on groundwater quality. Column leach experiments were conducted to investigate the potential of chemical and biological processes for restoration. The addition of phosphate was used to immobilize U(VI) by chemical precipitation. Sodium lactate was used as an electron donor for the activation of sulfate and metal reducing bacteria, and a control column without a chemical or biological reductant was used to interpret results differences. Given column experiment results, effluent concentrations of U and co-constituents for chemical and biological treatments are similar to those of the control, suggesting limited mixing between the contaminated groundwater and amended restoration fluid. Groundwater restoration should consider hydrodynamics, specifically the mixing that takes place in the interstitial pores within the aquifer.

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Chapter 1: Introduction

Mining of uranium (U) has been around since the 1950's. U.S. U resources estimates totaled 207,315 tU to 471,555 tU based on the forward cost of \$50 to \$100 per pound of U_3O_8 (yellow cake) respectively (EIA, 2016). Conventional U mining was prominent until In-Situ Leaching technology came into practice. Mainly due to availability of leachable deposits in NB, NM, TX, and WY, depletion of shallow U resources and the legacy issues created by conventional mines. In-Situ Leaching (ISL) of Uranium mining is the only current type of U mining in the US and has been adopted as a feasible approach for U extraction. It consists of circulating an aqueous extraction solution (lixiviant) through the ore formation using a series of injection and extraction wells. Soluble U is recovered at the surface and the barren lixiviant is then re-circulated back through the formation. Problems that are associated with ISL include: a) residual from water treatment at the surface; b) contamination of aquifers by U and trace elements; and c) ineffective immobilization of U and co-constituents post ISL mining. Compared to conventional mining, ISL mining minimized surface/subsurface contamination, human radiation/radon exposure, and further contamination from mills and tailings. Legacy issues by conventional mining have increased regulatory restrictions and the difficulty to mine U in the U.S. Uranium deposits are still available for ISL mining in the U.S., all regulatory restrictions have to be in compliance in order to mine U in the near future.

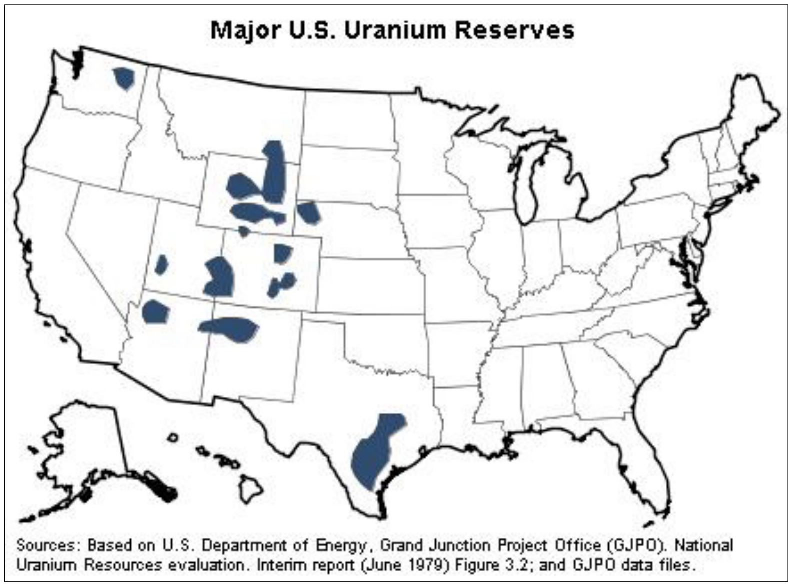
Nuclear power currently provides nearly 20 percent of the electric power in the U.S. Over 50 million pounds of U_3O_8 are imported into the U.S. each year as reported by the

National Mining Association (NMA, 2015), which is about 94% of the U required by nuclear power plants (EIA, 2016). Thus, development of domestic reserves is important to limit the nation's vulnerability to imported U. As mentioned, conventional U mining has left a legacy of surface soil and groundwater contamination that has represented a major challenge to clean up. Therefore, if U resources are exploited in NM, understanding the nature of contaminants that might be present and finding solutions to restore the aquifers after mining need to be addressed before practicing ISL U mining.

Uranium mining by the ISL process was created to reduce cost and recover U from deep deposits. Conventional mining peak production was of 16,800 tU in 1980 with more than 250 conventional mines in operation (WNA, 2015). As U resources depleted near the surface, conventional mining became more expensive and created more waste as more excavation was required. In-Situ Leach U mining (also called in situ recovery or ISR) was then developed to permit mining of deeper deposits while minimizing solid waste production and the impact on water resources. In-Situ Leach mining of U not only minimized surface waste but also increased the ability to mine low grade ore located hundreds of feet below the surface.

An evaluation of U resources conducted by the U.S. Department of Energy indicating that U is present in geologic formations throughout the western U.S. with large deposits in Arizona, Colorado, New Mexico, Nebraska, Texas, Utah and Wyoming, as well as in Washington as shown in Figure 1. Alaska, California, Idaho, Montana, Nevada, North Dakota, Oregon, South Dakota, Virginia also have significant U reserves (EIA, 2016).

Current and previous ISL U mining projects are located in Texas, Nebraska and Wyoming. A pilot study took place in New Mexico in the late 1970's, but no ISL mining was ever completed. Therefore, future and potential areas for ISL mining of U are Crownpoint and Church Rock, NM.



Major U.S. Uranium Reserves

Sources: Based on U.S. Department of Energy, Grand Junction Project Office (GJPO). National Uranium Resources evaluation. Interim report (June 1979) Figure 3.2; and GJPO data files.

Figure 1. Location of important U. S. Uranium reserves, (USDE)

New Mexico has some of the largest U reserves in the U.S. after Wyoming. Conventional mining took place in the Grants Mineral District from 1951-1980. Nearly 133,858 tU were mined and produced (McLemore, 2016). Mines, mills and tailings were all built in NM. All of which contributed to the contamination currently present in surface waters, soil and subsurface waters. Uranium mines, mills and tailings legacy in NM has and is affecting the population near these facilities.

The goal of ISL U mining is the recovery of U from ore deposits while minimizing impacts on groundwater quality. A number of contaminants are often associated with U ores including, arsenic, chromium, molybdenum, selenium and vanadium. It is important to understand the release of U and these co-constituents by ISL mining in order to develop effective methods for groundwater restoration following ISL mining. Knowledge about precipitation and redox reaction reduction to immobilize U and co-constituents by chemical and microbial processes is fundamental for groundwater restoration after ISL mining.

Therefore, this study consisted of two objectives that were intended to gather results that could have the best interpretation for future ISL mining in New Mexico. First objective was to investigate the release of U and metal co-constituents by ISL mining. This was completed by batch experiments that contained ISL lixiviant and crushed ore deposit from U mines in NM. The second objective was to evaluate groundwater restoration processes for U and co-constituents by chemical and biological processes. This was conducted in column experiments with ore deposits from Mt. Taylor mine and restoration amended fluids.

Chapter 2: Background

Summary of Uranium Industry in the United States

Conventional U mining consists of two methods: Open pit mining is used for U deposits that lie near the surface, and underground mines are used for deep deposits. Uranium mills are used to leach, extract and precipitate U (Merritt, 1971). Both processes produce waste that requires proper management. Mine wastes consist of water rock and wastewater from mine dewatering operations. Mill tailing consist of solids from the processed ore as well as highly contaminated wastewater from the milling process. Mill tailings piles also are a source of radon-222, a gaseous element that is a product of the U decay series. Overall waste in tailings contains mobile U, co-constituents, and radium or radon gases that arise from radioactive decay. Contamination can be hazardous through runoff, infiltration, spills to surface water, groundwater, and soil respectively.

New Mexico

Conventional surface and underground mining in NM was conducted in the Grants Mineral Belt located near the south boundary of the San Juan Basin. By far the greatest U production was from the Westwater Canyon member of the Morrison Formation. From 1951-1980 more U was produced in NM than any other state (McLemore, 2016). At a cost of $100 per pound of U_3O_8, 176,901 tU_3O_8 is the projected total of U resources in NM. It is estimated that 157,859 tU_3O_8 were produced from 1947-2002 in New Mexico with the remaining major deposits located near Crownpoint, Church Rock, and San Mateo, NM.

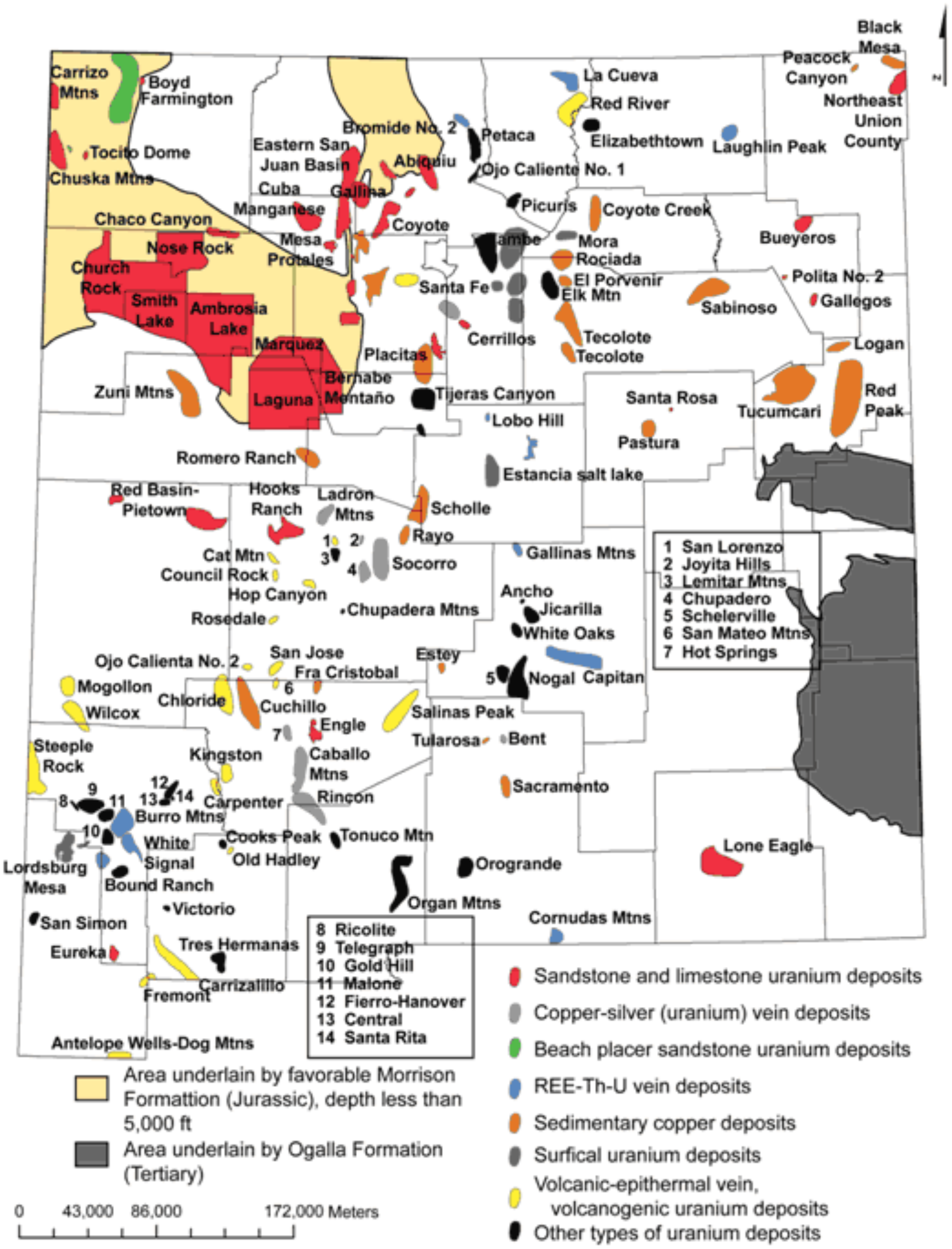


Figure 2. Uranium and Copper Mining regions in New Mexico (McLemore, 2016)

The Nuclear Regulatory Commission (NRC) licenses U mining in the U.S. The U.S. NRC has the authority to license mining of uranium for certain states. In New Mexico, The Title 10 of the Code of Federal Regulations, Part 40, gives the NRC regulatory authority over U processing operations, U milling, including ISL uranium recovery. Individual states can receive licensing authority from the NRC. Agreement states are able to exercise regulatory authority over U whereas mining in non-agreement states are regulated by the U.S. NRC. New Mexico is an agreement state but NRC has retained authority to license uranium recovery.

Prior to mining, the aquifer within the mining zone is exempted from human consumption and a baseline of constituent concentrations required by the NRC is established. Exempting the area as an underground source of drinking water, is in accordance with the Safe Drinking Water Act (NRC, 2009). Adjacent groundwater from the exempt location has to be protected and available for human use. State agency's also have the authority to create other constituent water quality standards if these agencies believe such constituents are a cause of concern (NRC, 2009). Baseline of constituents is determined by sampling four times over each season of the year for variability. When baseline water concentrations are near or well below the EPA standard, such concentrations are difficult to achieve during restoration (Hall, 2009). New Mexico also has similar ground water standards compared to the SDWA standards.

Groundwater is crucial/important in the state of New Mexico, where many New Mexicans depend on groundwater. If restoration is not effective, this could pose significant health risk to the human population in the surrounding areas. These areas are near Crownpoint (Table 10) and Churchrock, NM which are areas of interest for ISL of U mining. A pilot test completed in Crownpoint, NM showed positive results in mining U but complication of U and Mo immobilization.

Nebraska

Uranium ore deposits are located in northwestern Nebraska and are found in the Tertiary Basal Chadron member of the White River group. Nebraska recoverable U reserves add up to 9-13% of the US total (EIA, 2016). Uranium deposits range in depths from 60 to 300 m. Characteristics of the aquifer are low permeability, thin high grade ore intercepts all within an aquifer of good water quality. Specific problems are high levels of V, insufficient groundwater levels and winterization is required (Underhill, 1992). Crowe Butte ISL facility (Table 10) located in the county of Dawes, Nebraska implemented RO and IX for restoration of those wellfields that have been mined.

Texas

In-Situ Leach mining has been conducted in Texas since the 1960’s. The Texas Coastal Plain Uranium District has seen the greatest production of U by ISL accounting for 85% production in the US (Underhill, 1992). The Goliad Formation, Oakville Sandstone, Catahoula Formation, and Whitsett Formation create the Texas Coastal Plain. For the most part in south TX after ISL mining, groundwater was not restored to pre-mining conditions but to relaxed clean-up standards (Hall, 2009). After restoration, U concentrations exceeded the Environmental Protection Agency (EPA) Safe Drinking Water Act (SDWA) standard of 30 µg/L U at most of the ISL mines but the state of Texas has allowed restoration to be more feasible compared to EPA standards. For background TDS exceeding 3000 mg/L, the aquifer is exempted from EPA's SDWA. The state of Texas also has its own ground water standards allowing the restoration criteria to be less stringent, it applies to mines that are located over 0.5 miles from population and avoids human exposure to high TDS from groundwater resource (Texas Commission on Environmental Quality, 2010). Uranium is not the only metal of concern, other metals that are frequently associated with ISL mines are Mo, Se, V and P (Davis, 2007). Uranium minerals are also associated with phosphates, vanadates and silicates (Davis, 2007). Most ISL facilities located in Texas have used groundwater sweep, Reverse Osmosis and recirculation, chemical addition and deep well injection for restoration of disturbed aquifers.

Wyoming

The largest reserves of U in the US are located in Wyoming as shown in Figure 1 with reserves totaling 84,618 tU to 171,545 tU, which is 41% and 36% respectively recoverable reserves in the US (EIA, 2016). Wyoming was the first state to implement ISL mining of U beginning in 1963. A sulfuric acid leach system was used and approximately 577 tU were recovered in this period (Underhill, 1992). Today, many ISL plants operate or are near operation in the state of Wyoming (Table 10). Deposits are located in the Powder River Basin and consist of the Fort Union formation, the Paleocene age, Wasatch from Eocene age, and the Wind River formations. Most deposits consist of low permeability, thin ore deposits that are located within good water quality aquifers at depths of 60-300 m (Underhill, 1992). The major U ore mineral is coffinite ($USiO_4$) associated with pyrite, marcasite, hematite, ferroselite, native selenium, and calcite

(Davis, 2007). The principle problems related to ISL mining in Wyoming are insufficient water levels, high levels of Vanadium. Because of very cold climate, winterization is required. These facilities have introduced restoration methods by chemical and biological processes along with groundwater sweep, RO and recirculation.

Geochemistry of Uranium and Related Co-constituents

Uranium is commonly found in a reduced U(IV) and oxidized U(VI) in aqueous systems. Reduced U can be commonly found as Uraninite (UO_2), and Coffinite ($USiO_4$) which is a solid mineral located in the ore bodies at the subsurface. However, many other U minerals exist and contain high concentrations of co-constituents including chromium, molybdenum, selenium and vanadium. In-Situ Leach of U mining may dissolve and mobilize these co-constituents resulting in GW contamination that is difficult to remediate. For instance, the presence of carbonate can promote the dissolution of UO_2 exposed to oxic conditions. If mobilization of these constituents occur greater contamination of the aquifer is expected. These constituents are of importance due to their abundance in and around U ores and commonly found in New Mexico. The redox, complexation and acid base chemistry of U and co-constituents is important in order to understand the impacts of U mining and alternatives for subsequent aquifer restoration.

Redox Chemistry of Uranium

The geochemistry of U and its transport in aqueous solutions is strongly dependent on its oxidation state. The most common oxidation states of U are U(IV) and U(VI), but U can also be found as U(V). Most U(IV) minerals are sparingly soluble. The redox chemistry of U is summarized in (Figure 3) which considers U equilibrium with the U(VI) soluble phases and two common minerals, Coffinite ($USiO_4$) and Uraninite (UO_2). Under oxidizing conditions U(VI) is present, commonly found as Uranyl ion (UO_2^{2+}), that is more soluble and is easily mobilized when complexed with carbonate. Uranium (VI) minerals are more soluble though there are several common sparingly soluble U (VI) minerals such as carnotite ($K_2(UO_2)_2(VO_4)_2{\cdot}3H_2O$) and tyuyamunite ($Ca(UO_2)_2V_2O_8{\cdot}(5\text{-}8)H_2O$) . Uranium (VI) forms strong complexes with carbonate species, this increases its mobility and increases the production of rich uranium (U_3O_8). As described in (Mason et al., 1997) U (IV) might not be dissolved by carbonate, but can be oxidized by strong oxidizing agents such as carbon potassium permanganate and peroxides or most importantly dissolved oxygen.

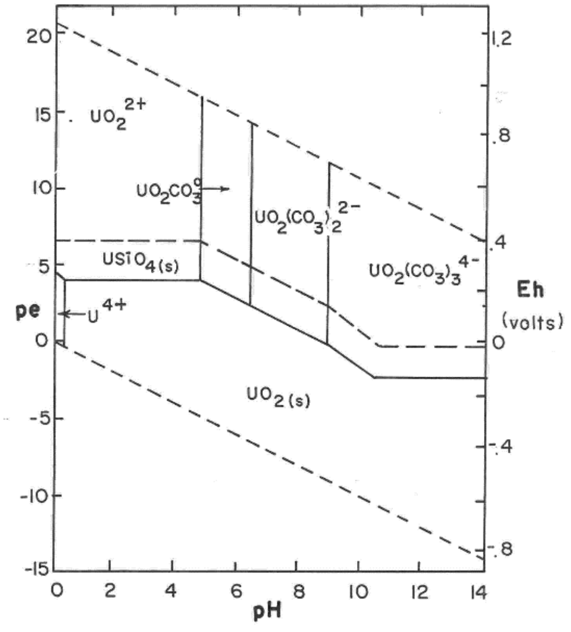


Figure 3. pe-pH equilibrium diagram for U showing oxidation-reduction and complexation of Uraninite and Coffinite, total U concentration is 10^{-6}M and the total dissolved CO_2 and H_4SiO_4 concentrations are 10^{-3}M. Created by Thomson, B. M.

Acid Base Chemistry of Uranium

Most ISL of U mining plants add carbonate such as sodium bicarbonate ($NaHCO_3$) to their lixiviant in order to increase the recovery rate of U. The concentration of U(VI)-carbonate species as a function of pH is summarized in Figure 4. If concentrations of DIC increase, the amount of U (VI) extracted also increases (Mason et al., 1997) (Zhou and Gu, 2005). This is understandable as many ISL plants add more carbonate and or bicarbonate to increase solubility. Also (Zhou and Gu, 2005) explained that stable complexes with carbonates such as $UO_2(CO)_3^{2-}$ or $UO_2(CO)_3^{4-}$ which are poorly retained by soil sediments and thus highly mobile in soil and groundwater. Compared to acid the carbonate specie is an effective chemical to recover U and its friendly to the aquifer by minimizing the mobilization of co-constituents.

The equilibrium solution chemistry of U (VI) can be summarized using log C vs. pH diagrams of U prepared using the MINEQL+ (Westall and Morel, 2014) program (Figure 4). The diagram shows that the dominant U species are carbonate complexes above pH of 5.6.

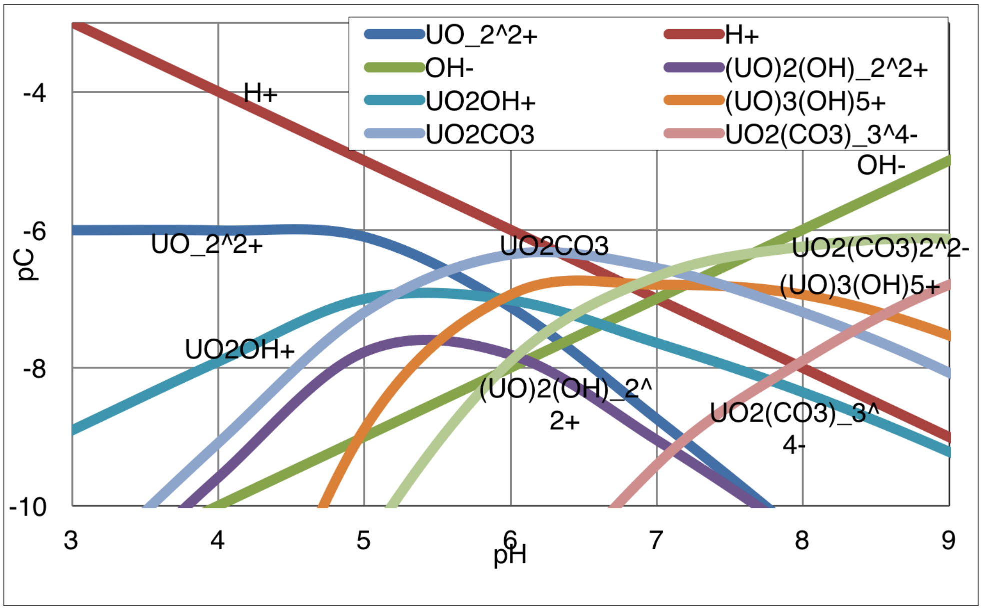


Figure 4. pH vs. pC of Uranyl Species, MINEQL diagram results, MINEQL+. Total U concentration is 10^{-6}M.

The objective of ISL mining is to recover U, but studies such as (Kumar and Riyazuddin, 2011) explain that the high soluble Se (VI) species is present where concentrations of bicarbonate are also high in the range of (73-650 mg/L). This comes to show that U co-constituents are mobilized by carbonate species used in ISL mining.

Solubility/Dissolution

The aqueous geochemistry of U strongly depends on its oxidation state. In particular U(VI) phases are generally much more soluble than U(IV). Therefore, hexavalent U has to be present in order for solubility/dissolution to take place. Solubility can also take place where certain ore deposits might not require an oxic environment as U (VI) will be present therefore extraction of U without oxidation.

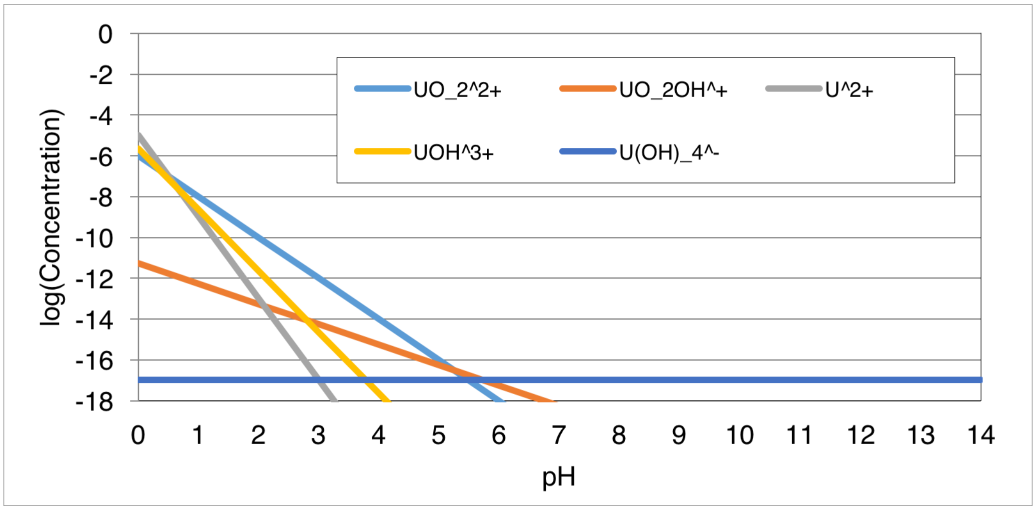


Figure 5. Solubility diagram showing uranyl hydroxyl phases.

Common Uranium Deposits and Minerals in New Mexico

New Mexico has the second largest U reserves in the U.S. (EIA, 2016). Most U deposits are located within the Grants Mineral/Uranium District. Sub-districts of interest from the Grants Mineral Districts are the Laguna, Ambrosia Lake and Church Rock-Crownpoint districts. Each sub-district contain similar but distinct deposits as shown in Figure 2 (MCLeMoRe et al., 2013). Common types of U ore deposits include those from the Morrison Formation which are; primary tabular sandstone U-humate deposits, redistributed sandstone U deposits, and remnant sandstone U deposits. Other sandstone U deposits are redistributed U deposits in the Dakota Sandstone, Roll-front sandstone U deposits in Cretacesous and Tertiary sandstones, and Beach Placcer, thorium-rich sandstone. Limestone U deposits in the Toldito Formation. Lastly, collapse-breccia pipes (including clastic plugs) from vein-type uranium deposits (MCLeMoRe et al., 2013).

Over 100 U minerals have been identified (De Voto, 1978). Common minerals found in NM are shown in Table 1 (McLemore, 2016).

Table 1. Common U mineral deposits in New Mexico (McLemore, 2016)

Common U Minerals	
Minerals	Formula
Oxides	
Uraninite	UO_2
Phosphates	
Autunite	$Ca(UO_2)_2(PO_4)2\bullet 10\text{-}12(H_2O)$
Silicates	
Coffinite	$U(SiO_4)_{1-x}(OH)_{4x}$
Uranophane	$Ca(UO_2)2SiO_3(OH)2\bullet 5H2O$
Vanadates	
Carnotite	$K_2(UO_2)2V2O8\bullet 3(H_2O)$

Chemistry of Co-Occurring Constituents

Arsenic is sometimes found with U ores, in low concentrations and not as a mineral. Arsenic may occur as three oxidation states (+5, +3 and -3). As (III) and As (V) are most common in water. Arsenate (V) is known to be as soluble compared to Arsenite (III) as described by (Nordstrom and Archer, 2003). The Eh-pH diagram shown below in Figure 6, suggest that the As present at oxic and near reducing condition will be dissolved in water, and As at reducing conditions will be precipitated. Therefore, As dissolution would be favorable under U oxic/near reduction state conditions.

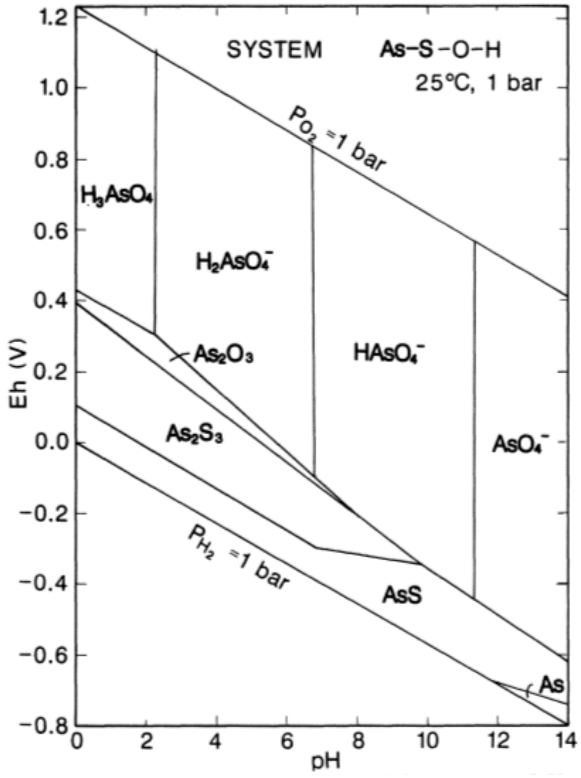


Figure 6. Eh-pH diagram of As (Brookins, 1988)

Molybdenum (Mo) is commonly found in IV or VI oxidations states. It is found in some NM U ore deposits, notably near Crownpoint, NM. It forms at least one mineral with U, umohoite $(UO_2)(MoO_4)4H_2O)$. Molybdenum is soluble as a molybdate (MoO_4^{2-}) and insoluble under reducing conditions (Figure 7). A sulphide phase, molybdenite (MoS_2) is shown in Figure 7.

These diagrams do not consider other constituents such as oxygen, nitrogen, sulfide and carbon. These constituents tend to restrict redox systems and mobilization of U and co-constituents could potentially vary if considered.

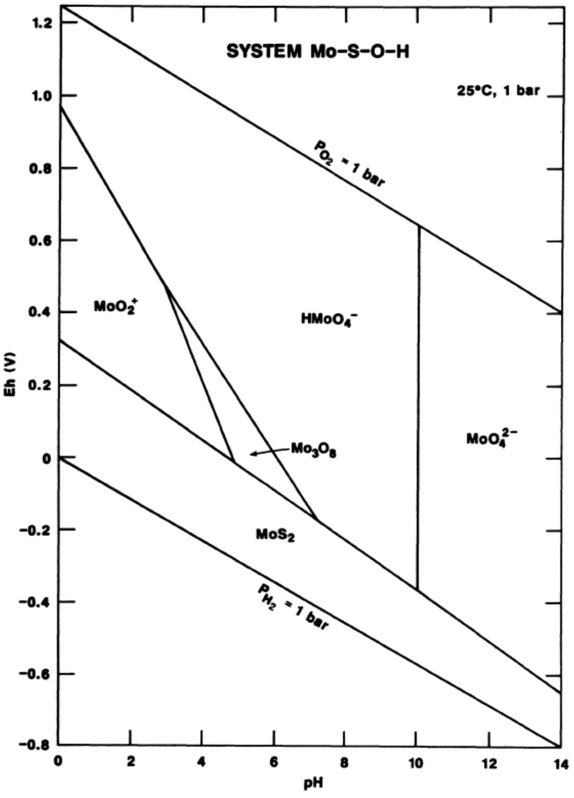


Figure 7. Eh-pH diagram of Mo (Brookins, 1988)

Another constituent frequently associated with U is Selenium (Se). Selenium is commonly found in four oxidation states in groundwater; selenide (Se (-II)), elemental selenium (Se(0)), selenite (Se (IV)) and selenite (Se (VI)) (Kumar and Riyazuddin, 2011). Figure 8 shows an Eh-pH diagram of Se, Se (VI) and (IV). Note that both Se (IV) and Se (VI) species are soluble whereas elemental selenium is insoluble. Common minerals under reducing environments such as Haynesite $(UO_2)_3(SeO_3)_2(OH)_2 \bullet 5(H_2O)$, are commonly found as crusts on sandstone.

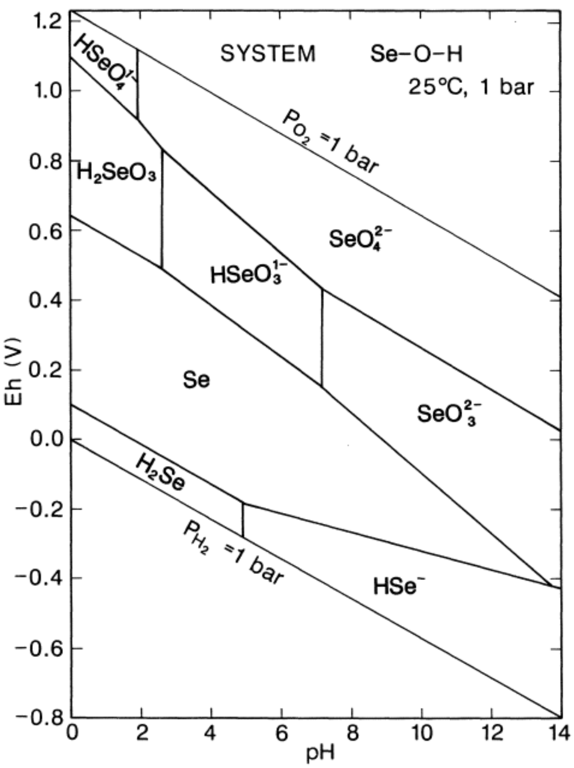


Figure 8. Eh-pH diagram of Se (Brookins, 1988)

Vanadium (V) is found within or around the U ore. There are three common oxidation states (III, IV, V). Vanadium (III) is insoluble and mostly found in reducing environments, V(IV) is commonly found in reducing environments but is more soluble compared to V(III), and V(V) is most common under oxic conditions making it the most soluble V specie (Telfeyan et al., 2015). There are several common U-V minerals which may contain either U (VI) or U (IV). An Eh-pH diagram that summarizes V redox is shown in Figure 9. Under oxic conditions V(V) is thermodynamically stable as a vanadate, while an insoluble oxide is stable under reducing conditions Karelianite (V_2O_3) is shown here.

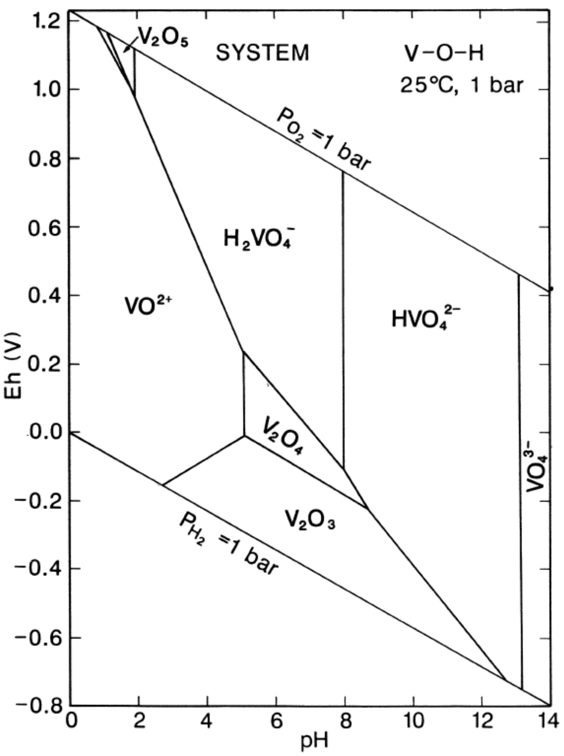


Figure 9. Eh-pH diagram of V (Brookins, 1988)

In-Situ Leach Uranium Mining

Introduction of a Lixiviant to Mobilize Uranium in a Well Field

In-Situ Leach U mining is a process in which a leaching solution (lixiviant) is injected into the ore formation through a set of injection wells as shown in Figure 10 and Figure 11. The lixiviant is typically composed of natural groundwater to which is added an oxidizing agent, such as oxygen, and a U complexing agent, usually bicarbonate/carbonate (America, 2016; UPA, 2016). Experimental work (Zhou and Gu, 2005) has shown that under aerobic conditions a greater fraction of U was extracted than under anaerobic conditions. This is due to the oxidation of U(IV) mineral to more soluble U (VI) phases. Once oxidized, U(VI) forms soluble carbonate complexes that is highly mobile. In order to optimize the mobilization of U, injection wells have to be properly installed trough out a well field.

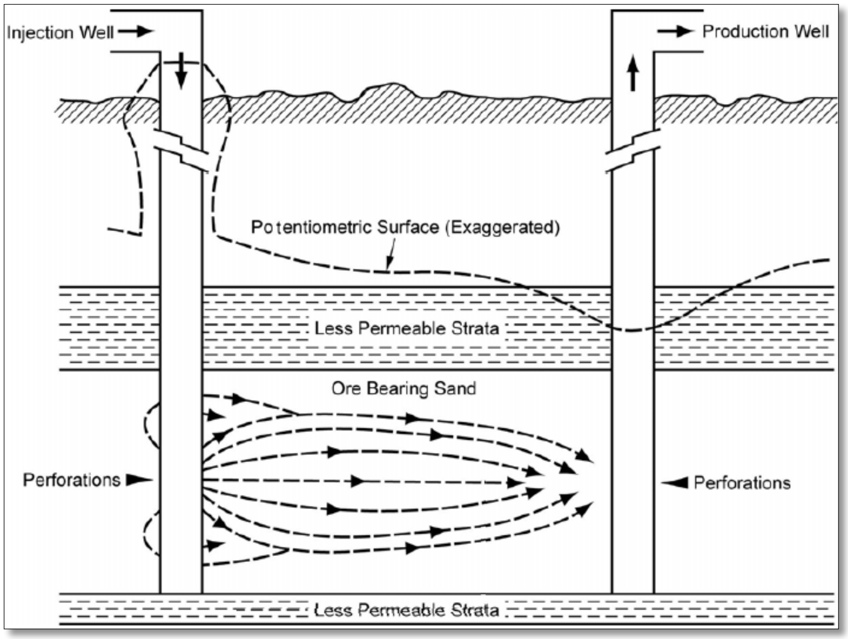


Figure 10. In-Situ Leach Cross Section illustrating ore formation geology and injection/production wells (NRC, 2009).

A five-spot or seven-spot pattern of injection and extraction wells are used (Figure 11) consisting of a central extraction (production) well surrounded by 4 or 6 injection wells respectively (NRC, 2009). Well field patterns depend on the shape of the U ore body and surface topography. Many roll front deposits are irregular and therefore the layout of the well fields tend to be irregular (NRC, 2009).

Recovery of U is usually composed of two processes. As aforementioned the first process involves the oxidation, complexation and the mobilization of U throughout the well field. Second process is composed of a set of production wells that extract the leachate (pregnant/uranium-bearing solution) to the surface for U recovery and enrichment. The production well pumps out more water than the injection wells pump in, this create a cone of depression and a circulation system that contains the leachate within the well field. A continuous injection and extraction takes place until the extractable U (cut-off grade) has been removed from the ore deposit. The uranium-rich solution is extracted through the pump well that is connected to a water treatment facility. (WNA, 2015)

Monitoring wells as shown in Figure 11 are placed around the ISL well field to monitor excursions (NRC, 2009). Sampling monitoring wells is an important duty and needs to be completed at least every two weeks (NRC, 2009). If leakage occurs the flow to the injection wells and from the extraction wells can be adjusted to draw this water back into the mine.

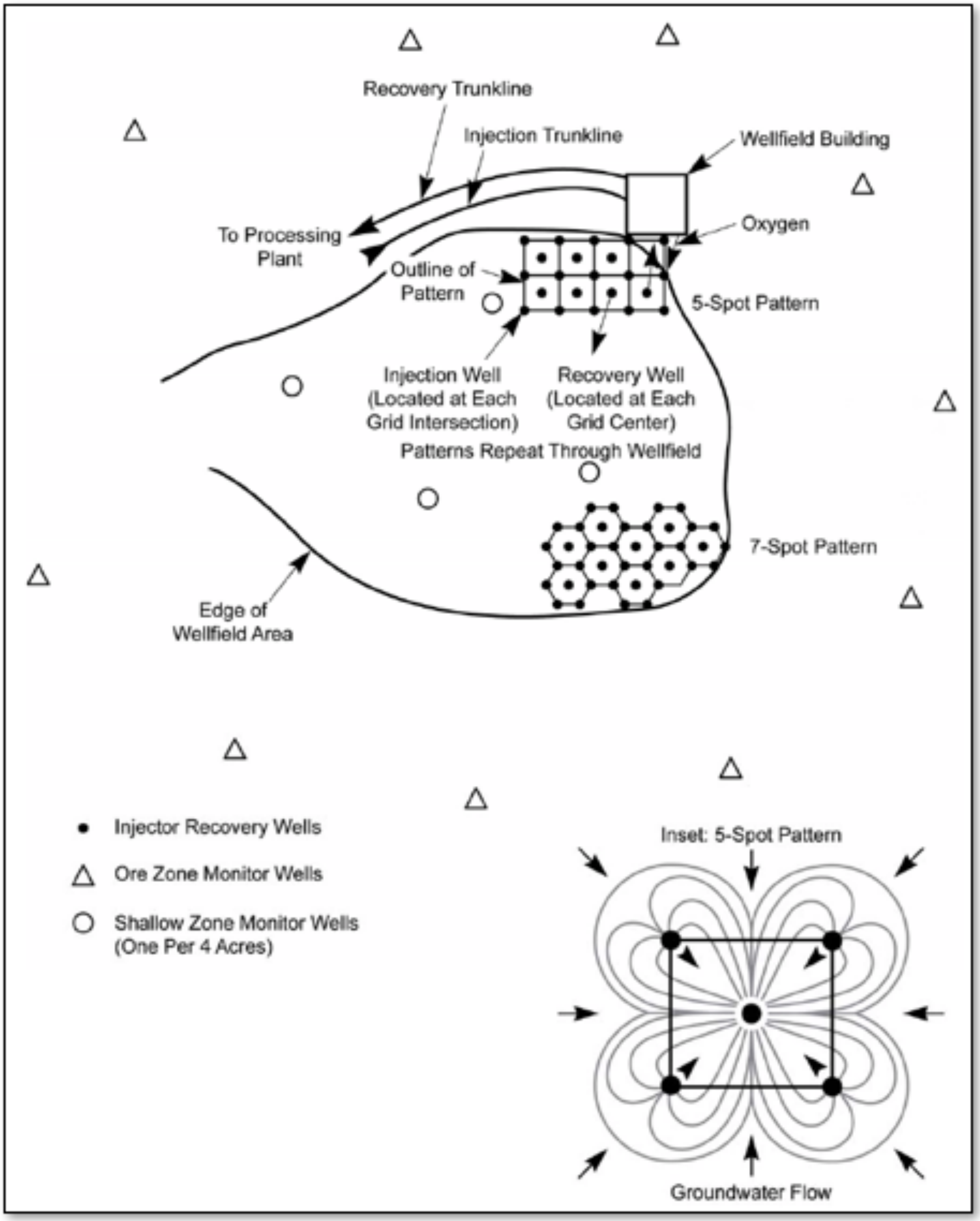


Figure 11. 5 and 7 Spot In-Situ Leach Wellfield Pattern. Schematic also illustrates the location of injection, production, and monitoring wells (NRC, 2009)

Uranium Enrichment for Recovery

Uranium, is recovered from the pregnant lixiviant at the surface and is processed into form of yellowcake (U_3O_8) (NRC, 2009). Uranium is first removed from the lixiviant typically by ion exchange (IX) columns (Figure 12). When concentrations of U are near 120-150 mg/L, approximately 95% of the uranium is extracted from the bearing solution during IX (NRC, 2009). The barren solution is then replenished with oxidant, and DIC if needed and pumped back into the mine. Elution, a process that washes the U (eluted) from the resin throughout a circuit with a concentrated salt solution (NaCl). The regenerated resin is then loaded back into IX columns for further adsorption of U. After the elution circuit, precipitation, drying and packaging of yellowcake (U_3O_8) is completed. The eluant is acidified with hydrochloric acid (HCl) or sulfuric acid (H_2SO_4), oxidized with hydrogen peroxide (H_2O_2) that produces a uranyl peroxide precipitate (NRC, 2009). This slurry is then dried in a yellowcake dryer. Dryers tend to reach temperatures of 400-620 °C (750-11550 °F). Some facilities have vacuum dryers that dry yellowcake at much lower temperatures 150 °C (250 °F). Once dried, yellowcake is placed in barrels for transportation and storage.

Figure 12. Ion Exchange Vessels in an ISL Facility (NRC, 2009).

Groundwater Restoration Methods following In-Situ Leach of U Mining

Restoration of the aquifer is conducted following completion of ISL U mining. An unresolved issue with ISL mining is whether the aquifer must be restored to meet ground water quality standards or to pre-mining water quality conditions. Restoration criteria are set on a state by state basis (Catchpole and Kuchelka, 1993). There are many approaches to restore the aquifer such as groundwater sweep, surface water treatment and recirculation, in-situ stabilization using biological or chemical methods, and natural attenuation (Catchpole and Kuchelka, 1993). An old rule of thumb for restoration is cost for restoring a mined aquifer and decommissioning the mine is about one dollar per pound of uranium recovered (Catchpole and Kuchelka, 1993) however, there are so many uncertainties with hydrogeologic conditions and restoration requirements that its not clear if this guideline is truly applicable.

Groundwater Sweep

The simplest method of groundwater restoration is groundwater sweep phase. This process consists of continuing to pump water from the mine after mining stops and allowing outer fresh ground water to enter the wellfield (Figure 13), therefore removing and diluting U and co-constituents (Catchpole and Kuchelka, 1993). The contaminated water must then be treated at the surface, typically by removing U by IX (NRC, 2009). Treated water may be disposed of in lined evaporation ponds, or via deep well injection (NRC, 2009) (Catchpole and Kuchelka, 1993). Large volumes of water are used in groundwater sweep measured in units of pore volume. One pore volume is equal to the volume of water in the interstitial pores within the mine (Catchpole and Kuchelka, 1993).

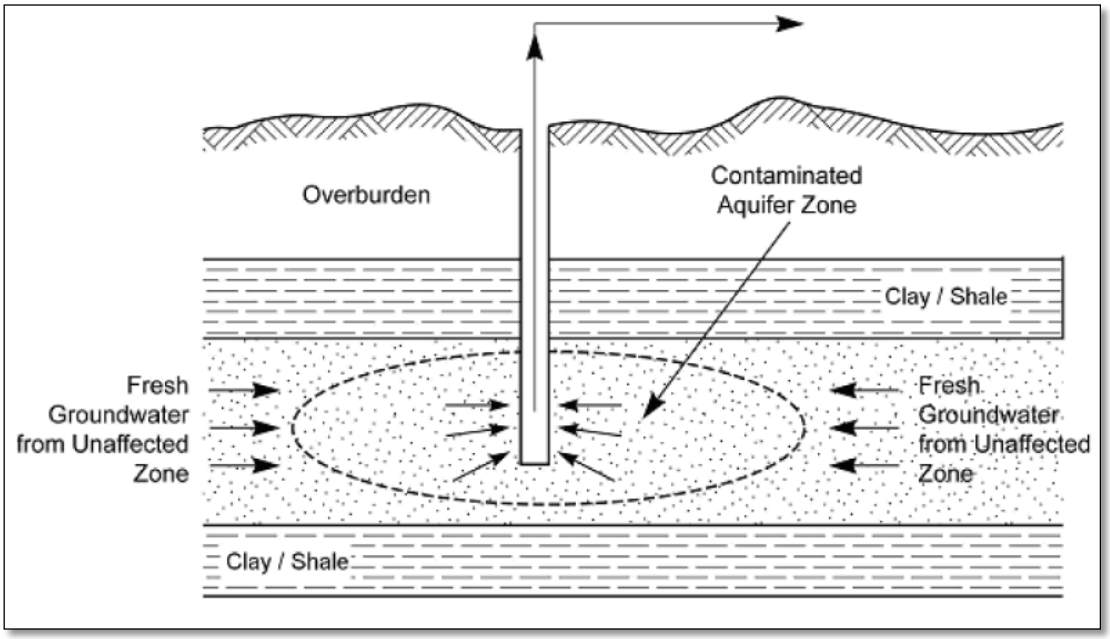


Figure 13. Illustration of groundwater sweep (NRC, 2009)

Surface Treatment and Recirculation

Surface treatment and recirculation is another slightly more aggressive restoration method. It is similar to groundwater sweep, but the recovered water is treated to remove all dissolved constituents by a desalination process such as reverse osmosis (RO) or electrodialysis (ED). The permeate can be reinjected but the concentrate from the desalination process requires disposal either in evaporation ponds or injected into deeper aquifer (Catchpole and Kuchelka, 1993). Facilities that cannot afford the net withdrawal of 30-50%, add a second treatment unit. This unit is a brine concentrator and reduces the net withdrawal by allowing the injection of more clean water and vice versa decreasing the amount disposed of in evaporation ponds. Groundwater sweeping and RO treatment is an effective method of restoration but very expensive (Borch et al., 2012a). One complication is that many metals in the subsurface formations are subject to dissolution and release as the desalinated groundwater is reinjected and passed through the ore body.

Chemical Reductant

In principle chemicals can be added to try reduce soluble U(VI) to insoluble U(IV) state or to achieve precipitation of the U(VI) phases. To achieve reduction, the oxidant must be removed and an anaerobic environment created. A chemical reductant may be added to the water (Catchpole and Kuchelka, 1993) such as hydrogen sulfide, to try to establish pre mining conditions. Addition of hydrogen sulfide (H_2S) has been tried but with little success (Borch et al., 2012a). Additionally, the formation of U(VI) bicarbonate and carbonate complexes was believed to be the reason for the lack of U immobilization (Borch et al., 2012a).

Alternatively, chemicals may be added to precipitate U. Addition of phosphate (PO_4^{3-}) will lead to formation of secondary metal-phosphate (Murray et al., 1983) Hydroxyapatite ($Ca_5(PO_4)_3(OH)$ has been used as the phosphate source and U concentrations decreased substantially with apatite addition (Arey et al., 1999b). The addition of apatite also caused the dissolution of dissolved organic carbon which caused U concentrations to remain higher in organic rich sediments (Arey et al., 1999b).

Immobilization of U(VI) has been shown by adsorption and precipitation using calcium and phosphate in batch studies was studied by (Mehta et al., 2016a). Column studies that focused on the adsorption of U(VI) by goethite (FeO(OH))-coated sand demonstrated the importance adsorption has in natural systems (Cheng et al., 2007). Such studies have shown that phosphate addition can substantially immobilize U by precipitation and adsorption but not completely. Furthermore, phosphate addition was conducted in batch studies only and has little effect on co-constituents, especially the oxyanions Mo, Se, and V.

Metal and Sulfate Reducing Organisms

Metal reducing bacteria have been shown to have a short term impact on U immobilization (Anderson et al., 2003). The ability of Iron-reducing and sulfate-reducing bacteria to reduce U(VI) with subsequent precipitation has been shown, suggesting that microbial reduction may be used for aquifer restoration (Elias et al., 2003).

Biological restoration approaches are based on achieving reduction of U(VI) with subsequent precipitation of insoluble U(IV) phases. Metal and sulfate reducing bacteria achieve U(VI) reduction, though it's not clear whether this is actual part of the microbial respiration process or simple enzymatic reduction (Uhrie et al., 1996). Since U is present at very low concentrations in groundwater, typically 10^{-5} to 10^{-7}M, it is likely that the organism receives little or no energy from the reaction and that electron acceptors at higher concentrations such as Fe(II), sulfate (SO_4^{2-}) or nitrate (NO_3^-) are more important. Pure cultures of Desulfovibrio desulfuricans, Geobacter metallireducens and Shewanella spp., have been shown capable of uranium reductive precipitation due to an enzymatic process. Microbial reduction has also been shown to reduce As, Se and V at a near neutral pH (Uhrie et al., 1996). Microbial sulfate reduction to produced reduced sulfide phases will establish a reducing environment with excess chemical reduction capacity that may prevent subsequent re-oxidation and dissolution of U (Borch et al., 2012a).

Considerable work has been done with geobacter, an iron reducing bacteria that is also capable of U(VI) reduction (Anderson et al., 2003). Stimulation of geobacter species by adding acetate was investigated to remove U from the contaminated aquifer located at the Rifle U mill tailings site in Colorado (Anderson et al., 2003). At pH of 7 across the Rifle, CO site, U (VI) concentrations decreased within a period of 50 days to levels below the prescribed limit. The U reduction was attributed primarily to the high 85% presence of Geobacter species, to the reduction of Fe (III) to Fe (II), and also to sulfate reduction (Anderson et al., 2003). This study from Anderson et. al. 2013 found that sulfate reducing bacteria can be predominant in the system. Beyond 52 days, 7% Geobacter species were present and sulfate reducing bacteria such as “Desulfobacteraceae” increased to 45%, this caused an increase in U concentration. This led to conclusion that sulfate reducing microorganisms may be less effective compared to Geobacter species in reducing U(VI) (Anderson et al., 2003).

Geobacter species were shown capable of removing U from groundwater as shown in (Ortiz-Bernad et al., 2004). The presence of one metal reducing bacteria is not optimal, therefore creating conditions for a mixed culture could potentially decrease concentrations of U more effectively. A mix of sulfate and metal reducing bacteria might potentially increase the performance of this restoration process.

No other literature review showed the removal of Mo, Se by metal-reducing bacteria. A set of batch experiments showed that acetate, oxalate, and citrate promoted the growth of sulfate reducing bacteria (Desulfovibrio desulfuricans) that reduced U(VI) to U(IV) by ligand complexation (Robinson et al., 1998). Lower concentrations of these ligands resulted in an increase of UO_2 precipitation (Robinson et al., 1998). No other studies have shown that reduction of U(VI) to U (IV) was attributed to organic complexing ligands.

Natural attenuation is often considered for groundwater restoration and is most effective in the long run. If subsurface conditions are such that reducing conditions might be re-established naturally in-situ restoration may not be required. Natural attenuation is considered as dilution, long term radioactive decay, adsorption and natural biogeochemical reactions. The success of natural attenuation is dependent on the subsurface microbiology, hydrogeology and geology (Mulligan and Yong, 2004).

Natural attenuation can occur by reduction of soluble U and other constituents by the use of organic matter. Adsorption of uranium ions onto organic material is a possible physical process that leads to U reduction (Spirakis, 1996). Thus, organic matter is capable of acting as an adsorbent and therefore reducing U. He also noted that organic matter is a stronger reductant than hydrogen sulfide (Spirakis, 1996). Organic matter is commonly present in many aquifers near U deposits and can aid natural attenuation. Most importantly, organic matter generates a reducing environment, which can protect geologic deposits from oxidation. Therefore, formations with high concentrations of natural organic material may provide sufficient reducing conditions that for natural attenuation provides groundwater restoration that is sufficient to meet regulatory criteria (Spirakis, 1996).

Monitoring Phase

Monitoring is required following restoration (also known as stability period). Before the stability period ground water recirculation for as much as 2 pore volumes until stable water chemistry is achieved may be necessary (Catchpole and Kuchelka, 1993). Stability period usually lasts for a period of six months to a year to make sure that the water does not deteriorate (Catchpole and Kuchelka, 1993). If U and other trace elements are detected in high concentrations further remediation methods need to be completed

Crownpoint, New Mexico In-Situ of Uranium Pilot Plant

A large scale pilot test of the ISL mining process was conducted in 1979 by Mobil Oil corporation near the village of Crownpoint, NM. The section 9 Pilot targeted the Westwater Canyon Member of the Morrison Formation near Crownpoint, NM in McKinley County located in the southern end of San Juan Basin. 40 miles Northwest of Grants and 40 miles Northeast of Gallup. Mobil oil conducted the pilot test then subsequently transferred ownership and resulting information to Uranium Resources, Inc (UPA, 2015).

The purposes of the pilot test were to 1) Test in-situ recovery of U at large depths of 2000 ft. or more, 2) Test viability of the carbonate/peroxide chemistry for recovery of U from the Westwater ore, 3) To assure hydrologic control, 4) Test above ground U concentration process, 5) and finally but most importantly was to test groundwater restoration. (UPA, 2015)

Prior to beginning the pilot test, water from 13 wells was tested for baseline water quality. Baseline water quality parameters are listed in Table 3. Native groundwater at the site met all NM ground water quality standards. Following completion of the mining phase it was determined that the groundwater restoration goals would be for ground water quality to meet NM water quality standards rather than attempting to return water quality to baseline levels. (UPA, 2015)

The well field was configured by four five-spot patterns. Allowing approximately 100 ft. between injection wells and 400 ft. between the well field and six monitoring wells. Injection of the lixiviant ranged from low 50 to 76 GPM targeting 60 GPM. This injection flow was reduced to 40 GPM once restoration took place.

A ten month ISL mining phase began in November of 1979. Lixiviants were composed of bicarbonate/peroxide solution mixed with groundwater. Carbon dioxide (CO_2) gas and 50% Sodium Hydroxide (NaOH) solution were also added to the groundwater for makeup. Carbonate ion level was maintained between 1500 to 2000 mg/l maintaining a pH of 8.3. 50% Hydrogen peroxide ($H_2O_{2)}$ was added to the injection line maintaining H_2O_2 concentrations of 1500 to 2000 mg/l. In May of 1980 the U concentration in water from the extraction wells was greater than 100 mg/l making the recovery of U feasible. (UPA, 2015)

A 12 moth restoration phase took place following the ISL mining phase. As shown in Table 3 nearly all parameters after ISL of U were greater than baseline average concentrations and also exceeded NM water quality standards. The sequence of operations during the restoration process are summarized in Table 2. Restoration primarily involved groundwater sweep and surface treatment, followed by recirculation of the treated ground water. Surface treatment consisted of RO to remove all dissolved constituents so that water recycled back into the mine had very low concentrations of U or other dissolved constituents (i.e. TDS). Sodium hydroxide paired with RO also gave a significant reduction of U and Mo amongst others. Other chemicals such as sodium sulfide and hydrogen sulfide showed no impact and mixed results respectively.

Table 2. Remediation Process on a step by step basis.(UPA, 2015)

Date	Description	Comment
October 1 to December 1, 1980	Stop chemicals	
December 1 to December 24, 1980	Lime treatment	No significant reduction of water quality indicators
December 24 to December 3, 1980	2,200,000 gallons of groundwater sweep	Significant reduction of Ca, Na, SO4, Cl, U
December 30 to late January, 1981.	RO preparation	No significant reduction of water quality indicators
Late January to July 1981	RO treatment of est. 26,000,000 gallons	Significant reduction of Ca, Na, SO4, Cl, U, Ra. No reduction of moly
July 1981 to May 1982	RO and calcium hydroxide treatment of est. 44,000,000 gallons.	Significant reduction of Ca, Na, SO4, Cl, U, Ra, Mo.
May to November 8, 1982	Ion exchange and “Clean Water” sweep	Major cations declined below restoration table except Moly
November 8 through April 15, 1983	Sodium sulfide circulation 9,000,000 gallons	No significant reduction of water quality indicators
April 15 to July 14, 1983	Sit and soak	No significant reduction of water quality indicators
July 14 to January 13, 1984	Groundwater sweep est. 3,300,000 gallons	Na and Cl reduced, not moly
January 18 to May 1, 1984	RO treatment of est. 7,200,000 gallons	Slight decrease in Cl and Mo
May 1 through March 18, 1985	Hydrogen sulfide treatment tests	Mixed results
March 18 to April 15, 1986	Sit and soak	Moly decreased to 7.7 mg/l. All other parameters stable.
April 15 to May 20, 1986	Groundwater circulation	
May 20 to present	Static	

This test demonstrated that all groundwater quality criteria could be met except for U and Mo as shown in Table 3. Even though the concentrations decreased, baseline concentrations were not achieved. It was believed that U standard was not met since not all available U in the ore body was completely extracted due to the short duration of the pilot test (UPA, 2015). Radium analyses were inconsistent and values were not considered reliable. Generally, the results of the restoration process were positive but better methods for U and Mo removal from groundwater are needed to assure restoration of ground water quality following ISL mining.

Table 3. Created by Uranium Producers of America, Parameter levels after the remediation process.(UPA, 2015)

Parameter	Unit	NM WQ Std.	Baseline Avgerage (Mobil 1986)	Before Restore (FEIS 1997)	Average	Color Code
Sulfate	mg/l	600	40	1176	47.6	🟩
Chloride	mg/l	250	25.3	1800	54.5	🟩
Nitrate	mg/l	10	0.08	0.17	0.556	🟩
Fluoride	mg/l	1.6	0.43	0.3	<0.5	🟩
TDS (180 c)	mg/l	1000	373	5500	356.2	🟩
pH		6-9	7.4		9.062	🟥
Aluminum	mg/l	5.0	0.2		0.808	🟩
Arsenic	mg/l	0.1	0.004	0.054	0.014	🟩
Barium	mg/l	1	0.2	0.1	0.277	🟩
Boron	mg/l	0.75	0.1	0.2	0.238	🟩
Chromium	mg/l	0.05	0.005	0.02	0.005	🟩
Cobalt	mg/l	0.05	<.05		0.021	🟩
Copper	mg/l	1	0.003	0.04	0.008	🟩
Cyanide	mg/l	0.2	0.1		<0.005	🟩
Cadmium	mg/l	0.01	0.007	0.01	0.006	🟩
Iron	mg/l	1	0.64	0.02	0.146	🟩
Lead	mg/l	0.05	0.003	0.005	0.016	🟩
Manganese	mg/l	0.2	0.066	5.85	0.035	🟩
Mercury	mg/l	0.002	0.00053	0	0.0003	🟩
Molybdenum	mg/l	1	0.238	62	1.118	🟥
Nickel	mg/l	0.2	0.02	0.09	0.022	🟩
Phenols	mg/l	0.005	0.011	0.09	0.008	🟦
Selenium	mg/l	0.05	<.01	4.6	0.006	🟩
Silver	mg/l	0.05	<.01		<0.05	🟩
Uranium	mg/l	0.03	0.013	145	0.3we19	🟥
Zinc	mg/l	10	0.01	0.39		
Radium	pCi/l	30	21.6(?)	150	59.94	🟥

Color Code Explanation	
🟦	Below Baseline
🟩	Below WQ Numeric Standard
🟥	Above BL & WQ Standard

Chapter 3: Research Methods

Sample Collection and Characterization

Samples were collected at three different locations within the grants mineral belt. Samples had to be collected from U mines in New Mexico and specifically those that were mined from the Morrison Formation. New Mexico U ore deposits that can be mined by ISL are within the Morrison Formation, therefore understanding the conditions that can result from leaching and restoration studies in the lab can potentially contribute positively to the mining of U in New Mexico by ISL process.

Samples collected were subjected to an extensive characterization process to determine their geochemical properties and elemental composition. They were then subjected to leaching studies to develop an understanding of the composition of lixiviants that would be expected during an ISL mining process. Finally, columns containing U ore samples were subjected to chemical and biological restoration processes to evaluate their effectiveness. These restoration processes were not implemented in the Crownpoint Pilot Test, and could potentially benefit future post ISL mining restoration in New Mexico.

Uranium Ore Deposit, Formation and Member

Most commercially viable U ore deposits in the Grants Mineral Belt are located in the Jurassic Morrison Formation. Grants (Section 11 Mine) and San Mateo (Mt. Taylor Mine) deposits are within the Westwater Canyon Member (WCM). Uranium ore deposits of Laguna (Jackpile Mine) are within the Jackpile Sandstone Member (JSM). Three types of deposits are known to exist in the Morrison Formation including roll front deposits, tabular and black shale deposits (Spirakis, 1996). WCM and JSM from the Morrison Formation are shown in Figure 14. Locations of interest to mine U by ISL in New Mexico are Crownpoint and Churchrock. Crownpoint deposits have been studied for ISL mining in the past and are similarly located within the WCM.

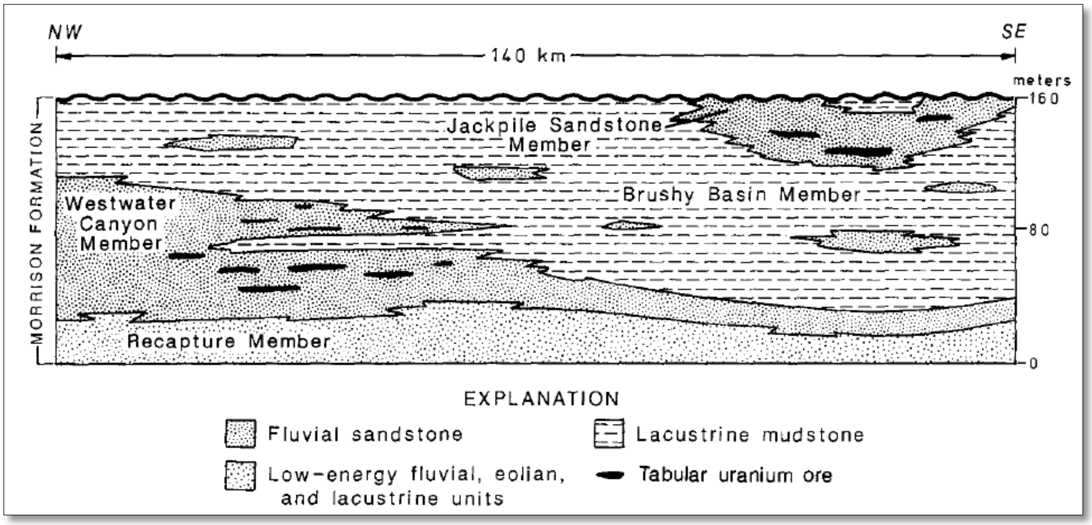


Figure 14. Depositional environment of the Morrison Formation in the Grants Mineral Belt (Spirakis, 1995).

Ore samples collected at the inactive Section 11 underground mine from the Ambrosia Lake were mined and placed in a low grade stockpile that has been exposed to atmospheric conditions. Mined from the Morrison Formation that is approximately 260 ft. from the surface and clear from the water table at 520 ft. The sample was categorized as low grade/waste ore by the section 11 mine manager Read Easterwood and photographs of the samples are shown in Figure 15.

Figure 15. Section 11 Ore Samples

Ore deposits collected at the Laguna sub-district came from the inactive Jackpile surface mine located 49 miles west of Albuquerque, NM. The Jackpile Mine was mined and operated from 1953 to 1982 by the Anaconda Minerals company, a division of Atlantic Richfield Company (ARCO) (EPA, 2016). Jackpile U ore deposits were collected from a tabular deposit that is exposed to atmospheric conditions. These samples displayed very different characteristics and were categorized according to their color as Black, Yellow and Gray in order to keep track and a consistency during experiments and analysis. Samples from the Jackpile mine had not been mined but were collected from exposed ore bodies (Figure 16).

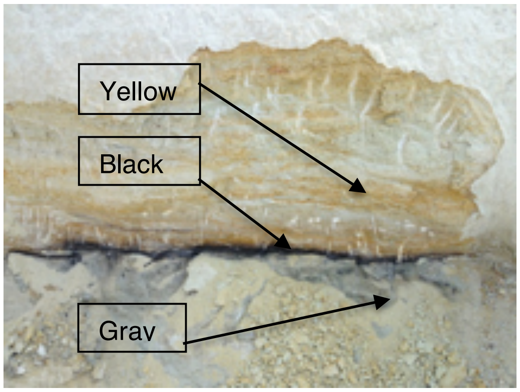


Figure 16. Jackpile mine ore samples (12” wide by 8” picture)

Uranium ore deposits shown in Figure 17 were collected at the inactive Mt. Taylor mine located near San Mateo, NM about 60 miles west of Albuquerque. Rio Grande Resources affiliated with General Atomics has identified Coffinite ($USiO_4$) as the primary uranium mineral. Ore grades range from 0.15% to 2.0% U_3O_8 according to Rio Grande Resources. These ore deposits from the Morrison Formation occur at 3000 ft. were mined 25 years ago have been exposed to the atmosphere but not to weathering as the material was stored inside a barrel located inside a warehouse.

Figure 17. Mt. Taylor Mine Ore Samples

Sample Characterization

Sample Preparation

All U ore deposits were gently broken and sieved. This was conducted in order to keep the samples integrity and have a proximate representation of the actual ore mineralogy and heterogeneity. Particles were sieved to pass Sieve # 40 (0.425 mm) and retained on the #200 (0.075 mm) for leach tests and acid digestion characterization. Samples that were sieved to pass through the #10 (2.00 mm) and retained on the #40 were used for the Mt. Taylor samples that filled the columns.

Acid Digestion

Samples were subjected to acid digestion to determine the metal acid extractable concentrations. Aqua regia was used which consisted of 3 parts chemical grade hydrochloric acid (HCl) and 1 part chemical grade nitric acid (HNO_3^-). Samples were placed in 50 mL vials and 50% aqua regia (half 18 MΩ water) was added to samples for a pre-digestion overnight (+/- 12 hours). Samples were then placed in a heat block for approximately 3 hrs at 90 °C. The solution was filtered with 0.45 μm to remove all suspended particles. The leach solution was then diluted and analyzed by Perkin-Elmer Optima 5300 DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) and PerkinElmer Optima NexION 300D Inductively Coupled Plasma- Mass Spectrometer (ICP-MS) elemental analysis.

Elemental Analysis

Leached solutions were analyzed for a batch of elements using ICP-OES. The ICP-OES instrument analyzed all major elements above method detection limit (MDL) (Table 11 in Appendix). If concentrations were below ICP-OES MDL, ICP-MS was utilized to determine trace element concentrations. The XRF (Rigaku ZSX Primus II Wavelength Dispersive XRF Spectrometer) instrument detects a mass majority of element concentrations, and only used for the Section 11 mine samples. Ion Chromatography (IC) (Dionex ICS-1100) with the IC Columns (Dionex Ion Pac AS9-HC) instruments used to determined anion concentration of phosphate and lactate after each pore volume through the column.

Loss on Ignition (LOI)

Organic materials are often associated and found in U ores. Because they are strong reducing agents it is important to know the amount of this material ISL leach and subsequent restoration studies. Organic matter was measured by Loss on Ignition (LOI). Sieved ore samples for leach studies were weighed and placed in a weighed crucible. Samples were dried in an oven at 105°C for one hour, cooled and weighed, and then placed in a muffle furnace at 550°C for an additional hour. Cooling time of 20 min took place in the transition phase and weighing phase. Moisture content was determined by the weight loss at 105°C and the mass of organic matter was determined by weight difference after ignition at 550°C. Note that a high concentration of carbonate minerals in a soil sample will cause a loss on ignition is both organic material and carbonate minerals. However, the U ore samples collected in this study had little carbonate material hence LOI is believed to be a representative measure of organic matter in the samples.

X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) analysis identifies the elemental composition on the outermost 10 nm of the surface. Once identified metal oxidation states can be determined. XPS was used in an attempt to determine the oxidation states of U in the ore samples. Oxidation state will almost certainly affect U leachability by the ISL process. XPS was also used to detect phosphorous (P) as phosphate (PO_4^{3-}) on the surface of the samples after chemical reduction remediation studies.

Leach Tests

Batch experiments consisted in reacting U ore deposits with lixiviant solution commonly used at ISL U facilities. Batch experiments were conducted under oxic conditions throughout the leaching process. Sodium bicarbonate ($NaHCO_3$) was mixed with 18 MΩ water to prepare 1, 10, 100 and 500 mM solution concentrations. The wide range of $NaHCO_3$ concentrations was used in order to understand at what magnitude was U leaching most effective and to understand the release of co-constituents. Aliquots were taken at 0, 2/3, 6, 12, 24 and 120 hours. For batch test sampled at time zero an aliquot (10 mL) was extracted in order to determine U and co-constituents concentrations dissolved with 18 MΩ water before mixing lixiviant. Duplicates and triplicates are indicated in Table 4 with additional details for each U ore deposit sample. Filtration of all samples was completed by using a 0.45 µm syringe filter.

Table 4. $NaHCO_3$ leaching studies setup and procedure.

Samples	Extractant Concentration (M)	Volume of Lixiviant	Mass of Sample	Sampling Times	Number of Replicates	Additional Comments
Grants, Section 11 Mine	1, 10 and 500 mM Sodium Bicarbonate	200 mL	10 g	2, 6, 12, 24 and 120 hours	3	Shaker before extraction at 100 rpm,
Laguna/Mt. Taylor	18 MΩ Water added 24 hours prior $NaHCO_3$ addition at time zero	200 mL	10 g	0 hrs	2	Shaker before extraction at 125 rpm
Laguna (Black, Yellow, Gray)	100 mM Sodium Bicarbonate	190 mL	10 g	3, 6, 12, 24, 120 hrs	2	Shaker before extraction at 125 rpm
Mt. Taylor	100 mM Sodium Bicarbonate	190 mL	10 g	2, 6, 12, 24, 120 hrs	2	Shaker before extraction at 125 rpm
Grants, Laguna, Mt. Taylor	Aqua Regia Acid Digestion	8 mL	1-2 g	Heat Block approx. 3 hours	3	Diluted acid by topping a 50 mL tube.

Column Tests

Column leach experiments were performed in 5 cm x 25 cm Plexiglas® columns packed with Mt. Taylor mine ore samples. Five columns were used, one to act as a control, and two each to provide duplicates for chemical and microbial stabilization experiments. Columns were prepared: columns were fed with synthetic groundwater (SGW) (Table 5) solution that was developed to simulate ground water quality from the ISL Pilot Plant in Crownpoint, NM (UPA, 2015).

Synthetic groundwater (SGW) is composed of Ca, Na, HCO^-_3, SO_4^{2-}, Cl^-. Concentrations were determined by post mining water conditions of the pilot test conducted in Crownpoint, NM. Table 5 shows concentrations of each constituent. Crownpoint groundwater conditions, are given by the post mining baseline limits shown in 2015, *The Section 9 Pilot Restoration Results Summary Report and Applicability to the Section 8 Site*, (UPA, 2015)

Table 5. Crownpoint Synthetic Groundwater

Constituents	Atomic Weight	Post Concentration 1986 (mg/L)	Molarity (mM)
Calcium	40.08	10.41	0.3
Sodium	22.99	110	4.8
Bicarbonate	61.01	160.7	2.6
Sulfate	96.07	40	0.4
Chloride	35.45	25.3	0.7

All 5 columns were first set to leach for an 11-day period to mobilize metals by the addition of SGW and 50mM sodium bicarbonate. After 11 days (Time: 0 days) stabilization experiments began by adding sodium phosphate and sodium lactate to columns 1-2 and 3-4 respectively. Ground water flow in an ISL mine is very slow. It was not feasible to pump water continuously through the columns at such a slow velocity so instead they were fed discontinuously by feeding 1 pore volume every 2 days for the chemical restoration experiments and every 7 days for the microbial restoration experiments. One pore volume was added through the control column every two days similar to the phosphate columns. A second leaching period took place with SGW only after restoration period. This second leaching period served as a test for re-mobilization of U and other metals. After the second leaching period, a set of 10 pore volumes were flushed through all the columns with SGW only. Table 6 contains a brief summary of the chemical and biological solution concentrations, equivalent flows and the duration of each set of column experiments.

Table 6. Procedure for restoration experiments.

Method	Synthetic Water	Chemical Restoration	Biological Restoration
Solution	Crownpoint SGW	SGW + Phosphate	SGW + Lactate
Concentration	SGW	0.10mM	3 mM
Pore volume/ time	1/2 days	1/2 day	1/7 days
Approximate Flow mL/day	70	70	20
Duration	64 days	68 days	91 days

Samples of effluent from each column were collected when the columns were fed. Forty mL were filtered with a 0.45 μm syringe filter to inhibit further dissolution of metals and for instrumental analysis preparation. Twenty mL were preserved by adding chemical grade nitric acid for cation analysis and the other 20 were refrigerated for nonmetal analysis.

Two types of restoration methods were simulated, chemical restoration using a PO_4^{3-} solution and biological stimulation achieved by stimulation of biological reducing organisms. Chemical restoration process consisted on the addition of phosphate to precipitate U as a Uranyl-Phosphate or precipitation by adsorption mechanisms. The feed water solution consisted of synthetic groundwater Table 5 with addition of PO_4^{3-} or lactate instead. This feed solution did no longer contained 50 mM instead a 2.6 mM $NaHCO_3$. Phosphate was added in the form of basic phosphate (Na_2HPO_4) at a concentration of 100 μM (10 mg/L) of PO_4^{3-}, a concentration similar to that used in previous studies ((Arey et al., 1999a; Mehta et al., 2016b). Sodium Lactate 60% ($C_3H_5NaO_3$) was chosen for biological restoration experiments. Sodium lactate ($NaC_3H_5O_3$) at a concentration of 3 mM was used to stimulate growth of naturally occurring anaerobic sulfate and metal reducing organisms.

In the ISL restoration experiments, synthetic ground water containing PO_4^{3-} was added to the columns at the rate of one pore volume every two days. Because microbial growth is much slower than the precipitation reactions expected with PO_4^{3-} addition, the feed rate for the synthetic groundwater amended with lactate was one pore volume every seven days.

Chapter 4: Results & Discussion

1. Characterization and Composition of Ore

The concentration of elements of interest for the ore samples used in this study is summarized in Table 7 and in an illustration (Figure 18). Given acid digestion results, all samples that contained significant U concentrations were considered for subsequent batch studies. The results show widely varying Mo, U and V concentrations. More V (24-512 mg/Kg) is available for extraction compared to Mo (0.70-90.5 mg/Kg) and Se (8.4-12.3 mg/Kg) in all of the samples. Acid extractions also show that Mo and Se are present at higher concentrations for the WCM samples than in the JSM samples. The highest U concentrations were measured in the Mt. Taylor mine ore samples (10767 mg/Kg U) and in samples from the organic rich black zone collected from exposed ore formation at the Jackpile mine (7602 mg/Kg U).

Table 7. Concentration of selected elements and organic matter as measured by loss on ignition in ore samples used in this study.

	Concentration (mg/kg)				
Sample	Mo	Se	U	V	LOI*
Section 11 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	BDL*	7602.	24.0	21.8
Laguna Mine – Grey	0.00	BDL*	1050.	50.7	0.56
Laguna Mine - Yellow	1.20	BDL*	38.4	BDL*	1.74

*LOI = Loss on ignition, *BDL=Below Detection Limit

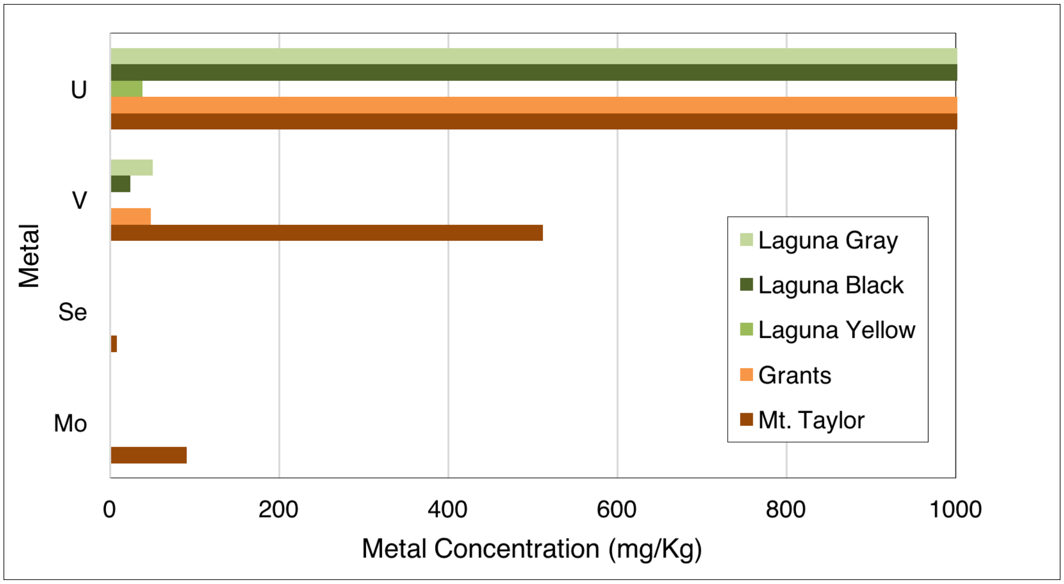


Figure 18. Total metal extracted by acid digestion (Aqua Regia: 3 parts HCl, 1 Part HNO_3)

Organic Content

Organic matter (OM) as measured by loss on ignition decreased the amount of U that was leached by $NaHCO_3$ lixiviants. The content of organic matter did not decrease leaching percentages in U ore deposits that contained 0-4% OM but did show a significant role when the percentage was as high as 20% OM. The fraction of total acid extractable uranium leached by $NaHCO_3$ solutions ranged from 4-50%. Tabular deposits from the Jackpile mine contained 21.8 % OM, but $NaHCO_3$ solutions only leached 5.4 % after five days. Organic matter percentage of Jackpile mine gray samples was as low as 1.74% and nearly 50% of the acid extractable U was leached by $NaHCO_3$ solutions. Figure 19 shows U leaching percentages that range from 29-50% and only contained 0.5-4% of OM. A significant leaching percentage results solely due to the OM%.

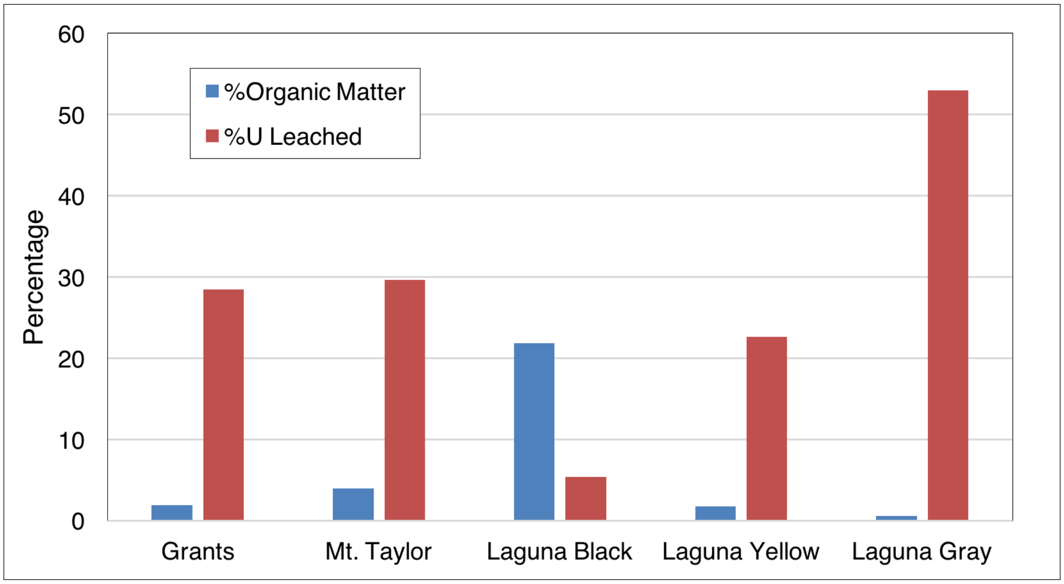


Figure 19. Percent organic matter and fraction of acid extractable U leached from oxidized ore from Grants (500 mM $NaHCO_3$), and from Mt. Taylor and Laguna (100 mM $NaHCO_3$).

Oxidation State of Uranium

X-ray Photoelectron Spectroscopy analyses found that uranium was predominately present as U(VI), which is more mobile than U(IV) (Table 8). Results show that U(VI) percentage was 75.2% and 24.8% U(IV) for Mt. Taylor U deposits. The XPS results for the gray and black samples from Jackpile mine and Section 11 mine samples also contained a high percentage of U(VI). Elemental composition of Mo, Se, and V was not determined by XPS. Detection of these elements composition are mostly in parts per thousand (g/Kg), Mo, Se, and V concentrations were in the low parts per million (mg/Kg) and therefore not detected by the instrument.

Table 8. Valence states of U in ore samples determined by XPS results.

Sample	U(VI)	U(IV)
Mt Taylor	75.2	24.8
Grants ore	60.8	39.2
Laguna ore black	59.3	40.7
Laguna ore gray	59.3	40.7

2. Uranium and Co-occurring Metal Release: Batch Experiments

Metals Dissolved by ISL Lixiviants

The purpose of the leaching tests was to develop an understanding of the solution chemistry that would likely result from the ISL mining process. Batch aerobic leaching experiments were conducted using Section 11 mine samples to determine the leachability of the U and co-constituents using different HCO_3^- concentrations ranging from 1 mM, 10 mM and 500 mM $NaHCO_3$. Results demonstrate that higher concentrations of $NaHCO_3$ leached more U and metal co-constituents (Figure 20 and Figure 21). Overall this set of batch studies show that as concentrations of bicarbonate increase, the release of U and other metals increased.

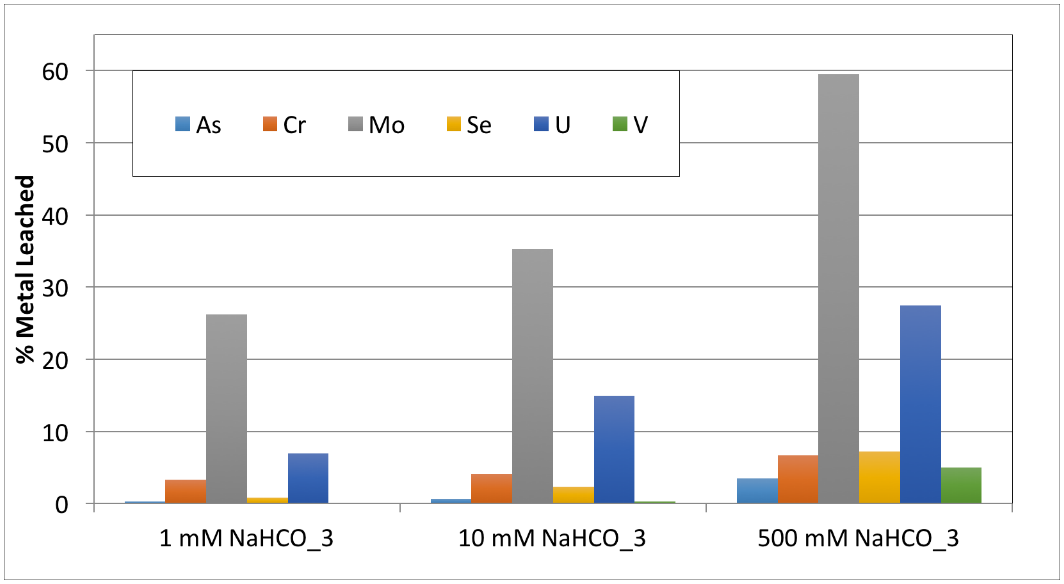


Figure 20. Fraction (%) of metal leached from Section 11 ore sample after five days of leaching with different sodium bicarbonate concentrations.

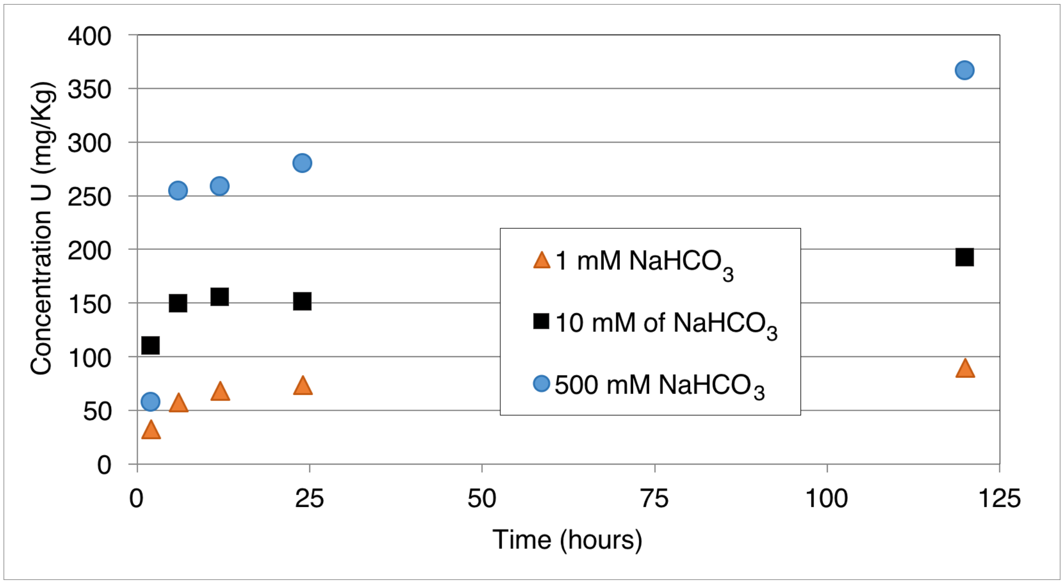


Figure 21. U released from Section 11 ore samples after five days of leaching with different concentrations of $NaHCO_3$.

A 100 mM $NaHCO_3$ concentration was selected for subsequent studies that included Jackpile and Mt. Taylor mine U ore deposits. This concentration was selected in order to mobilize U and simultaneously understand the release of co-constituents into solution.

Release of U within 24 hours was found in all batch studies (Figure 22). This rapid release is likely due to the amount of U(VI) available as shown by XPS results. After 24 hours the release rate of U decreased, with little subsequent dissolution occurring after 5 days. Although a decrease in the release rate of U is observed, most of the total acid extractable U was not leached within 5 days. Therefore, the effectiveness of the lixiviants is also dependent on the amount of U VI) available.

The leach tests showed that the release of U from oxidized ore deposits is effective using $NaHCO_3$ concentration of 100 mM. Jackpile mine ore deposits did not release high concentration of other metals leaching a maximum of 50% total acid extractable U after 5 days. Leachate concentrations of U were as high as 3190 mg/Kg (213 mg/L) after only five days of leaching Mt. Taylor deposits. Most operating ISL plants achieve U concentrations of 100 mg/L in their pregnant extracted solution (UPA, 2015). Although batch studies do not clearly represent a real aquifer, these studies demonstrate the effectiveness sodium bicarbonate has for leaching U from oxidized ores.

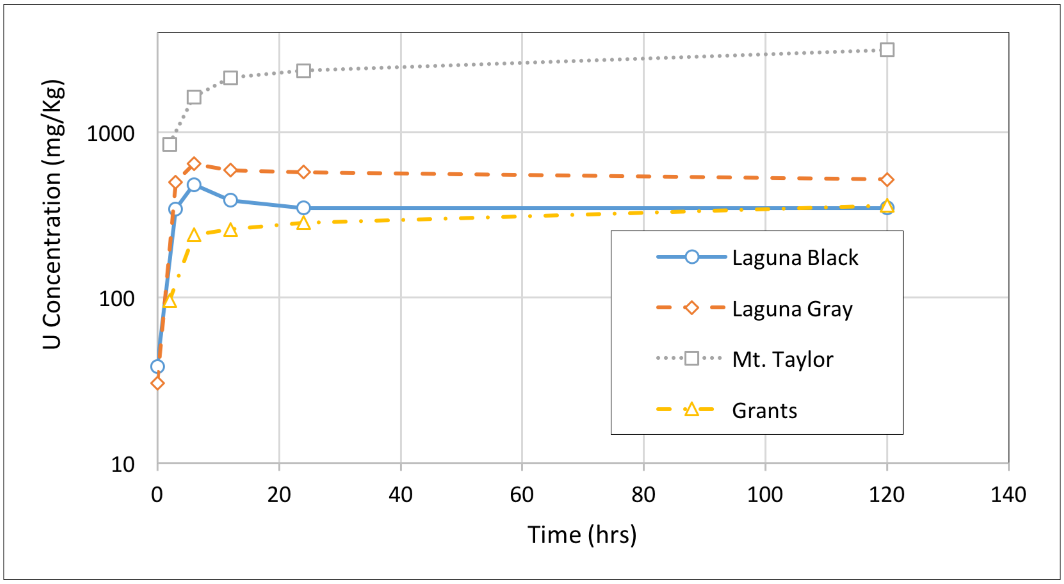


Figure 22. Dissolution of U for three different U ore deposit collected in the Grants Mineral Area.

As U is released in these experiments, co-constituents are also released and cause a concern for restoration after ISL of U mining. Molybdenum, Selenium and Vanadium were also leached by $NaHCO_3$ solutions. Overall these constituents were more consistent in their release with a $NaHCO_3$ solution throughout all deposits.

Vanadium was also released from the Jackpile mine ore deposit (10.4% of V). Section 11 mine release studies showed high leaching percentages of Mo at 40.7% but leaching of other co-constituents was limited, in part due to their low total concentrations in the ore samples. Batch studies are not ideal representations of the effectiveness of ISL mining, but gives a first order estimate of what metals might be released.

The results of five days of batch leaching experiments for the Mt. Taylor WCM U ore deposits are shown in Figure 23. The concentrations after 120 hours of leaching are as follow: 35.9 mg/Kg of Mo, 6.9 mg/Kg of Se and 44.63 mg/Kg of V. Molybdenum, Se and V had similar release trends as U (Figure 35 in Appendices). Concentrations of Mo were the highest which suggests that recovery of Mo may be feasible if an ISL process was used for this ore. It also indicates that Mo may present a challenge for groundwater restoration following ISL mining as was found during the Crownpoint pilot test (UPA, 2015). An average of 40.7% of Mo, 89.0% of Se, 8.75% of V and 29.1% U was leached from the ore samples (Figure 23). The effectiveness of the leach process suggested that lower concentrations of $NaHCO_3$ could potentially be used for extraction of U in order to decrease the release of other metals.

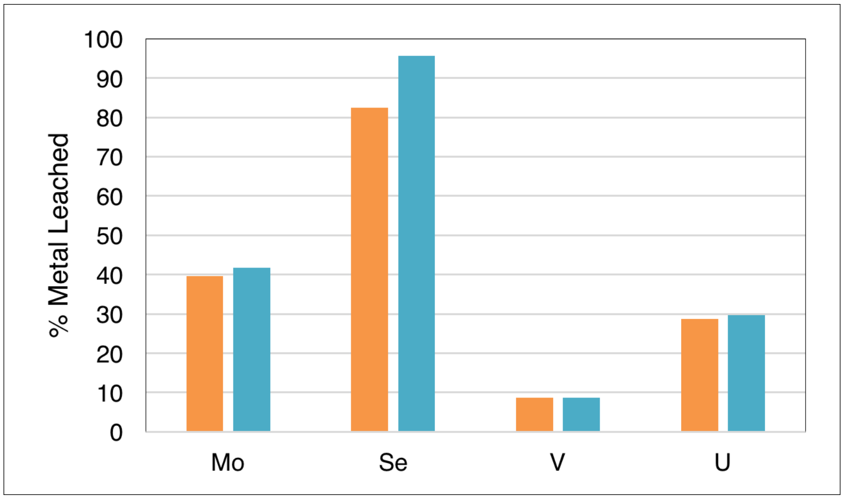


Figure 23. Fraction (%) of metal leached from Mt. Taylor ore after 5 day leaching with 100 mM $NaHCO_3$.

The fraction of total U leached depends on the concentration of $NaHCO_3$, U content in the ore, the oxidation state of the samples and especially the presence of organic matter in the ore sample. The black Jackpile mine samples contained high content of OM. Tabular deposits are coextensive with epigenetically introduced organic material (Spirakis, 1996). Organic matter is known to create a reducing environment and inhibit the oxidation of U(IV). This is illustrated in Figure 19 in which small portion of the total U was leached from the Jackpile mine black sample which had an organic carbon content of nearly 22%. These experiments also suggest that dissolution of U is dependent on the oxidation state of U. U ore samples were exposed to atmospheric conditions, therefore U(VI) was expected to dominate and was confirmed by XPS results. Other metals were not detected by XPS because of their very low concentrations, but similar dissolution to U that are interpreted as a possible high percentage of oxidized Mo, Se, and V. Because the Mt. Taylor Mine ore samples were amenable to leaching by $NaHCO_3$ solutions all subsequent tests were performed with this lixiviant.

3. Chemical and Biological Restoration: Column Experiments

Leaching of Uranium in Columns

The batch leach tests were conducted prior to running the column tests to select an appropriate bicarbonate leaching solution and to anticipate the concentrations of constituents in the leachate. Based on the batch test results, 50 mM $NaHCO_3$ was added to the SGW (Table 5) to serve as a leachate for the column tests. Columns were filled with Mt. Taylor crushed and sieved samples. Note that samples were intentionally not finely ground in order to retain some of the internal structure of the material to provide a more representative approximation of leaching that would occur in an ISL mine. The columns were filled with a 50 mM $NaHCO_3$ solution and allowed to stand for 11 days to initiate leaching from the ore samples prior to initiation of restoration experiments. An average concentration of all constituents following the 11 day equilibration period are presented in Table 9. The extremely high U concentration reflects the high concentration of U in the Mt. Taylor ore and its high leachability as shown in the batch tests (Table 7). Uranium levels in the effluent after 11 days were as high as 1600 mg/L. These concentrations can be caused by the higher ratio of solids to liquids than in the batch tests.

Although 50 mM $NaHCO_3$ was added to the leach solution corresponding to an alkalinity of 50 meq/L, the initial alkalinity of the lixiviant following the 11 d equilibration period was less than half that. The decrease in alkalinity and the relatively low pH are believed to be due to acid produced by partial oxidation of sulfide minerals such as pyrite (FeS_2), as a result of weathering reactions that occurred in the stockpiled ore. After 11 days of equilibration the effluent had a noticeable yellow color, possibly due to the presence of iron and manganese.

Table 9. Average concentration of cations, anions and metals of concern in column leachate prior to stabilization tests. Initial pH ≈ 6.4.
[1]Units of mg/L $CaCO_3$

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

<u>Metals & Non Metal Mobilization and Immobilization</u>

The aquifer restoration experiments began after the 11 day equilibration period. Two methods were evaluated, a chemical stabilization process and a microbial stabilization process. Chemical stabilization was investigated by adding 100 µM $NaHPO_4$ to the synthetic groundwater which was passed through the column at a rate of one pore volume every two days. Microbial stabilization consisted of the addition of 3 mM sodium lactate to the synthetic ground water to stimulate growth of dissimilatory sulfate and metal reducing organisms. The lactate solution was passed through the column at a rate of one pore volume every week. The slower rate of addition was used in recognition of the slower rate of microbial reactions in comparison to the purely chemical reactions associated with PO_4^{3-} addition.

The results of the restoration process using the PO_4^{3-} addition are summarized in Figure 24 which plots U concentration and pH in the column effluent versus pore volumes of synthetic ground water fed to each column. The figure presents data for two replicate columns (C1 & C2) and a control column (CC) leached only with synthetic groundwater to simulate restoration by groundwater sweeping. During the leaching tests 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.

After 18 pore volumes through each column, concentration of Mo and U and V are 0.56 mg/L, 17.7 mg/L and 3.75 µg/L respectively. The final concentration of As was 6.1 µg/L, Cr concentrations were not detected in the effluent. Selenium concentrations ranged from 17 to 34 µg/L. Other metals such as aluminum, iron, magnesium, manganese, and lead were all analyzed and present through each pore volume. After 18 pore volumes all metals except U were still present at concentrations below state ground water standards

Figure 24. The effluent concentrations of U in the columns receiving stabilization treatment were nearly identical to those in the control column.

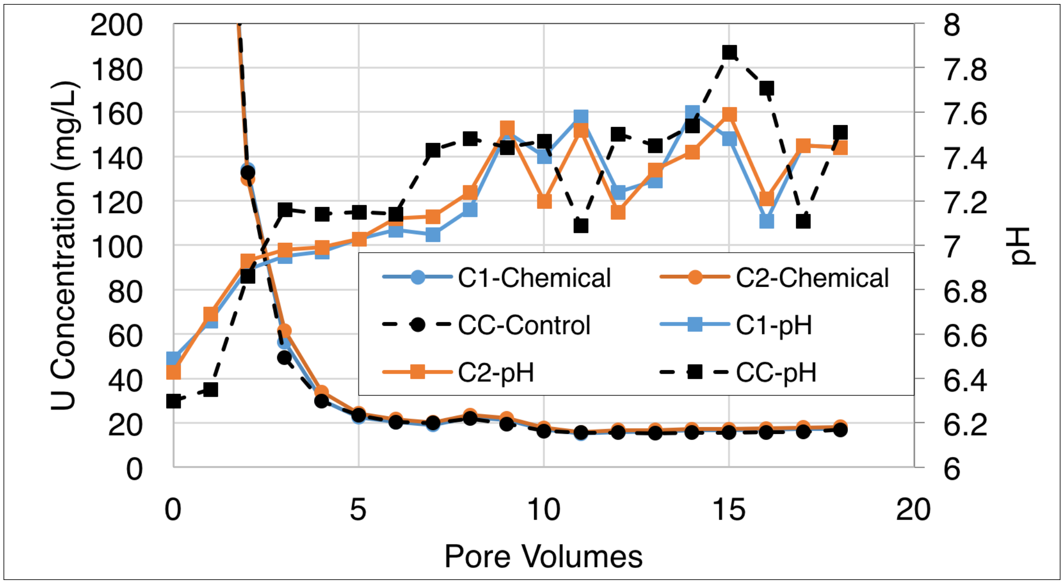


Figure 24. U Concentrations and pH plotted against pore volumes of effluent solution for columns fed a 100 µM PO43- solution.

The results of the restoration process using the PO_4^{3-} addition are summarized in Figure 25 which plots non-metals concentration in the column effluent versus pore volumes of synthetic ground water fed to each column. The figure presents data for columns (C1 & C2) and a comparison to the control column is found in Figure 36 located in the Appendix. At time zero high concentrations of sulfate are observed, that contributed to the low pH caused by acid produced by partial oxidation of sulfide minerals. Phosphate was not detectable by ion chromatography in the column effluent (Figure 25), however, XPS analysis show phosphate on the surface of the solid samples that were located near the inlet of the column (Figure 28).

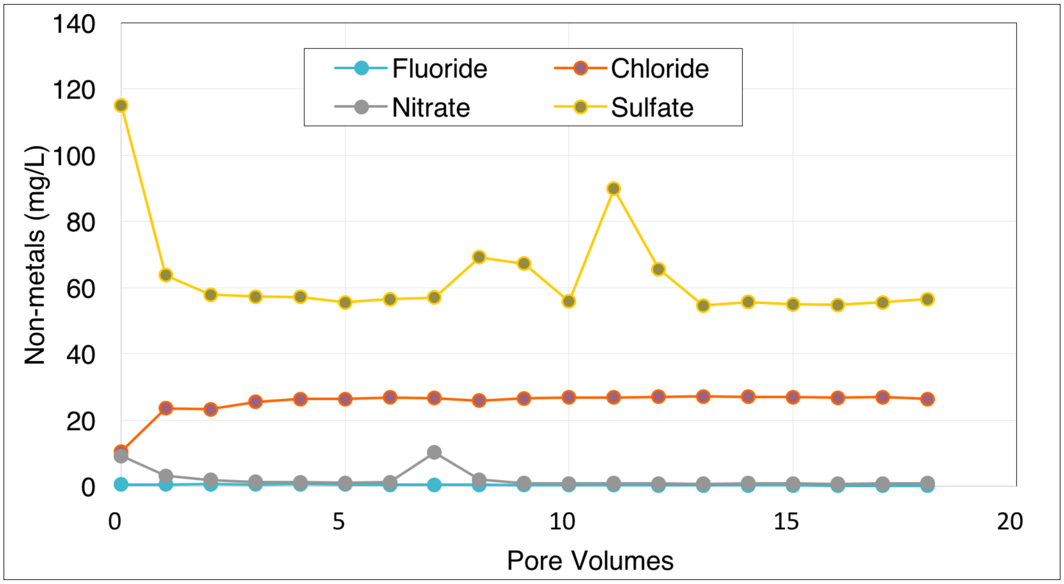


Figure 25. Average anion concentrations against pore volumes of effluent solution for columns fed a 100 µM PO43- solution

The XPS data show that phosphate was in fact precipitating at the surface of the samples near the inlet of the columns (Figure 28). Compared to the results for samples not used in columns (Figure 26), and samples located at the outlet of the column (Figure 27), phosphate is clearly present at the surface of the samples that were located near the inlet. The phosphate is either adsorbing/precipitating within the column, and is consistent with the lack of detectable PO_4^{3-} in the column effluent.

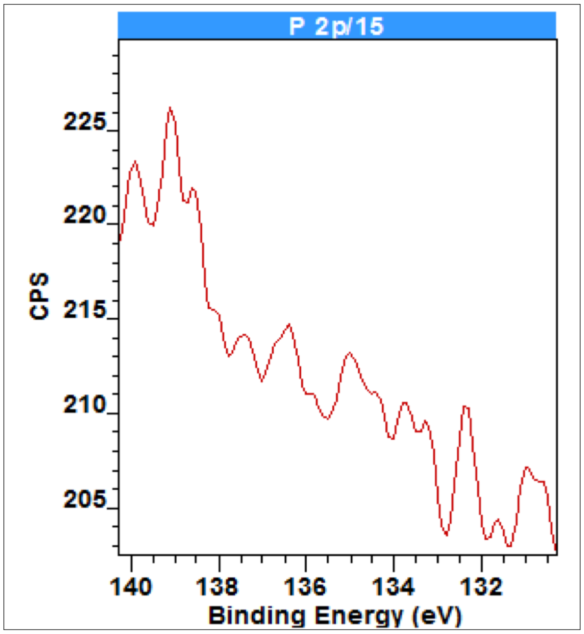


Figure 26. P 2p spectra by XPS did not detect Phosphorous in Mt. Taylor samples not used in column studies.

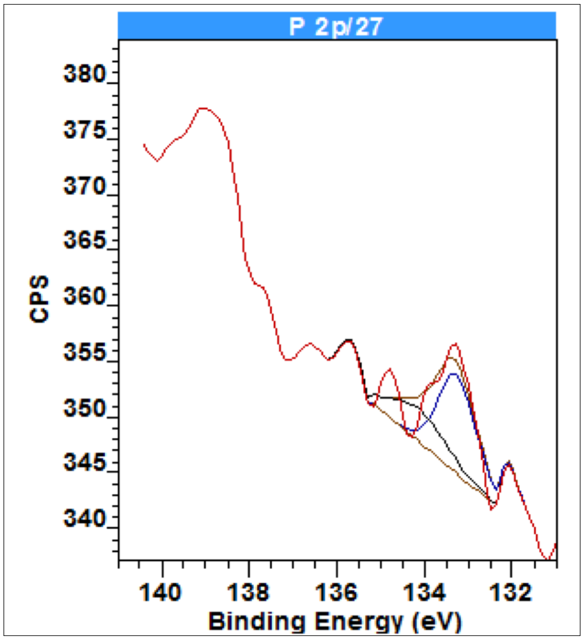


Figure 27. P 2p spectra by XPS for Mt. Taylor samples located at the outlet of the column.

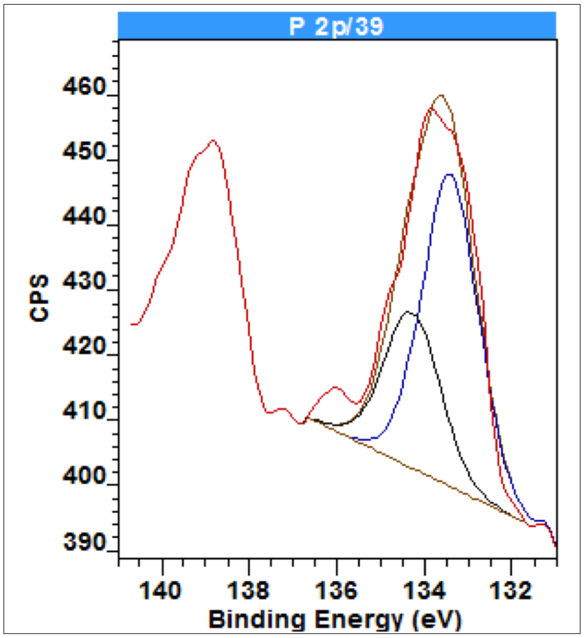


Figure 28. P 2p spectra by XPS detected Phosphorous as phosphate near the inlet of the column.

The results of the microbial restoration process in which lactate was used to stimulate growth of anaerobic microbial populations are summarized in Figure 29. Figure 29 presents data for two replicate columns that were fed lactate to stimulate microbial growth (C3 & C4) and a control column (CC). As with the columns stabilized by PO_4^{3-}, effluent concentrations of U in the columns receiving lactate were nearly identical to those in the control column (Figure 24 and Figure 29). After 18 pore volumes through each column, concentration of Mo and U and V are 0.42 mg/L, 16 mg/L and 3.6 µg/L respectively. Arsenic final concentration was 3.25 µg/L, Cr concentrations were not detected. Selenium ranged from 15-30 µg/L. One particular difference was the stability of the lactate columns compared to the control. The concentrations of metals in the lactate fed columns seemed to decrease over the whole experimental period.

For all of the columns it is suggested that the residual U concentration was the result of continuing dissolution reactions from the ore material. It may be associated with slow diffusive transport of soluble U species from in the interior of rock materials to the bulk fluid.

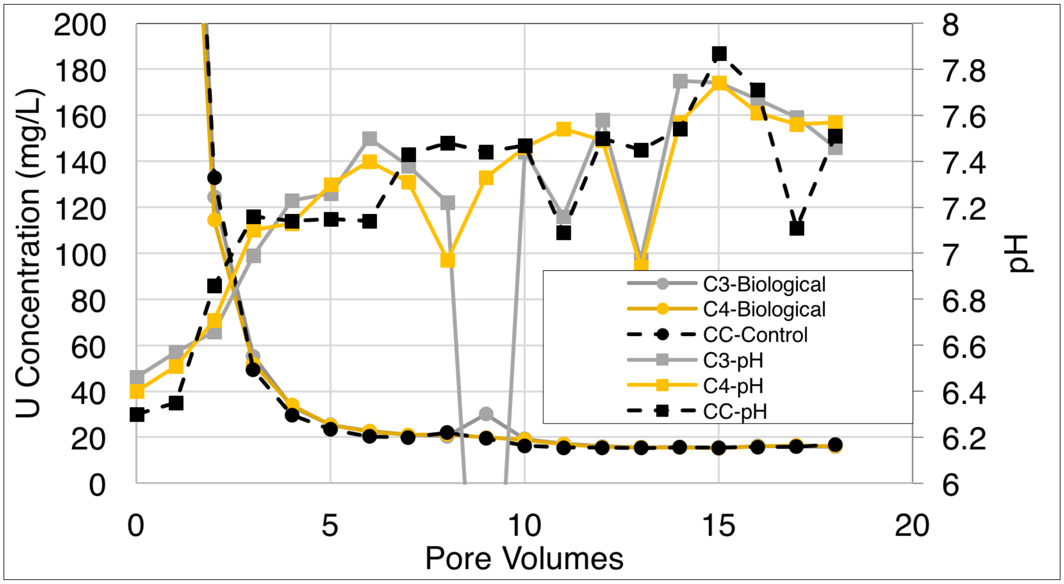


Figure 29. U Concentrations and pH plotted against pore volumes of effluent solution for columns fed a 3 mM lactate solution to stimulate biological growth.

Anion analysis results of the microbial restoration process are also summarized in Figure 30. Figure presents data for columns (C3 & C4) and a comparison to the control column is also found in Figure 36 in the Appendix. Concentrations of fluoride were detected in the lactate column effluent Figure 30. The column effluents were not analyzed for lactate. However, organic acids co-elute with fluoride in an ion chromatograph using an AS9-HC column at about 1 min elution time. All of the chromatograms showed very large peaks at this time which is consistent with the expectation that much of the lactate passed through the columns.

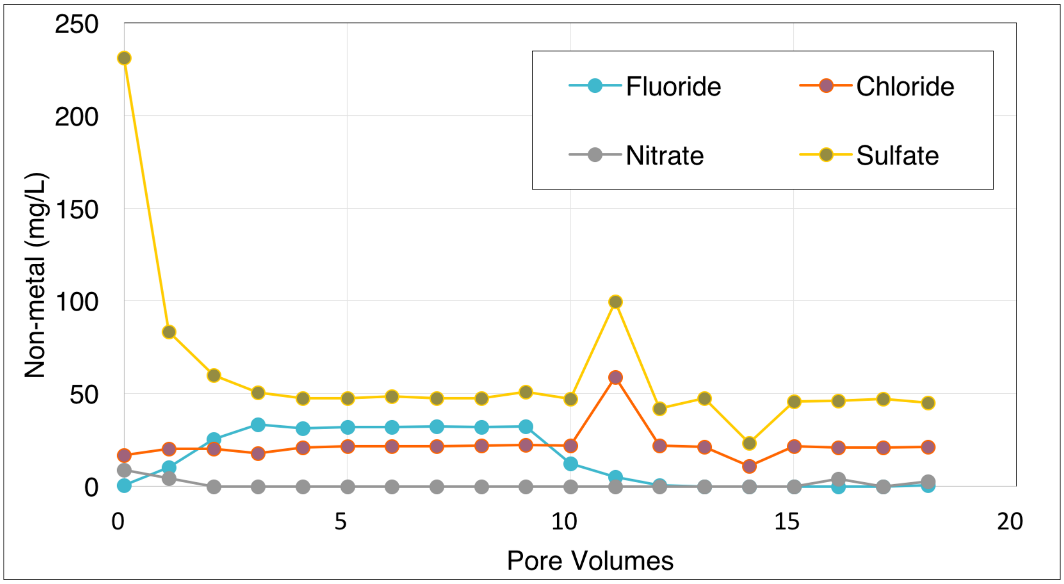


Figure 30. Average anion concentrations against pore volumes of effluent solution for columns fed a 3 mM lactate solution to stimulate biological growth.

Groundwater Sweep Effectiveness and Solute Transport

Groundwater sweep will remove soluble constituents from a soil column by simple flushing. The concentration profile for a non-reactive conservative tracer present in a column filled with porous media flushed with clean water will resemble that shown in Figure 31. The effluent concentration of a column used to simulate ground water sweep can be calculated using an analytical solution to the 1-D advection-dispersion equation (Equation 1) (Fetter and Fetter Jr, 1999). The longitudinal dispersion coefficient (D_L) was computed using the diffusion coefficient D_d of uranyl dicarbonate (UDC) given by (Liu et al., 2011) and the Peclet No. Given all other parameters interstitial velocity (v_x), time (t), and length of column (L) the results are then presented in Figure 32. This front also known as the mixing zone has been studied through quantitative 1-D transport analysis. As shown in Figure 32 as much as 5 cm can be affected such that phosphate or lactate is mixed with mobile U in this 5 cm mixing zone. Mixing within 5 out of 25 cm is limited, therefore minimal mixing between mobile U and the stabilizing solution resulted in less U immobilization. Figure 24 and Figure 29 describe this phenomena as neither the chemical or microbial studies show differences compared to the control column.

Equation 1. Analytical Solution of the Transport Equation

$$\frac{C}{C_o} = \frac{1}{2}\left[erfc\left(\frac{L - v_x t}{2\sqrt{D_L t}}\right) + exp\left(\frac{v_x L}{D_L}\right) erfc\left(\frac{L + v_x t}{2\sqrt{D_L t}}\right)\right]$$

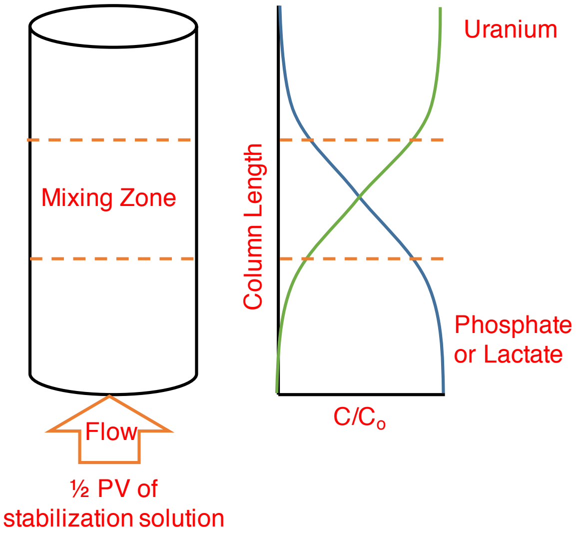


Figure 31. Illustration of interaction of stabilizing solution and concentrated bearing solution. Schematic also shows a mixing zone that represent front curves as shown in Figure 32.

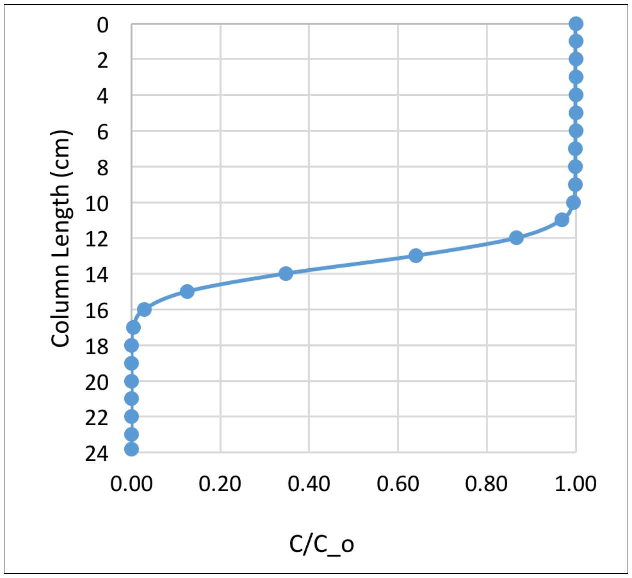


Figure 32. Solute front curve shown by 1-D solute transport analytical solution of advection-dispersion equations.

Other metals such as Mo, and V behaved in the same manner as U. This suggests that the metals in columns were removed by simple flushing rather that by chemical or biological reaction. The flushing process can be dominated by advective transport or convection since most dissolved solids are carried along with the flowing groundwater as explained in (Fetter and Fetter Jr, 1999).

The mixing zone is therefore considered a sharp front curve that does not allow much interaction between the effluent and influent. The behavior of each column is controlled by advective transport during the addition of a pore volume to the column. This theory can be similar to how groundwater tends to flow in aquifers, mainly as a 1 D flow that does not account for major vertical flow within small distances.

The most important conclusion from these results is that neither chemical addition nor microbial reduction provided measurable reduction in U concentrations due to chemical or biological reaction in groundwater passing through an ore body that had been mined by the ISL process. The U concentrations in columns leached by groundwater amended with PO_4^{3-} and lactate were essentially identical to that from a column flushed by groundwater alone. It is not apparent that any chemical reactions nor biological reactions took place which would immobilize U or other metals in these experiments. It is also important to recognize that approximately 90% of the total extractable U in the ore was still present within the columns. Similar results were given for the rest of the columns. Mass balance analysis (Figure 33) gives a clear representation of the given U concentrations in the effluent and the percent of U leached.

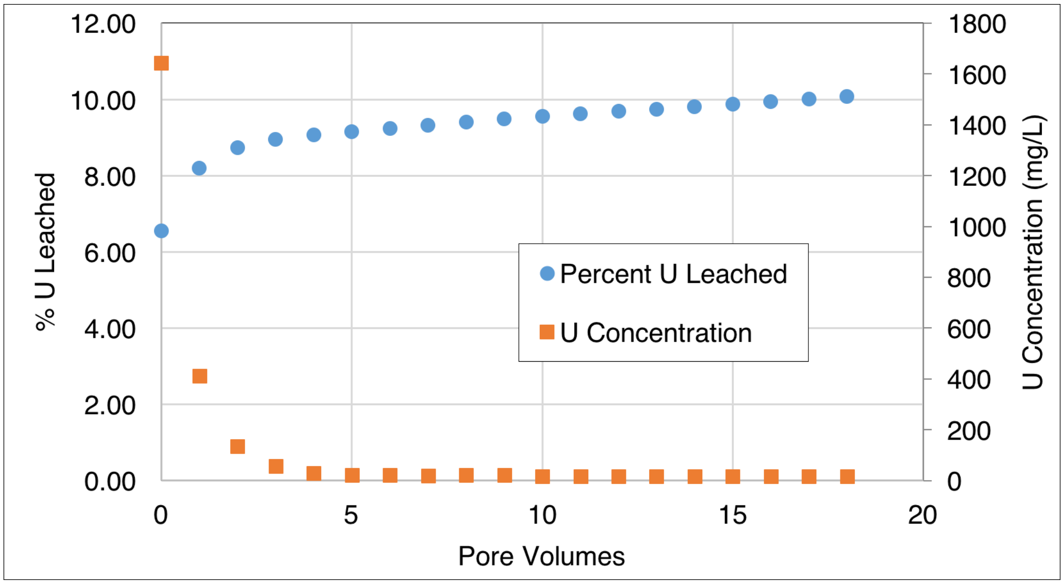


Figure 33. Column 1 U mass balance of 18 pore volumes.

In comparing the results reported here with those reported by others it is important to recognize this study utilized 1-dimensional packed columns to simulate ISL mining and subsequent aquifer stabilization methods. Chemical stabilization through PO_4^{3-} addition described by (Arey et al., 1999) and (Mehta et al., 2016) was studied in batch systems in which the principal objective was to identify the chemical and geochemical reactions, not simulate groundwater restoration methods. Similarly, microbial reduction studies such as those described by (Williams et al., 2013) have been done in batch systems for the purpose of understanding the microbial and geochemical processes associated with microbial reduction. Transport through a porous U ore media was not considered.

A potentially explanation for the lack of U stabilization found in this study is that it is due to the hydrodynamics of groundwater flow. Specifically, flow through a porous media occurs with little mixing and can therefore be characterized to a large extent as 1-dimensional plug flow. Therefore, in the experimental system used in this study there was little interaction between the restoration fluids with PO_4^{3-} or lactate and the ISL lixiviant containing high concentrations of U and other elements. In short, water amended with soluble reactants (i.e. PO_4^{3-} or lactate) has little mixing with contaminated groundwater. Classical dispersion calculations such as those presented by (Charbeneau, 2000) can be used to show this limited mixing. This may in part explain the poor performance of a field test in which H_2S, a strong precipitating and reducing agent was added with little effect on ground water quality (Borch et al., 2012)

Chapter 5: Conclusion

There are two notable conclusions from this study. The first is that bicarbonate leaching of U from an ore sample strongly depends on the nature of the U ore. In a 5-day batch test between 20% and 50% of the acid extractable U could be leached by a 100 mM $NaHCO_3$ solution for most samples. Rapid release of U within 24 hours are likely due to the amount of U(VI) in the deposits as shown by XPS analysis. Results have shown that as the concentration of $NaHCO_3$ increases the release of metals increases. High concentrations of Mo, Se and V were observed in the Westwater Canyon Member but not in the Jackpile Sandstone member. The lixiviant is effective but also leaches other constituents of concern that will have to be considered for restoration. Less than 5% of the acid extractable U was leached from an ore sample containing 21.8% organic material. As shown by the black tabular deposit from the Jackpile mine, U release is inhibited by the %OM in the deposit. Though this was not the objective of the study, it is a reminder that careful consideration of U ore characteristics are important to the success of an ISL mining project. These results represent different deposits with different characteristics. Therefore, the release of U and co-constituents depends on; 1. ore deposit, 2. the presence of organics, 3. degree of oxidation of the ore sample.

The second conclusion was gathered from column studies that 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^{3-} 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 and other metal reducing organisms. Neither method decreased the concentration of U or other constituents any more effectively than the control column, indicating minimal chemical/biological effect on restoration. Potentially due to minimal 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. These results show that both methods behaved similar to the control column flushing technique that is similar to groundwater sweep restoration process. Although phosphate was adsorbing/precipitating on the surface of samples near the inlet, concentration of U or co-constituents did not show relative difference that distinguished the chemical and control columns. This finding emphasizes the importance of groundwater hydrodynamics in addition to biogeochemistry when developing in-situ restoration strategies.

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

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Appendix

Table 10. Licensed Uranium Recovery Facilities, NRC

Site Name	Licensee	Location	Type of Facilitie	Agreement State
Crow Butte	Crow Butte Resources, Inc.	Chadron, Nebraska	ISR	Yes
Crownpoint	Hydro Resources, Inc.	Crownpoint, New Mexico	ISR	Yes
Dewey Burdock	Powertech Uranium Corporation	Fall River & Custer Counties, South Dakota	ISR	Non
Lost Creek	Lost Creek ISR, LLC	Sweetwater County, WY	ISR	Letter of Intent-AS
Moore Ranch	Uranium One Americas, Inc.	Campbell County, Wyoming	ISR	Letter of Intent-AS
Nichols Ranch	Uranerz Energy Corporation	Campbell and Johnson Counties, Wyoming	ISR	Letter of Intent-AS
Ross	Strata Energy, Inc.	Crook County, WY	ISR	Letter of Intent-AS
Smith Ranch	Power Resources, Inc.	Douglas, Wyoming (Converse County)	ISR	Letter of Intent-AS
Sweetwater	Kennecott Uranium Co.	Sweetwater County, Wyoming	Conventional Uranium Mill	Letter of Intent-AS
Willow Creek	Uranium One U.S.A.	Johnson & Campbell Counties, Wyoming	ISR	Letter of Intent-AS

Table 11. ICP OES Method Detection Limits (MDL)

Element	IDL (mg/L)	MDL (mg/L)
Al	0.0280	0.280
As	0.0250	0.250
B	0.0048	0.048
Ba	0.0013	0.013
Be	0.0007	0.007
Ca	0.0100	0.100
Cd	0.0027	0.027
Co	0.0070	0.070
Cr	0.0071	0.071
Cu	0.0054	0.054
Fe	0.0062	0.062
K	0.0500	0.500
Li	0.0500	0.500
Mg	0.0030	0.030
Mn	0.0014	0.014
Mo	0.0079	0.079
Na	0.0690	0.690
Ni	0.0150	0.150
Pb	0.0420	0.420
Se	0.0750	0.750
Si	0.0120	0.120
Sr	0.0008	0.008
V	0.0064	0.064
Zn	0.0018	0.018
P	0.0760	0.760
U	0.3000	3.000

IDL = Instrument Detection Limit
Can use 0.500 ppm as MDL for U
MDL = Method Detection Limit
MDL = IDL * 10

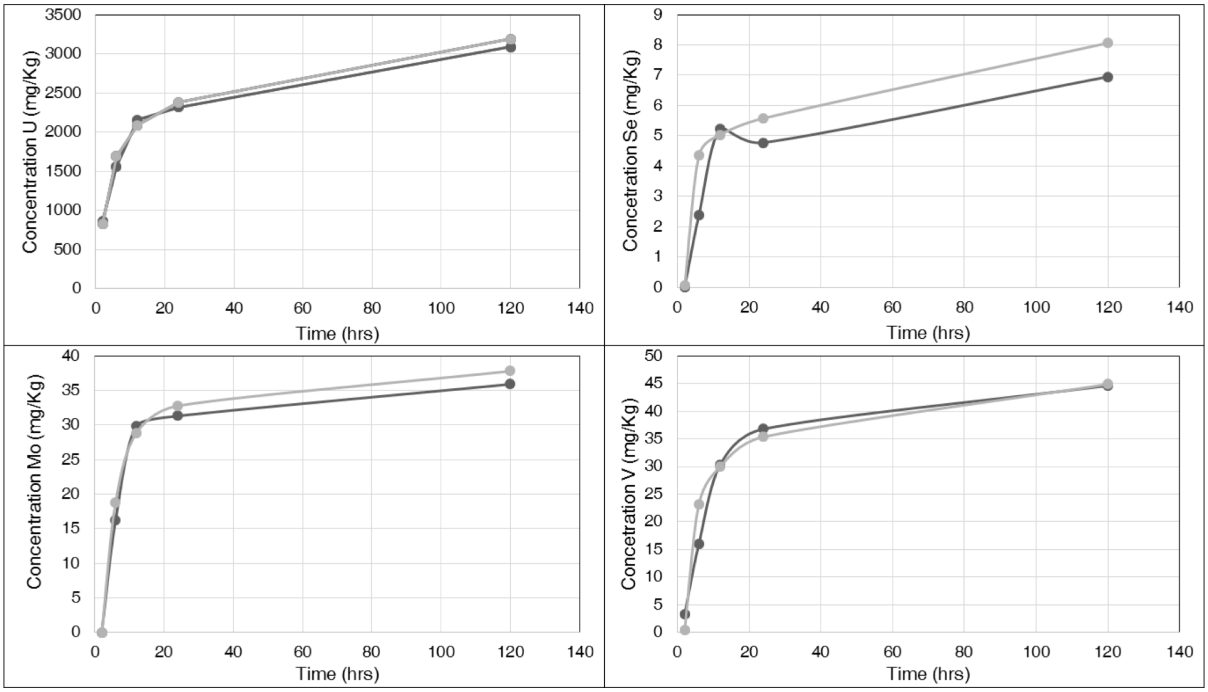

Figure 34. Dissolution of Mo, Se, U and V for Mt. Taylor Mine U ore deposit collected in the Grants Mineral Area.

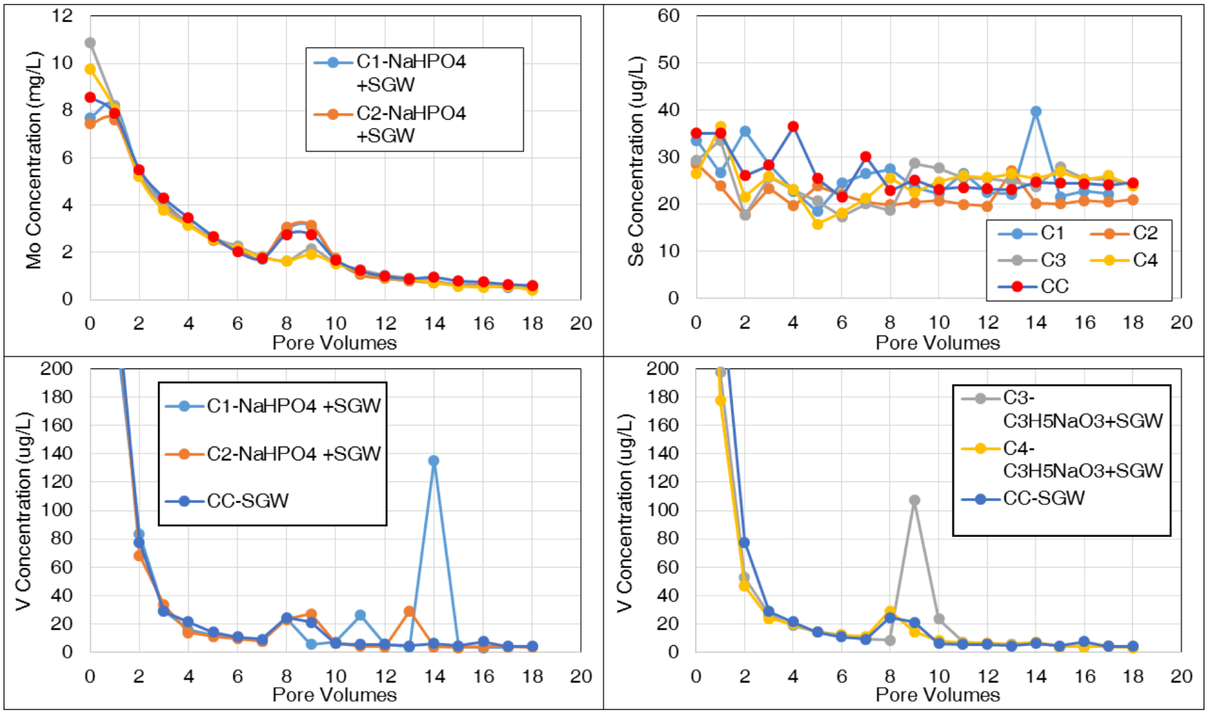

Figure 35. Metal concentrations plotted against pore volumes of effluent solution for columns (C1 & C2) fed a 100 µM PO43- solution and 3 mM lactate solution to stimulate biological growth (C3 & C4). Control column (CC) was only fed SGW. .

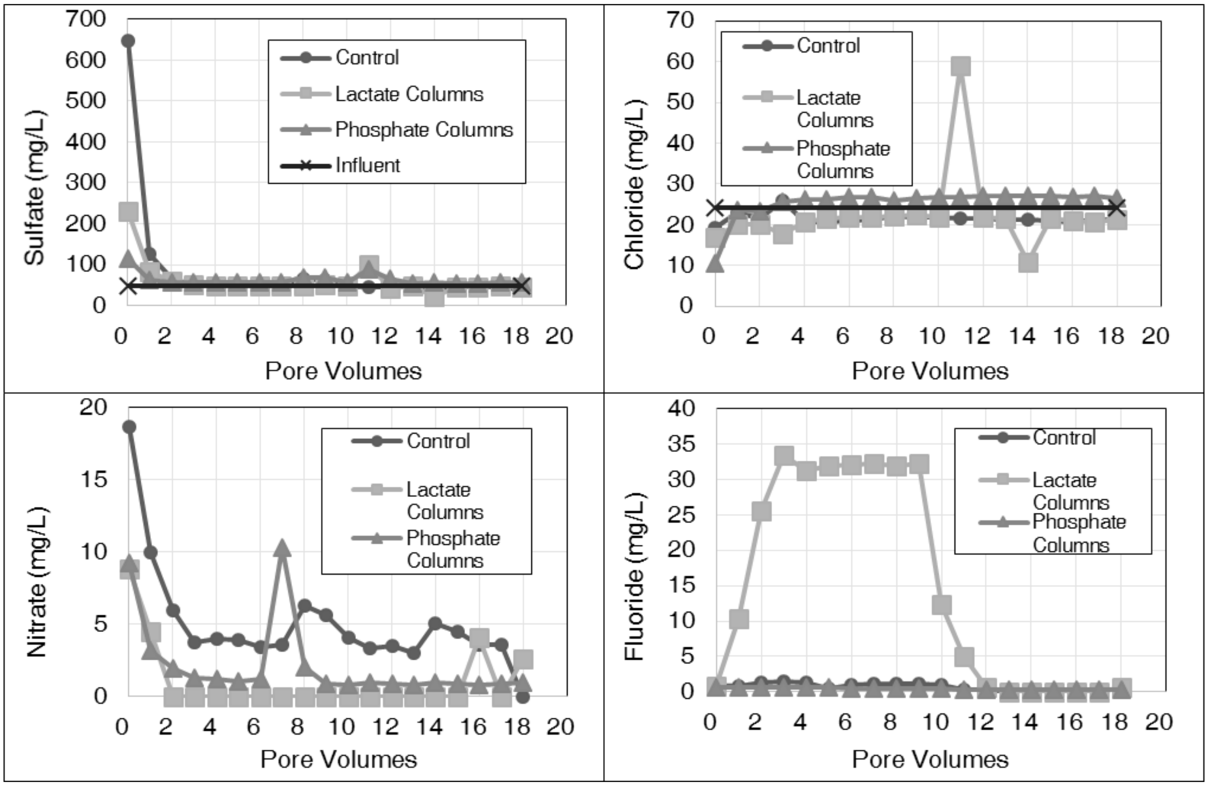

Figure 36. Anion concentrations against pore volumes of effluent solution for columns fed a 3 mM lactate solution to stimulate biological growth and 100 µM PO43- solution. Control column was a fed only SGW.