

HEAVY ELEMENT RELEASE TO GROUNDWATER  
AT IN-SITU URANIUM MINING SITES: PHASE I

Michael J. Humenick  
William L. Dam  
James I. Drever

August 31, 1983

Department of Civil Engineering  
College of Engineering  
Department of Geology  
College of Arts and Sciences  
University of Wyoming

Research Project Technical  
Completion Report (A-037-WYO)  
Agreement No. 14-34-0001-2154

Prepared for:  
U. S. Department of the Interior

The research on which this report is based was financed in part by the U. S. Department of the Interior, as authorized by the Water Research and Development Act of 1978 (P.L. 95-467).

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Wyoming Water Research Center  
University of Wyoming  
Laramie, Wyoming

## ABSTRACT

This laboratory experimental research project evaluated the mechanism and kinetics of release of heavy elements to groundwater from sandstone ores which have been mined by an in-situ leach process and subsequently subjected to groundwater flow through the mined area. Ore from Wyoming and Texas were examined during the work, and heavy elements of interest were uranium, molybdenum, vanadium, arsenic and selenium.

The mechanism of release was found to be controlled by diffusion. The kinetics of release were modeled by an overall mass transfer relationship. Under conditions of the experiments, the heavy elements were calculated to be anionic in nature. Data were obtained and processed to provide required information to simulate field conditions when evaluating heavy element migration at uranium solution mining sites.

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## ACKNOWLEDGMENTS

The following persons and groups provided their expertise to make this project possible:

Steve Boese analyzed rock and water samples for uranium and built a glass manifold. Tom Cogswell of the University of Wyoming Research Corporation offered his time, interest, and provided training in the analysis of water samples using a Plasma Atomic Emission Spectrophotometer. Laura Crossey and Ray Kablanow prepared and examined rock samples using a Scanning Electron Microscope. Dean Logan built several columns, often at a moment's notice. The Wyoming Mineral Corporation donated a core and baseline water analyses.

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Introduction

This study was designed to provide information on the geochemistry of heavy metals in groundwater that flows through a previously leached in-situ uranium mine. The method of in-situ solution mining has been used on the production scale in Wyoming, and other western states, and has several environmental advantages over conventional mining including the reduction of radiation and dust pollution. A major disadvantage to the method is the potential for the contamination of groundwater by leach fluid excursions and metals that are ubiquitous in the sandstone ore deposits. Kirkham (1979) states, ".....there is, however, a significant potential for ground-water contamination, but it can be minimized by successive restoration of the mined aquifer....." This study used cores from in-situ mines and was designed to provide information on the fate of elements in the groundwaters that pass through an in-situ mine that has had no, or very minimal, restoration. The Wyoming Mineral Corporation's Irigaray Mine in Johnson County, Wyoming was one site that had temporarily been abandoned without reclamation (Ogle, Personal Conversation, 1983) and experiments were conducted using a core from this mine site. It must be stressed that this study provided a methodology for the experimental measurements of the mobility of metals in groundwater and a model describing the rate of mass transfer of the metals released from the rock to the fluid. The study was not designed to make conclusions regarding a specific location. Future investigations are planned to integrate the results of this study into a

mathematical model that will be used to simulate the release of metals in actual in-situ uranium mines.

#### Purpose and Objectives

The purpose and objectives of the study was to determine the mechanism(s) of the release of heavy elements from post-uranium in-situ mines into flowing groundwater, to determine the mathematical relationships and kinetic parameters which describe the release, and to examine the aqueous geochemistry of the heavy elements of interest under the experimental conditions in relation to factors which control this release.

#### Scope

Experimental apparatus was constructed to leach the sandstone followed by groundwater circulation under anoxic conditions and controlled flow rates. Arsenic, molybdenum, selenium, uranium, and vanadium were the elements of primary concern in the study due to their occurrence, abundance, solubility, and environmental significance in uranium sandstone deposits. Also, additional elements were analyzed to provide data for geochemical models. The WATEQFC computer program made calculations to provide information on the speciation and saturation of the heavy elements in the groundwater. The kinetic model that was used to interpret the data was based on the assumption that waters pass through smaller pores in the rock at a rate slower than through larger pore channels and that heavy elements were released to the groundwater from the fluid in the smaller pores.

## SECTION I

## Previous Investigations

To the knowledge of the authors, no other experimental investigations have been conducted on the subject of the kinetics and mechanisms for the release of metals in the groundwaters that flow through a previously leached uranium in-situ mine. Several researchers have investigated various aspects of leaching technology and geochemical effects of leaching and restoration. A good bibliography on in-situ leaching technology and topics of research and development can be found in Larson (1978).

Much of the original work for the design of the experiments was conducted by Kidwell and Humenick (1981). Their experiments examined the extent of solubilization of trace elements during in-situ mining and groundwater circulation through the leached area. Several mechanisms were to control the uranium concentration in the leach and restoration solutions including reduction, precipitation, and adsorption. Molybdenum was found to solubilize quickly when the oxidation potential of the solution was increased by the addition of hydrogen peroxide. Arsenic, selenium, and vanadium were analyzed in the leach and restoration waters and were not found to be significantly high in concentration. The study of Kidwell and Humenick (1981) compared the concentrations of metals in restoration waters whereas the current study examined the concentration of metals in groundwaters without restoration.

Tweeton and Peterson (1981) suggested that contact between the ore and the lixivient would be more complete in column leaching experiments than in

actual in-situ leaching. Applying their study to the current investigation suggested that the amount of contact of artificial groundwaters with the rock would be much higher in the column experiments than what would be expected in the field.

Galichon and others (1977) examined some of the chemical and physical factors that affect in-situ uranium extraction. They state that the rates of uranium dissolution are related to the uranium available for leaching which is attached to the substrate. The authors propose that the simplest expression for the rate of uranium dissolution is:

$$\frac{\partial W}{\partial t} = -K_R(W - W_1)$$

where  $W$  is the mass of uranium per mass of substrate and  $W_1$  is the mass of uranium which is not accessible for leaching (or dissolution). The rate constant,  $k_r$ , depends on several factors including the oxidizing potential of the leach solution, the rate of mass transfer and the flow rate of the solution. From column experiments, they found that the dissolution rates of uranium were limited to uranium dissolved during leaching and variations in flow rates were independent of the dissolution of uranium. Their experiments showed considerable variation in using 100 g samples during duplicate runs and suggested the use of larger quantities of ore.

Geochemical factors that affect in-situ leaching have been investigated by Potter (1976). Some of the effects that an alkaline leach solution may have on the ore-bearing rocks include hydrolysis of feldspars which decreases the permeability, oxidation of pyrite which consumes oxidant or may reduce other species, precipitation of calcite, and the removal of uranium from solution due to ion exchange on clay sites.

## Deposition and Mineralogy of Metals in Sandstone Deposits

Uranium roll-type deposits are found in gently dipping, permeable sandstone units that are hydraulically confined between units of lower permeability such as clays or shales. The general shape of the deposits are concentric in cross-section and elongate along the altered sandstone (Harshman, 1974). Several investigators have described the theory and field relations of the roll-type deposits (Adler, 1974; Harshman, 1974; Granger and Warren, 1974; and Childers, 1970). The Wyoming Powder River Basin deposit from which samples were used in the experiment has a prominent redox interface (Adler, 1974) and may consist of three separate roll fronts separated by impermeable clay lenses extending over 110 vertical feet (Lueck, 1978).

The ore-bearing solution was probably an oxygenated, high bicarbonate groundwater that carried dissolved arsenic, molybdenum, selenium, uranium, vanadium and other elements. As the solution moved deeper into the reducing environment, the oxidation potential (Eh) was lowered from  $H_2S$  generated by sulfate-reducing bacteria in the host rocks and from dissociation of unstable sulfur species (e.g.  $SO_3^{2-}$ ) that formed as intermediate by-products of pyrite oxidation (Granger and Warren, 1969). Dissociation reactions produced  $H_2S$  and  $HS^-$  which lowered the solution Eh and selenite ( $SeO_3^{2-}$ ) was reduced to elemental selenium which was precipitated at the margin of the oxidized host rock (Howard, 1977). Other species of uranium, vanadium (Garrels and Christ, 1965), molybdenum, and iron moved to more reducing environments beyond the zone of accumulation and were deposited (Howard, 1977). Harshman (1974) constructed an Eh-pH diagram that depicts the sequence of deposition for various minerals as shown in Figure 1.

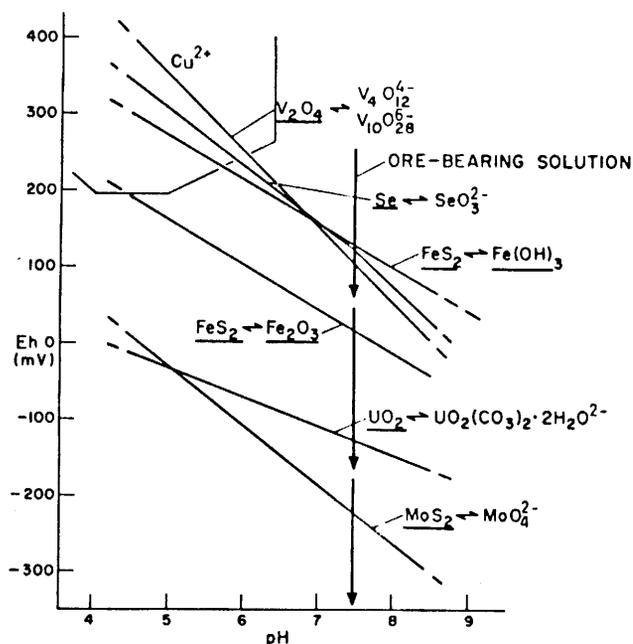


Figure 1. Eh-pH Diagram of Mineral Deposition

Figure 1 corresponds to the field relations of minerals from several locations in Wyoming, South Dakota and Texas that all showed similar depositional patterns of the metals. Arsenic was found to have no consistent field relations to the other elements in several deposits (Harshman, 1974). Arsenic is typically found in the deposits as arsenopyrite ( $\text{FeAsS}$ ) where arsenic has substituted for a sulfur atom in the pyrite ( $\text{FeS}_2$ ) lattice Boyle and Jonasson, 1973). Molybdenum is typically found in reduced sandstone as jordisite ( $\text{MoS}_2$ ) adjacent to the outer edges of uranium and pyrite bearing zones (Harshman, 1974). However, molybdenum was not detected at the Highland mine in the southern Powder River Basin (Langen and Kidwell, 1971) and no mention of molybdenum was made for the

Shirley Basin district (DeNault, 1974). Selenium is concentrated in the deposits as native selenium and selenide minerals such as ferroselite ( $\text{FeSe}_2$ ) (Howard, 1977). Vanadium and uranium are often found together as carnotite ( $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2$ ) or in vanadiferous and uraniferous clay minerals. Giblin (1980) found that in solutions containing up to 70 mg/l uranium, uraninite is extremely fine-grained, possibly colloidal, material when formed by reduction in the absence of any nucleating surface. DeNault (1974) also described uraninite as clay sized particles (less than two microns) that are coated on sand grains and fills interstices between grains.

#### Controls on the Concentration of Metals in an Aqueous Solution

Factors that control the mobility and concentration of metals in the aqueous environment include pH, redox conditions, adsorption, coprecipitation, complexation and kinetics.

#### pH and Redox Controls

The change in redox conditions can affect trace metals in aquatic systems by direct changes in the oxidation state of the metal ion and/or by redox changes in available and competing ligands (Leckie and James, 1974). Eh-pH diagrams are useful ways of displaying equilibrium solubility information. Drever (1982) provides a good summary of the methods of constructing Eh(pe)-pH diagrams, their advantages and limitations. The diagrams can be misleading when important variables are not represented. Such is the case for uranium which is generally soluble in oxidized waters and becomes very insoluble when traces (0.1 mg/l) of vanadium are present, hence the formation of carnotite as shown in Figure 2.

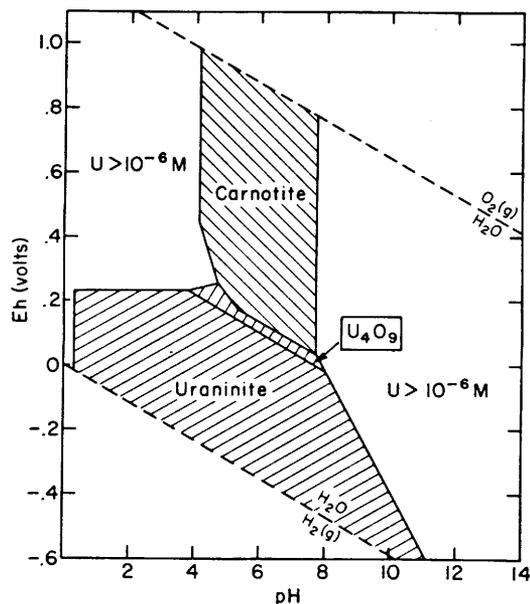


Figure 2. Uraninite-Coffinite Distribution

Above pH 8 the solubility of carnotite increases due to the formation of uranyl carbonate complexes as shown in Figure 3. Figure 4 presents the Fe-S-Se-U-H<sub>2</sub>O system but does not incorporate the large stability field of ferroselite (FeSe<sub>2</sub>) as is shown in Figure 5. Under reducing conditions at neutral to alkaline pH, selenite ions may form ferroselite. As the oxidation potential is increased (Eh = 0), native selenium and U(+6) are stable forms. At higher Eh, native selenium forms selenate which coexist

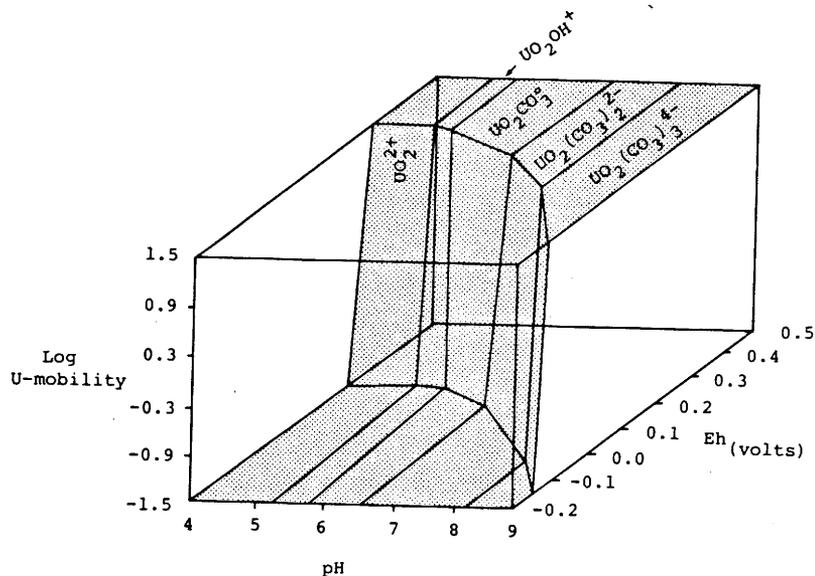


Figure 3. Eh-pH Diagram of Uranium Species.



with the mobile uranyl ions (Dall'Aglia and others, 1978 and Howard, 1977). Several investigators have reported that the oxidized selenate, Se(+6), could not be produced in experiments even under very highly oxidizing conditions.

Figure 6 shows various arsenic species and iron minerals. At pH 7 and high Eh,  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  are stable species in equal amounts and at pH 8,  $\text{HAsO}_4^{2-}$  is the dominant form (Frost and Griffin, 1977). Arsenous acid ( $\text{HAsO}_2(\text{aq})$ ) may be present in reducing environments (Hem, 1970). Molybdenum tends to occur as the soluble  $\text{HMoO}_4^-$  species under alkaline, reducing conditions as shown in Figure 7.

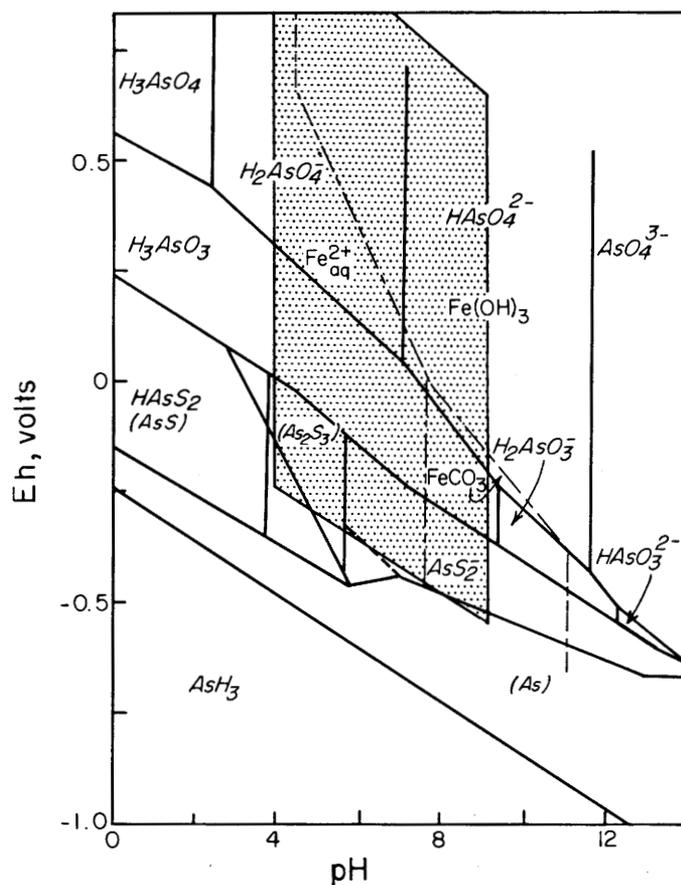


Figure 6. Eh-pH Diagram of Arsenic Species and Iron Minerals

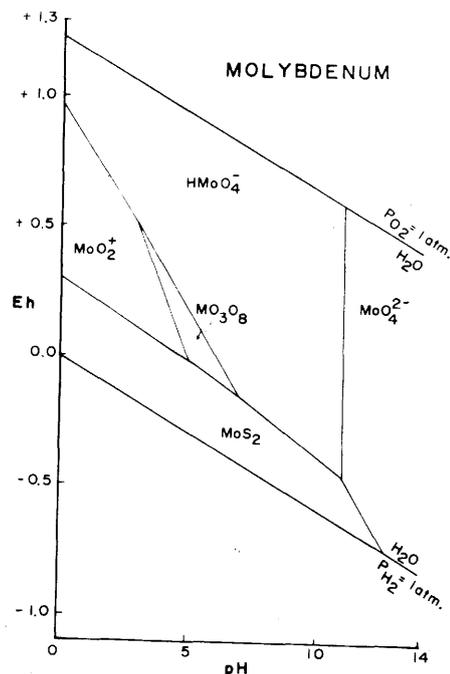


Figure 7. Eh-pH Diagram of Molybdenum Species

#### Adsorption, Coprecipitation, and Ion Exchange

Adsorption is a surface phenomenon that occurs at the interface between a solution and a mineral surface, and so the total available surface area of a particular mineral (such as a clay) is the most important property concerning adsorption (Giblin, 1980). Drever (1982, p. 310) states, "Adsorption occurs when a dissolved ion or molecule becomes attached to the surface of a pre-existing solid substrate." Several types of suspended solids, such as ferric oxides, carry a surface charge which may be strongly affected by pH. In general, at high pH, a negatively charged surface is formed and at low pH a positive surface charge on the solid is formed. The isoelectric point is the pH at which the net surface charge is zero (Stumm and Morgan, 1981). Hematite ( $\text{Fe}_2\text{O}_3$ ) commonly has an isoelectric point at pH 6-7 (Drever, 1982). Thus, in a solution with a pH

greater than seven hematite has a net negative surface charge. Mobile species in solution having a net positive charge (such as  $UO_2^{2+}$ ) will tend to be attracted, and possibly adsorbed, by hematite. Depending on the charge of the metal species in solution, the metal will be adsorbed or desorbed.

Several investigators have examined the adsorption of the five metals (As, Mo, Se, U, V) into ferric oxyhydroxides (Borovec, 1981, Gulens and others, 1979, Gupta and Chen, 1978, Holm and others, 1979, Langmuir, 1978, and Wagemann, 1978). Frost and Griffin (1977) found smectite to be more effective than kaolinite in removing arsenic and selenium from landfill leachate. The smectite has a larger surface area than the kaolinite and thus a larger area having a positive or negative surface charge available for sorption (Giblin and others, 1981). Arsenate tends to have a greater affinity for adsorption than arsenite although arsenate adsorption tends to decrease above pH 5. Arsenite tends to increase in the amount removed as pH increases (Frost and Griffin, 1977). These results were substantiated by Gupta and Chen (1978). Moran (1976) suggested that the mobility of selenium is largely controlled by adsorption on colloidal particles of hydrated ferric iron. Selenite is readily soluble as  $SeO_3^{2-}$  in solution but is easily adsorbed by iron oxides and clays (Dall'Aglio and others, 1978). Howard (1977, p. 1667) states, "Ferric-hydroxide adsorption, not the formation of insoluble selenite, is responsible for controlling the selenite concentration in natural waters."

Figure 8 shows the effect of mobile iron on the mobility of uranium in a solution containing 70 mg/l total iron (.45 microns and less), 200 mg/l kaolinite and 70 mg/l U. For a mobile iron concentration above 35 mg/l,

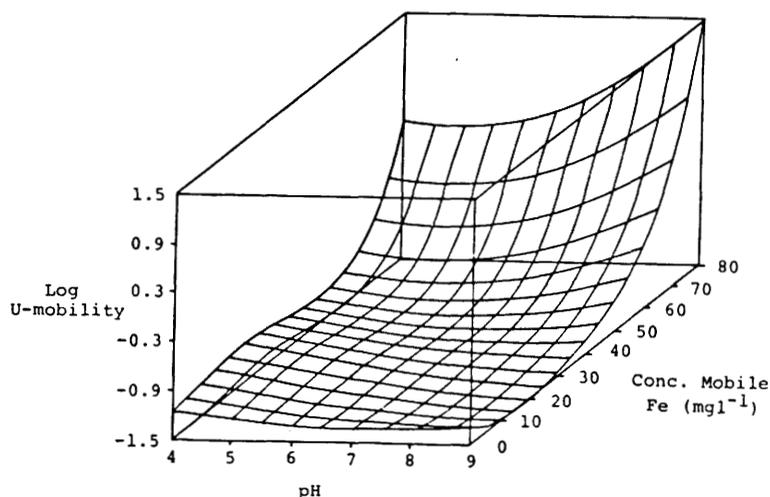
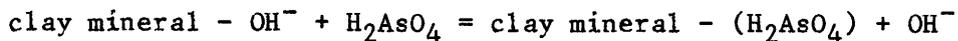


Figure 8. Plot of log Uranium Mobility, pH and Mobile Iron.

uranium mobility, pH and iron mobility all increase. This fits in with the idea of surface charge since the negative surface charge of hematite increases above a pH 7 and negatively charged uranyl tricarbonate  $\text{UO}_2(\text{CO}_3)_3^{4-}$  are desorbed and/or repelled from the iron oxide. Giblin and others (1981) concludes that kaolinite, which has the minimum adsorption capacity of most clays, exerts a major control on uranium mobility at low pH whereas iron is most significant at high pH values. Maximum adsorption of uranyl ion onto ferric oxides may be expected for a pH range 4-8 and desorption at pH 8 or greater when carbonate species are present (Van Der Weijden and others, 1976). Similar results were found for molybdenum adsorption. Mechanisms that control the availability of molybdenum in surface waters may be largely controlled by adsorption of  $\text{HMoO}_4^-$  and  $\text{MoO}_4^{2-}$  on ferric oxyhydroxides (Chappell, 1975 and Kaback and Runnells, 1980).

Coprecipitation may also have a significant effect on removing metals from solution. Drever (1982, p.311) states, "Coprecipitation occurs when a dissolved species is incorporated as a minor component in a solid phase as that phase itself is precipitated." Wilson and Hawkins (1978) found that arsenate becomes relatively immobile in weakly acid to basic solutions due to coprecipitation on hydrous iron oxides that form under these conditions.

A third mechanism for removal of metals from solution is ion exchange by clay minerals. Boyle and Jonasson (1973) point out the importance of clay minerals in fixing the concentrations of arsenic ions. Anion exchange may occur under slightly acidic conditions which replaces  $\text{OH}^-$  ions in the clay for soluble (mobile) arsenate ions as shown in the simplified equation:

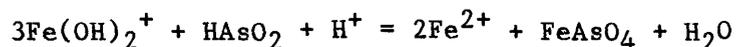


Brovoec (1981) examined the adsorption of uranyl species for kaolinite, illite and smectite and found that removal of uranium by clay minerals is more effective in a solution having low ionic strength.

#### Complexation

Complexation is an important process in determining the mobility of metal species. Carbonate, which is derived from atmospheric  $\text{CO}_2$  and carbonate minerals, is the most significant complexer of uranium (which is why in-situ solution operators typically use a carbonate to complex uranium in solution). Serebrennikov and Dorofayena (1980) examined the forms of uranium during solution mining in relation to Eh, pH and carbonate controls.

Gulens and others (1979) examined iron and arsenic reactions in solution and showed that arsenite and ferric iron may react to produce arsenate and ferrous iron as shown in the following reaction:



The authors suggest that the reaction may occur at the surface of iron hydroxides and affect the concentrations of free ions in solution. Both arsenite and arsenate form complexes with ferric iron in solution and the Fe(+3) - As(+3) complex tends to be more soluble than the Fe(+3) - As(+5) complex.

#### Kinetics

Kinetics is very important in determining whether a reaction will occur since even if a reaction is thermodynamically favored and is fast relative to geological time the reaction may never occur on a laboratory time scale. Good review articles can be found in Lasaga and Kirkpatrick (1981), Domenico (1977), Palciauskas and Domenico (1976), Berner (1978) and rigorous treatments of mass transfer and other kinetic equations can be found in Helgeson and others (1970) and Paces (1976). Unfortunately, very few studies have been conducted dealing specifically with rates of reaction for the metals of concern in this study.

From column elution studies, Gulens and other (1979) found significant differences in arsenite and arsenate concentrations corresponding with different redox conditions of the groundwater. In an oxidizing zone of pH 5.7, As(+3) was detected sooner and was eight times more concentrated than As(+5). The strong retention of arsenate is attributed to its adsorption by

ferric hydroxides in the sand. In column experiments with groundwaters between oxidizing and reducing conditions at pH 6.9, the relative amounts of arsenic species were unchanged and arsenate moved more rapidly than arsenite in the oxidizing environment. With reduced conditions where iron was immobilized as insoluble iron sulfide, arsenate greatly increased in mobility (possibly a desorption reaction) and both species were detected after one column volume was displaced (Gulens and others, 1979). The rate of oxidation of arsenite to arsenate appears to be very slow at neutral pH but is faster in acidic or alkaline environments (Ferguson and Gavis, 1972). Cherry and others (1979) found that the ratio of concentrations of arsenite to arsenate is very stable under a wide range of pH conditions and the rate of change of  $\text{As}(+3)/\text{As}(+5)$  is very slow on a laboratory time scale.

Howard (1977) found that bubbling air through a Fe-S-Se- $\text{CaCO}_3$  system for 15 days failed to oxidize elemental selenium to  $\text{SeO}_3^{2-}$  (selenite), and that elemental sulfur, which formed from oxidized FeS, was not appreciably oxidized to sulfate.

Grandstaff (1976) examined the rates of dissolution in uraninite and formulated an equation in which the variables included the specific surface area, other cations in the uraninite, dissolved oxygen content, total dissolved carbonate (or  $\text{pCO}_2$  for groundwater systems), and temperature. Capuano (1977) used data from the study by Grandstaff and proposed a mechanism for the formation of sandstone uranium deposits taking into account kinetic and thermodynamic considerations.

## SECTION 2

## Experimental Design

The procedures used in the experiments were designed to simulate the migration of natural groundwaters that pass through a previously leached in-situ uranium mine. The experimental apparatus, known as a recirculating batch reactor, was constructed to control the continuous circulation of waters that flow through unconsolidated sediments in an anoxic environment. Figure 9 shows a schematic of the experiment. Three sets of columns and reservoirs were constructed and were run simultaneously. In general, the experimental procedure consisted of leaching 100 g of uranium-bearing sediment with a one g/l ammonium bicarbonate-carbonate solution (pH = 9) and enough hydrogen peroxide to oxidize approximately one-half of the uranium. After the oxygen-consuming reactions were complete, the leach solution was drained and deaerated groundwater was added to the system. It was necessary to prevent contamination by atmospheric oxygen in the system while groundwater was circulated and samples were collected.

The experiments were run at flowrates that were much higher than actual groundwater flow rates. In the experiments, the rate of flow ranged between 0.5 and 10 ml/min whereas the groundwater velocity for the Irigaray mine site was reported to be between 11 and 20 ft/yr (3.4 to 6.1 m/yr) (Ogle, Personnel Conversation, 1983). Flow rates of 0.5 and 10 ml/min corresponds to flow velocities of 1702 and 34032 ft/yr, respectively.

## Columns

The design of the columns permitted the aqueous solution to flow through packed sediments under low nitrogen pressure. The columns were

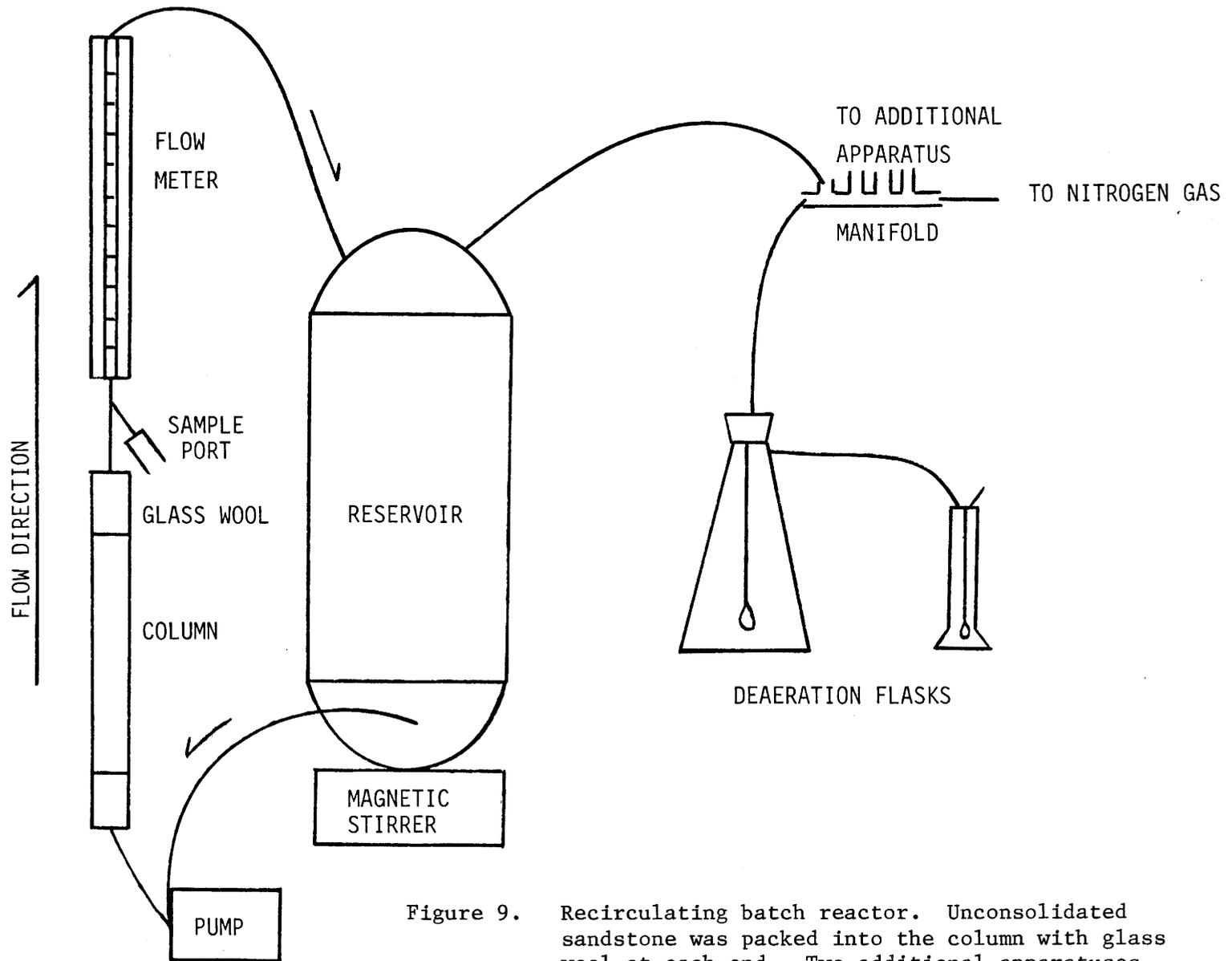


Figure 9. Recirculating batch reactor. Unconsolidated sandstone was packed into the column with glass wool at each end. Two additional apparatuses were connected to the manifold.

constructed from extruded, acrylic tubing and were clear to enable the visual observation of the rock-fluid interactions. The column dimensions were 2.54 cm I.D., 3.2 cm O.D., 18 cm long, and had a total volume of 91 cm<sup>3</sup>. The caps were 2 cm long and were lathed with a rim for a tight fit on the column. Connectors were screwed in at both ends of the caps and sealed with rubber adhesive.

The loading procedure consisted of gluing one cap with ethylene dichloride, adding 2 cm of glass wool, adding 100 g of sediment packed with a dowel rod, glass wool at the top, and sealed with ethylene dichloride which fused the plastic into a single piece.

#### Reservoirs

Reservoirs were built from schedule 40 PVC pipe. Each reservoir was 10.2 cm I.D. and 30 cm long with a 2.75 l fluid capacity. Fitted hemispherical caps were prepared with PVC cleaner, primer, and cement. Connectors for tygon tubing were placed in the caps and sealed with silicone adhesive. Magnetic stirring bars were placed into the tanks prior to sealing the caps. The reservoir sat on a ringstand with a magnetic stirrer below the ring.

#### Flowmeters

Three flowmeters from Gilmont Instruments, Inc. were used. The maximum flow rate capacities of the flowmeters were four, 36 and 295 ml/min. This corresponds to velocities through the column of 0.8, 7.1, and 58 cm/min. The accuracy was plus or minus 0.1, 1.0, and 5.0 ml/min, (or .02, .20 and .90 cm/min) respectively. It was necessary to use the

same flowmeter to prevent air contamination for leaching the sediment (at high flow rates) and circulating groundwater (at slow flow rates) although this caused problems due to difference in flow rate. Experiments were run to maximize accuracy of the flowmeters. The largest flowmeter was used for the fastest groundwater flowrates (10 ml/min).

#### Pumps

Masterflex peristaltic pumps and standard heads from the Cole Parmer Company were used in the experiments and ran continuously for several months without problems.

#### Tubing

Two types of tubing used in the experiments were pump tubing and tygon tubing. Silicone pump tubing was the most durable tubing. Degradation of pump tubing at high speeds (e.g. 40 ml/min) was a persistent problem in the experiments and it was necessary to change the position of the pump tubing on the pump every day for flow rates above 25 ml/min.

Tygon tubing was used to connect the apparatus. Pipette tips were used to connect the tygon tubing to the pump tubing and the connections were tightened with cable tie. The cable ties were found to be the most effective when pulled tight with pliers.

#### Gas Pressure System

The purpose of adding nitrogen was to prevent air from entering into the system by keeping a positive pressure on the inside of the system and to detect any leaks in the apparatus. Standard grade nitrogen (99% pure) was used in the experiments. Tygon tubing was fit from the nitrogen gas

regulator to a glass-blown manifold which enabled each apparatus to have an individual gas line.

#### Uranium Sandstone Cores

The two types of uranium sandstone core used in the experiments were from the Powder River Basin in Wyoming and from South Texas. Table I shows a comparison of the trace metals from the two locations.

TABLE I  
Metal Concentrations of Cores in Study

	<u>Wyoming (PPM)</u> (This Study)	<u>South Texas (PPM)</u> (From Kidwell and Humenick, 1981)
Uranium	560	3560
Arsenic	26.5	100
Molybdenum	<2	120
Selenium	0.55	20
Vanadium	143	50

As shown in Table I, the concentrations of the five metals except vanadium were much more abundant in the South Texas sandstone than in the Wyoming sandstone. From Appendix D, it was apparent that the concentrations of arsenic and selenium were more abundant in a southern Powder River Wyoming sandstone uranium deposit than that represented by the Wyoming sandstone used in the experiments. Thus, the Texas ore was used to obtain higher concentrations of arsenic and selenium in the groundwater for analytical convenience and accuracy and to collect data on molybdenum concentrations.

#### Wyoming Uranium Bearing Sandstone Ore

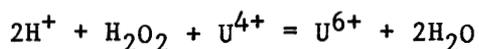
A three meter section of core from the Wyoming Mineral Corporation's Irigaray mine site in Johnson County, located in the Powder River Basin 25 miles northeast of Kaycee, Wyoming, was used in the experiments. The core was taken from Well No. KP-45C at the 68-71 m depth interval within the mineralized portion of the Upper Irigaray Sandstone. The five cm diameter core was collected and placed in five sections and wrapped with plastic to help minimize exposure to the air. The light gray core was 95% coarse grained sandstone with 5% dark shale. Silica was the primary cementing agent with minor calcite cement. The core was generally poorly cemented and easily disaggregated. A representative sample of the ore was lightly ground, blended, and stored in an air tight container.

X-ray diffraction showed the clay sized particles to consist of the smectite group (which includes montmorillonite), kaolinite and illite. Clay analysis was done on a Philips XRG 3100. The larger grains were predominately quartz, feldspar, and calcite.

The average percentage of clay in the core was 2.6% for the lightly ground samples used in the experiments and 10.6% clay when pulverized with a shatter box. The higher percentage may have been largely due to the powdering of quartz and feldspar grains. The percentage of clay was measured from a known sample mass which was liquefied, sonified, and centrifuged. The procedure was repeated several times until the suspended liquid was clear. The sample was then dried in a petri dish and reweighed. We feel the ground sample best depicted existing field conditions because only the packing of the grains had been rearranged in the columns.

#### Leach Solution

The alkaline leach solution consisted of ammonium carbonate-bicarbonate and hydrogen peroxide added to distilled water. The amount of solubilizing agent used was based on concentrations used by in-situ mining operators and generally consisted of one to five g/l (Tweeton and Peterson, 1981). In the experiments 0.5 g/l  $\text{NH}_4\text{HCO}_3$  and 0.5 g/l  $(\text{NH}_4)_2\text{CO}_3$  was used. The concentration of hydrogen peroxide was based on the stoichiometric quantity required to oxidize one-half of the uranium in the 100 g sandstone as shown in the following formula:



The Wyoming ore contained 560 ppm uranium and the Texas ore that was used contained 3560 ppm of uranium.

#### $\text{H}_2\text{O}_2$ Content Used in Wyoming Ore

$$0.056\% \text{ U}^{4+} = (.00056 \text{ g}) \times (100 \text{ g}) = 56.2 \text{ mg U}^{4+}$$

$$56.2 \text{ mg U}^{4+} \times 34.01 \text{ g/mole H}_2\text{O}_2 / 238 \text{ g/mole U} = 8.03 \text{ mg H}_2\text{O}_2$$

Using 30%  $\text{H}_2\text{O}_2$  with a mass of 8.03 mg is equivalent to a volume of 0.027 ml  $\text{H}_2\text{O}_2$ .

$\text{H}_2\text{O}_2$  Concentration Used for Texas Ore

$$0.356\% \text{ U}^{4+} = (.00356 \text{ g}) \times 100 \text{ g U}^{4+} = 356 \text{ mg U}^{4+}$$

$$356 \text{ mg U}^{4+} \times 34.01 \text{ g/mole H}_2\text{O}_2 / 238 \text{ g/mole U} = 50.9 \text{ mg H}_2\text{O}_2$$

The 50.9 mg's  $\text{H}_2\text{O}_2$  is equivalent to a volume of .17 ml.

Actual volumes of  $\text{H}_2\text{O}_2$  used in the experiments for both the Wyoming and Texas ore was one-half of the calculated volume so that only one-half of the uranium in the ore was oxidized.

One assumption made in the calculations was that the uranium in the sandstone used in the experiments was still in the reduced form. The sandstone appeared to be reduced judging from the characteristic gray color of the rock. A second assumption for the  $\text{H}_2\text{O}_2$  calculations was that uranium was the only mineral which significantly consumed oxygen and other minerals (such as pyrite) did not consume oxygen. If oxygen was consumed by other minerals, then a fraction less than one-half of the uranium would have been oxidized. However, the oxidation of less than half of the uranium would not affect the results or interpretations of the experiments since the purpose of the study was not to leach the ore quantitatively.

#### Addition of Leach Solution

The leach solution was added to the reservoir with a funnel through the top connector while the gas line was disconnected. To pressurize the system, the solution was pumped until the fluid had recirculated back into the reservoir. The pump was turned off, the clamp was closed on the reservoir inflow tube and nitrogen gas was added to a pressure of five psi.

The clamp on the gas line was closed to the reservoir, gas was turned off, and the solution was pumped as the clamp on the inflow tube to the reservoir was opened. The direction of flow was up-column. The flow rate during the leaching stage varied from 4 to 50 ml/min depending on the flowmeter that was used.

#### Measurement of Leaching Time

The time required to leach the uranium was dependent on the kinetics of the oxygen-consuming reactions within the closed system. One method to determine when the reactions terminated was to measure the dissolved oxygen concentration of the solution with time until there was an absence of oxygen, or a constant oxygen concentration, in the leach solution. Several problems occurred in measuring the dissolved oxygen of the solution. Wet chemical methods were not very sensitive at low dissolved oxygen concentrations. A dissolved oxygen meter was found to have good sensitivity at low oxygen concentrations while the sample was open to the atmosphere. Unfortunately, the electrode behaved poorly when placed in a closed environment. Various techniques to cover the electrode from the air were used including rubber balloons and a sealed glass tube so that the sample could be injected into the electrode without air contamination. Removing the surrounding air in the electrode resulted in very erratic readings of dissolved oxygen due to the change in the partial pressure at the membrane surface. It was found that the meter could only be used in an open environment with large (100 ml) samples. In actual in-situ mining of uranium, the leaching of the uranium is terminated when the dissolved oxygen content of the solution is at, or below, 8 mg/l oxygen. In the experiments, the dissolved oxygen content of the leach solution solution

change from 10 mg/l to approximately 2 mg/l from the start to the finish of the leaching stage. The leaching stage was typically run for at least ten days at 30 ml/min to ensure that the oxygen had been consumed in the closed system.

The pH of the leach solution generally changed from 9.0 to 8.5 from the beginning to the end of the leaching stage and was measured with a Fisher Accumet meter. The accuracy of the meter was plus or minus 0.2 pH units. The temperature of the solution was 25<sup>o</sup> C. Once the leaching stage was complete, the pump tube was separated from the tygon tube and the fluid was pumped out into a flask. Pore fluid was removed from the column by reversing the pump and displacing the fluid with gas into the reservoir. Extreme care was taken to ensure that oxygen did not enter back into the reservoir.

#### Artificial Groundwater Calculations

Using baseline water quality data from groundwater collected at the Irigrary Mine Well No. KP-44 (located approximately 70 feet of core hole KP-45C where the Wyoming ore was cored) the quantities of compounds added to distilled water were calculated to replicate the natural groundwater. Only the major anions and cations were used for making the artificial groundwater. Baseline groundwater analyses are given in Appendix E and were averaged over three sampling dates in constructing the groundwater. The baseline analyses were converted to molarity (M) and equivalents (Eq Wt) as shown in Table II. The charge balance for the cations was  $6.89 \times 10^{-3}$  M and  $6.98 \times 10^{-3}$  M for the anions which was a negligible difference. Highly soluble salts were mixed in distilled water. Calculations to find

TABLE II

## Major Ions Used for Artificial Groundwater

	<u>Mg/ℓ</u>	<u>M x 10<sup>-4</sup></u>	<u>Eq Wt x 10<sup>-4</sup></u>
Ca <sup>2+</sup>	10.5	2.62	5.24
Mg <sup>2+</sup>	1.15	0.47	0.95
Na <sup>+</sup>	143	62.2	62.2
K <sup>+</sup>	2.1	0.537	0.537
CO <sub>3</sub> <sup>2-</sup>	18.9	3.15	6.3
HCO <sub>3</sub> <sup>-</sup>	75.5	12.375	12.375
SO <sub>4</sub> <sup>2-</sup>	232	24.17	48.3
Cl <sup>-</sup>	10.0	2.82	2.82

the mass of each compound are shown in Table III. The formula weight was divided by two for complexes that have two moles per cation.

TABLE III

## Calculations of Artificial Groundwater

	<u>g/mole x</u>	<u>M x 10<sup>-14</sup></u>	<u>ℓ=</u>	<u>g</u>
K <sub>2</sub> SO <sub>4</sub>	174.27/2	0.537	10	.047
MgSO <sub>4</sub>	246.498	0.95	10	.234
+7 H <sub>2</sub> O				
CaSO <sub>4</sub>	136.14	5.24	10	0.713
NaCl	58.44	2.82	10	0.165
Na <sub>2</sub> CO <sub>3</sub>	105.99/2	6.3	10	0.334
NaHCO <sub>3</sub>	84.01	12.375	10	1.04
Na <sub>2</sub> SO <sub>4</sub>	142.04/2	40.71	10	2.89

## Dearation and Addition of Groundwater

To remove oxygen from the synthetic groundwater and to prevent air from contaminating the solution, a double set of glass containers with diffusion tubes were set up as shown in Figure 9. The end of the gas manifold was connected by tygon tubing to a tube with a diffusion stone inside a rubber stoppered flask. The 1000 ml flask was connected with tygon

tubing to a 40/50 Pyrex cylinder that had a built in gas dispersion tube. Pump tubing was sealed into the tygon tubing and ran to the flask so fluid could be pumped out without air contamination. The gas traveled from the nitrogen bottle through the manifold, into the flask and was dispersed as small bubbles in the fluid. The gas moved from the fluid into the water in the cylinder and then out to the air. It was found that the total time needed to deaerate the groundwater was two hours by measuring the change in dissolved oxygen with time using a dissolved meter. The groundwater was deaerated to less than 1 mg/l dissolved oxygen. Once the groundwater was deaerated, the valve to the pump tubing into the flask was opened and a few drops of solution were allowed to drip out. The tubing into the flask was hooked up to the pipet tip on the pump tubing. The pump was reversed and the fluid was added while nitrogen continued to deaerate the groundwater. Five hundred ml of groundwater were added in the experiment. Once the fluid was added to the reservoir, the pump was switched to forward, the tubes were disconnected, and some of the fluid was taken out of the pump tubing. The lines were hooked back up to the original set-up. The pressurization step followed using the same procedure as described for the leaching stage.

#### Sample Collection and Analysis

A MPL multidraw needle, which is used for blood collection, was found to be very useful in the experiments. The needle was injected into the tygon tubing in the direction of flow and sealed with silicone adhesive. The two-pronged needle had a rubber diaphragm valve that opened only when an evacuated tube was inserted. The tubes were evacuated by withdrawing air out of the tube with a syringe. This sampling method was preferred over

the septum-type sampling port due to clogging problems of the needle and the necessary reduction in the tubing size. Approximately six ml samples were collected and put into polyethylene, seven ml minivials (Cole Parmer) with screw-on caps. The samples were preserved to a pH of two as recommended by the EPA for preserving trace metals (U.S.E.P.A., 1974).

Problems with the type of sample containers used include adsorption and replacement of elements on the walls of the container. Plastics were recommended for all the trace metals that are the subject of this report. However, some authors have reported losses of arsenic when stored in plastics and recommended the storage of arsenic solutions in glass (Cherry and others, 1979). In the experiments, both plastic and glass sample containers were used.

The prevention of sample contamination, especially in trace metal investigations, is extremely important. All sample test tubes were cleaned with nitric acid. Samples were not filtered for analysis following the recommendations of Danielsson (1982) who cites errors including adsorption onto filters, leaching of metals which increases the concentration of the filtrate, and contamination among samples. Furthermore, the use of filters to separate the particulate and dissolved fractions at 0.45  $\mu$  is an artificial boundary and not an absolute boundary between immobile and mobile species in waters. Thus, the data represents total concentration of particulates and dissolved fractions for each species. Since the samples were very clear and glass wool was used in the columns, the amount of particulate matter in the liquid samples was minimal.

Two types of analytical methods were used in the analysis of trace elements. A fluorometric technique specific for the analysis

of uranium required approximately five ml samples and was a difficult and dangerous procedure. A second technique was used for the analysis of trace metals and appeared to be the best method for rapid analysis of several elements using small volumes. Several samples were analyzed at the University of Wyoming Research Corporation (UWYRC, previously the Laramie Energy and Technology Center) using an Inductively Coupled Argon Plasma (ICAP) emission spectrometer. Several current papers describe the methods of analysis using the ICAP (Crock and Lichte, 1982, Taggart and others, 1981). The ICAP had the capability of analyzing 42 elements using only six ml of sample with five replicate analyses per sample. Each sample was averaged for the five replicates and statistical parameters were reported. Data using this analysis procedure were found to be inconsistent among samples possibly due to the averaging of the five replicate analyses. The method of analysis was modified for experimental Runs J and N so that each sample was analyzed 10 times and values for each replicate analysis were reported. The 10 replicates were then lumped as the median concentration to eliminate inconsistent analyses caused by particulate matter or other sources that resulted in high or low values. The detection limits were calculated as two times the standard deviation of the blank for each element. The detection limits for the trace elements improved during the study due optimization of the instrument and replacement of parts. The ICAP was connected to a Digital PDP-11 minicomputer which fit calibration curves to measured intensities so that all samples were analyzed within the linear working range. Chemical interferences between elements were negligible on the ICAP due to the operational temperature used by the instrument (10,000°K). Caution was taken for elements having

similar spectral wavelengths if there existed a large variation in absorbance which might have caused incorrect measurements.

#### Kinetic Model

The kinetic model assumed that after leaching the concentration of heavy elements in all pores of the rock were uniform. In the experiments, the fluid in the large pores was removed so leach and groundwater solutions were not significantly mixed. However, some leach fluid was held in the pore spaces due to surface tension. With the introduction of groundwater, the heavy elements in the large pore spaces may be swept out. Heavy elements may exist in higher concentrations within the smaller pore spaces and either diffuse or disperse into the groundwater flowing through the larger pores. If molecular diffusion is assumed to control the exchange of elements then fluid velocity should not affect the rate of mass transfer from small pores to large pores. If hydrodynamic dispersion is assumed to control the elemental exchange, then the rate of mass transfer should be a function of fluid velocity. In these experiments the variation of mass transfer coefficient with flow velocity can be used to infer the rate-controlling process. Figure 10 shows that the concentration of a particular metal in the fluid of the smaller pore spaces was designated  $C^*$  and the concentration of the heavy elements in the bulk groundwater was designated as  $C$ .

Conservation of mass in the larger pores where dispersion is not a factor in the larger pores is shown in Equation 1.

$$\frac{\partial C}{\partial t} + v \frac{\partial C}{\partial x} = K(C^* - C) \quad \dots \dots \dots 1$$

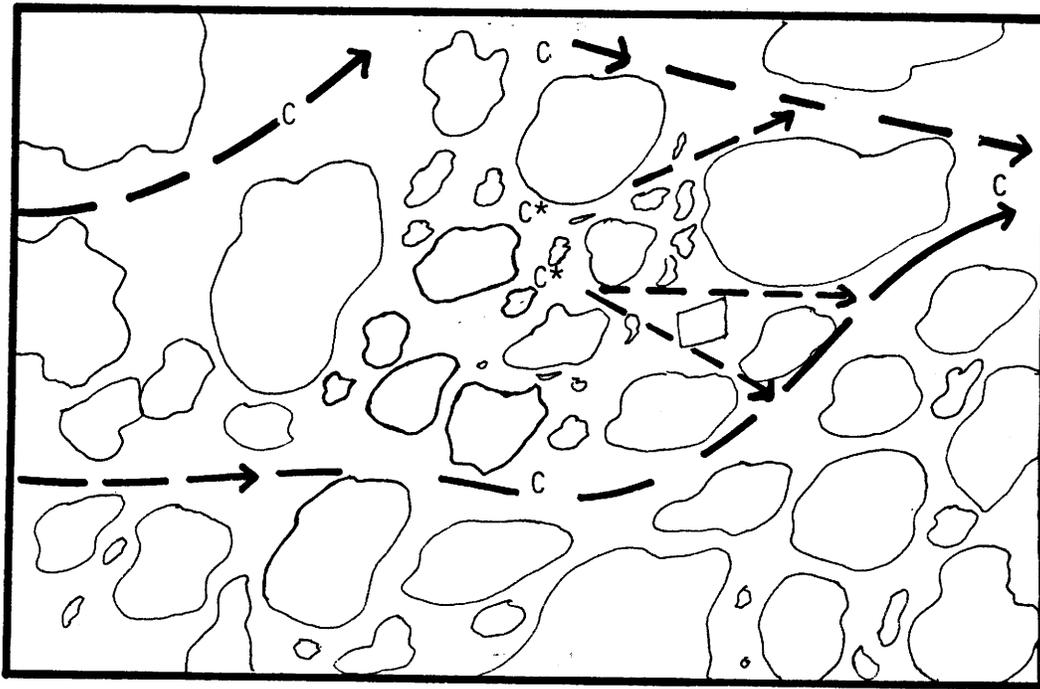


Figure 10. The kinetic model assumed that heavy elements were concentrated in the fluid in smaller pore spaces ( $C^*$ ) and were released to the bulk groundwater that had heavy element concentrations ( $C$ ).

For a short column, as used in the experiments, the change in concentration with distance is approximately zero so Equation 1 is reduced to the form shown in Equation 2.

$$\frac{\partial c}{\partial t} = K(C^* - C) \quad \dots \dots \dots \quad 2$$

Equation 2 states that the change in concentration of the bulk fluid with respect to time equals the rate of mass transfer between the smaller pores in the sandstone and the groundwater. The coefficient of mass transfer ( $k$ ) has the units of the reciprocal of time ( $t^{-1}$ ). Letting the two variables ( $C - C^*$ ) equal a third variable  $\bar{C}$

$$\frac{d\bar{C}}{dt} = -K\bar{C}$$

Integrating both sides of the differential equation

$$\bar{C}(t) = \bar{C}_0 e^{-Kt}$$

$$\text{or: } C - C^* = (C - C^*)_0 e^{-Kt}$$

Since there were no metals in the pore fluid initially ( $C_0 = 0$ )

$$C(t) = C^*(1 - e^{-Kt})$$

$$\text{or: } \ln(C^*/C^* - C) = Kt$$

If the natural log of  $(C^*/C^* - C)$  is plotted against time, the slope of the line is the coefficient of mass transfer ( $k$ ).

The value  $C^*$  was obtained using a mass balance approach which took into account the amount of the metal that was released into solution for each sample. Appendix C shows the method used to calculate  $C^*$  and a

Fortran program used to process the data efficiently. Slopes were calculated using linear regression for the line of best fit. At the end of the experimental run,  $C^*$  equalled  $C$  so the value of  $\ln(C^*/C^* - C)$  tended towards infinity. Only the values that approximated a straight line were used in the linear regression.

#### Geochemical Modeling

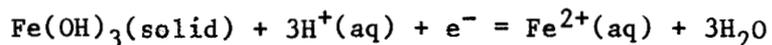
The computer program WATEQFC was used for speciation-saturation calculations of the experimental data. The original program (WATEQ) was written by Truesdell and Jones (1973) and then written in Fortran IV and expanded by Plummer and others (1976) who renamed the program WATEQF. Lueck (1978) added uranium to the model using the best available thermodynamic data compiled primarily by Langmuir (1978). Runnells and Lindberg (1981) added molybdenum and vanadium, expanded the uranium distribution, and renamed the version WATEQFC.

The program required an accurate chemical analysis of major anions and cations, pH, Eh, and temperature. Input of various other elements was necessary for calculations of minerals that contain that element. For instance, an analysis of aluminum was required for consideration of aluminosilicates (which includes several clay minerals) in the program. From the input water analysis the program calculated the theoretical distribution of species of an element in solution, the activities and activity coefficients of dissolved species, and the degree of saturation of the solution with respect to the various solid phases.

This version of WATEQFC solved the simultaneous equilibria for 47 chemical elements represented by approximately 540 minerals and solid

compounds and 650 aqueous species (Runnells and Lindberg, 1981). Stumm and Morgan (1981) have reported significant discrepancies between calculated predictions from chemical equilibrium models and actual chemical compositions, possibly due to limited or inconsistent thermodynamic data, poor chemical analyses, slow rates of chemical reaction, and problems of defining the redox state.

Probably the most important and most difficult to measure or define parameter used in speciation-saturation models is the oxidation potential (Eh). In general, Eh is measured in volts by an electrode and expresses the activity of electrons in solution. The problems of measuring Eh are discussed by Stumm and Morgan (1981). These basically involve poor response of the electrode to most of the redox pairs in natural systems and the problem of measuring mixed potentials (more than one reaction occurring at one time). All this often results in a meaningless measurement of Eh. WATEQFC has several methods of defining Eh and calculating pe (the negative log of the activity of electrons) from a redox reaction. For instance, the dissolution of limonite to form ferrous iron is shown:



This equation can be written in terms of pe:

$$pe = \log[\text{Fe}^{2+}] + 3 \log a_{\text{H}_2\text{O}} - 3 \text{pH} - \log K$$

pe and Eh are related by the equation  $pe = F/(Eh * 2.303 * RT)$  where F is the Faraday constant (23.06 kcal/volt gram) and R is the gas

constant (.001987 kcal/deg mole) and T is the absolute temperature. Thus, an estimation of Eh can be obtained from calculating pe which requires that an analysis is made of the species of the redox pair. For example, if the above iron reaction is used, one must have a chemical analysis of ferrous iron and make the assumption that all of the iron in solution is in the reduced state and that  $\text{Fe(OH)}_3$  is present. Other redox reactions can be used including  $\text{SO}_4^{2-}/\text{H}_2\text{S}$  and  $\text{N}_2/\text{NH}_4^+$ . For a further explanation of the theory and application of redox chemistry, detailed discussions may be found in Drever (1982). Lueck (1978) presents the several methods used in WATEQFC to estimate Eh. These limitations must be taken into account in interpreting the output of the computer model. Despite the many limitations, several authors have proven the applicability of the model to exploration of uranium ore deposits and in-situ uranium mining (Runnells and others, 1980, Runnells and Lindberg, 1981).

## RESULTS AND DISCUSSION

The results are presented in four sections. The first section shows the data used to identify the mechanism of heavy element release. The second section examines the results of the kinetics of release. The third section presents the relationships needed to perform mass balances in subsequent simulation model studies. Finally, section four discusses theoretical aspects of heavy element release, transport, and implications related to the geochemistry of the groundwater system.

### Mechanism of Release

Preliminary studies were performed to establish the mechanism of release for the heavy elements. The procedure used was to leach the sandstone ore in the recirculating system until the oxidant was used up. Then the lixivient was drained and deoxygenated groundwater was placed in the reservoir and circulated until the concentration of heavy elements in the recirculating fluid became constant. Next, the fluid in the reservoir was removed and a new batch of deoxygenated groundwater was placed in the reservoir and circulated through the column containing the sandstone ore. Again, concentration as a function of time and volume throughout was determined. The response of the concentrations vs time plots for subsequent elutions reveal the mechanism of release.

Figures 11, 12 and 13 show the results of two elutions of groundwater. These data were collected using Texas sandstone ore and a recirculation rate of 50 ml/min (142 m/day superficial flow velocity). This velocity was much higher than normal groundwater flow rates. However, the purpose

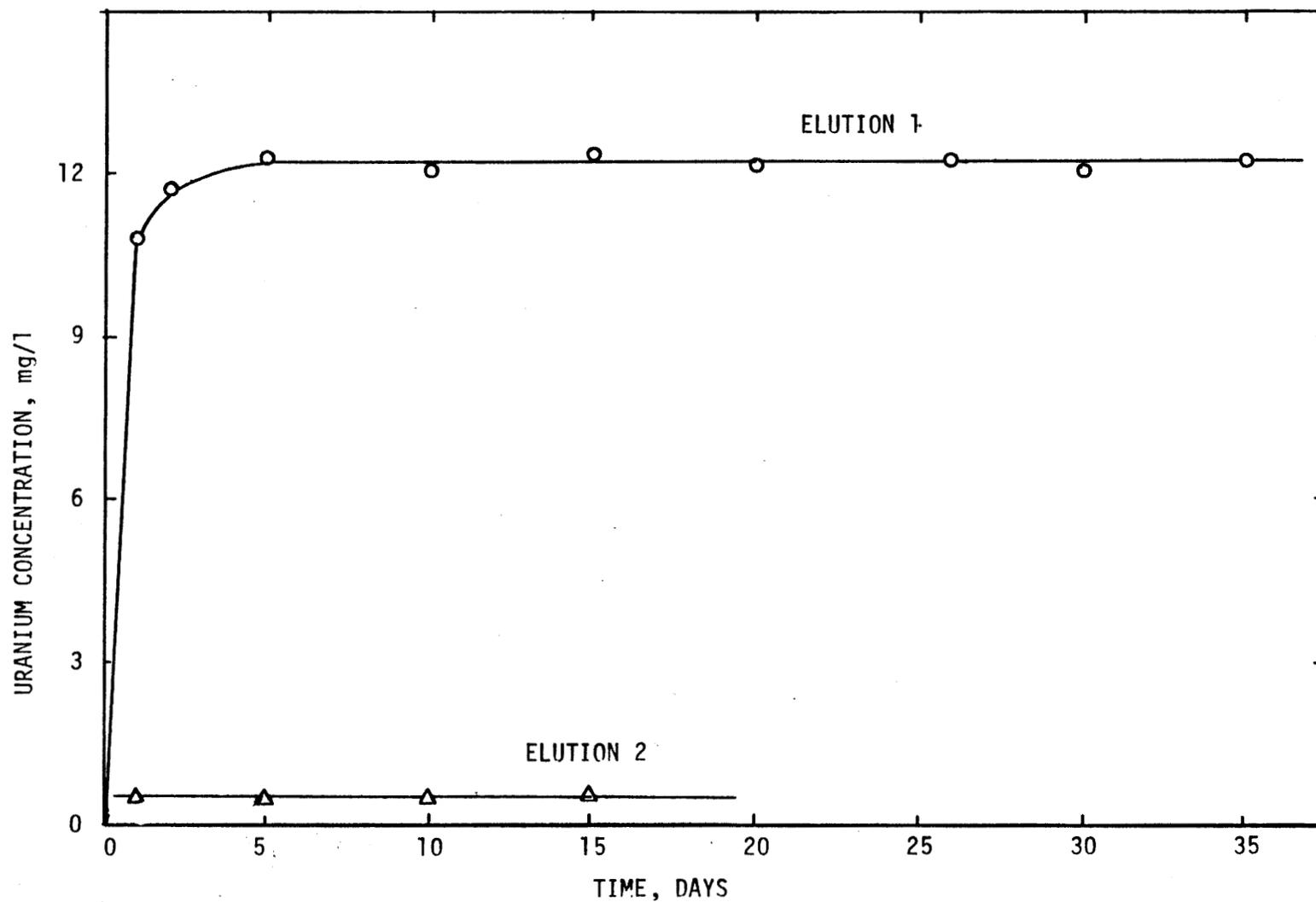


FIG. 11. URANIUM CONCENTRATION VS TIME. SUBSEQUENT ELUTIONS WITH GROUNDWATER.

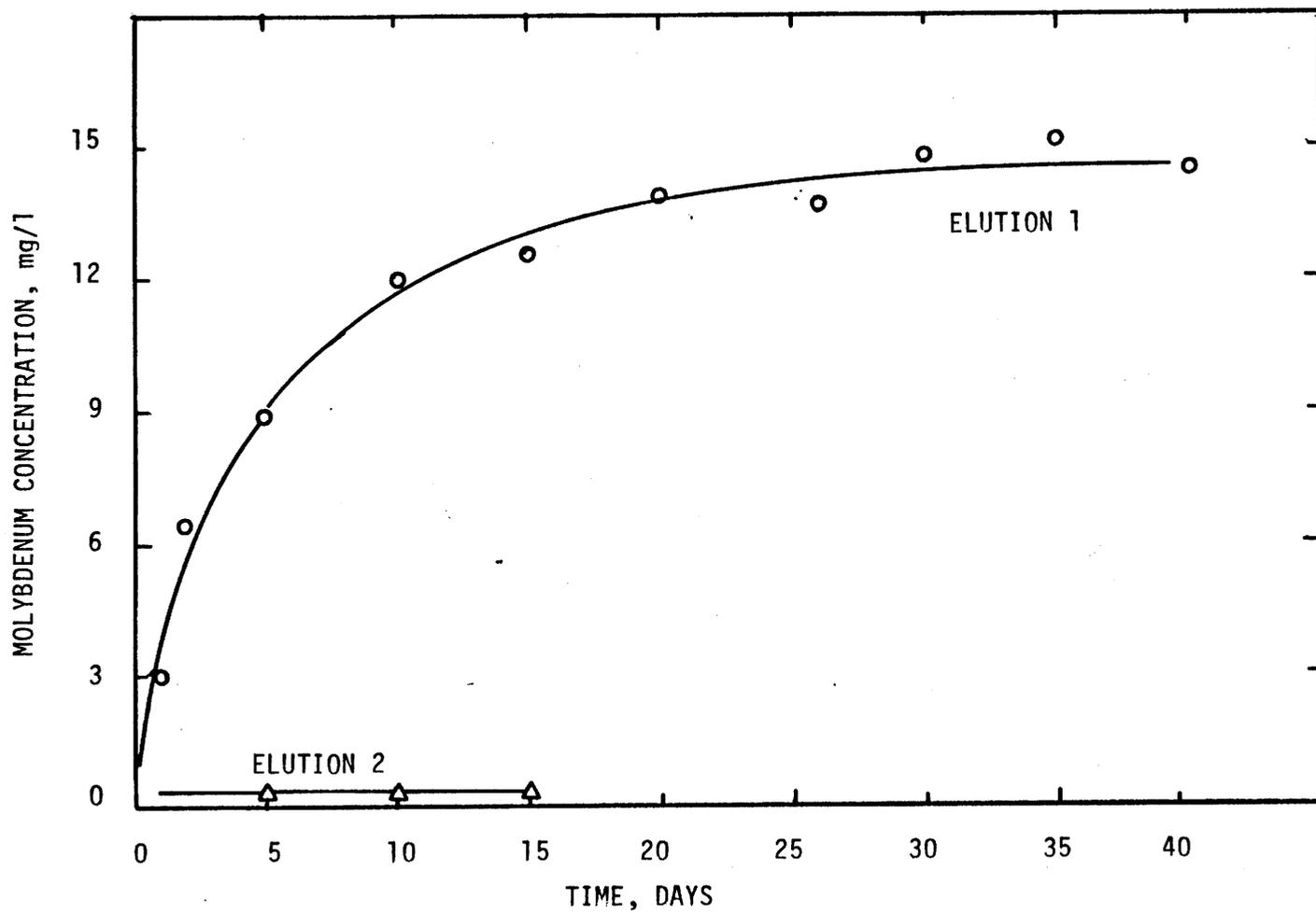


FIG. 12. MOLYBDENUM CONCENTRATION VS TIME. SUBSEQUENT ELUTIONS OF GROUND WATER.

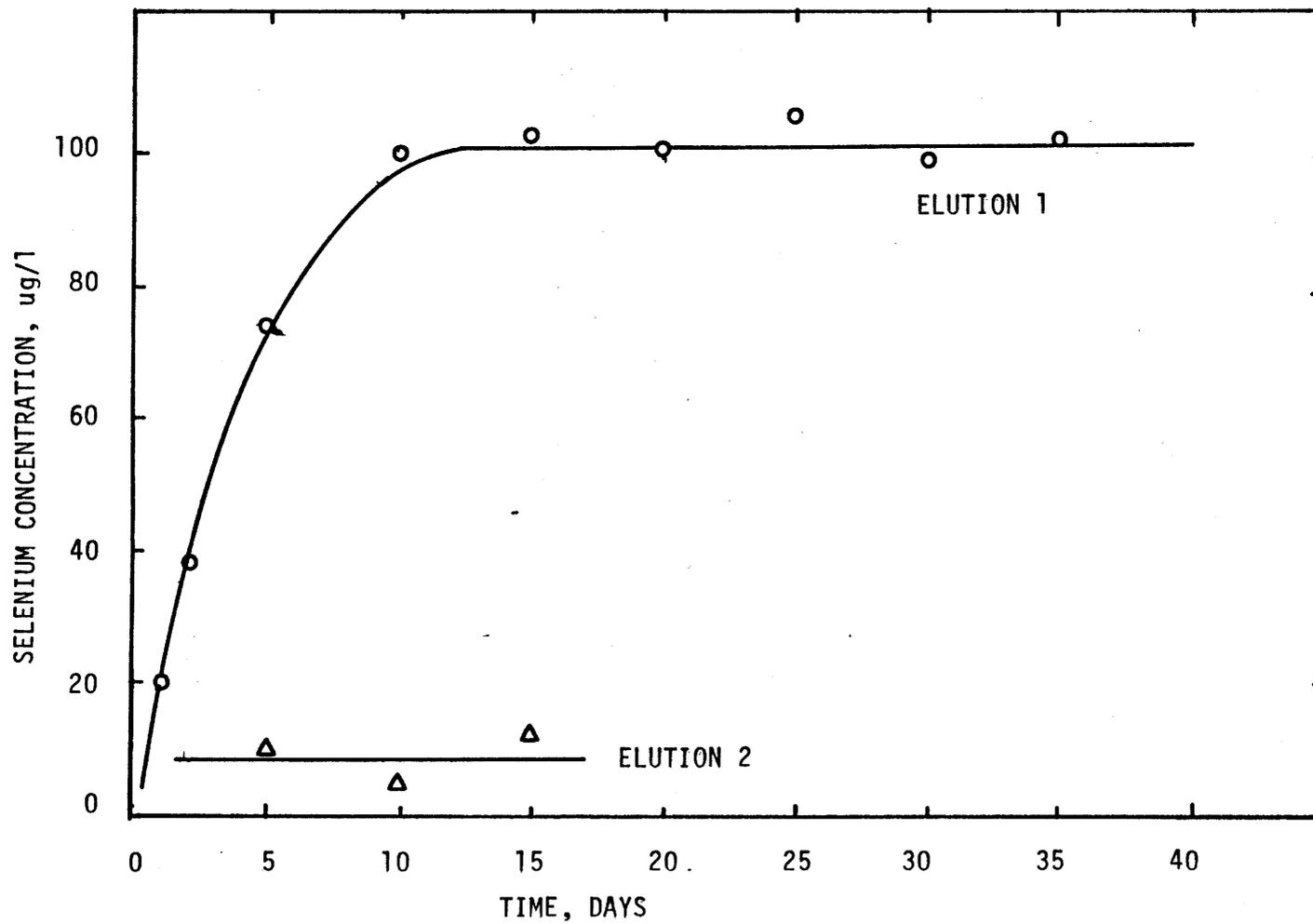


FIG. 13. SELENIUM CONCENTRATION VS TIME, SUBSEQUENT ELUTIONS OF GROUND WATER.

of these experiments was to identify the mechanism of release and not to obtain kinetic data.

As stated before, the shape of the elution curves indicate the mechanisms of release. For example, if each elution indicated an exponential rise in concentration to some limiting value, the limiting value would be controlled by an equilibration process such as adsorption, ion exchange, or solubility. Examination of Figure 11, 12 and 13 indicate that these equilibrium processes do not exist for the heavy elements shown (uranium, molybdenum and selenium).

Figure 11 shows the data for uranium. The first elution follows an inverse exponential rise to a maximum value. However, subsequent elutions with groundwater show no rise in concentration. The initial value for uranium on elutions two and three is due to the residual pore fluid which was not drained from the ore column between elutions.

Thus, the mechanism of release is proposed to be simple diffusion of oxidized and mobile heavy elements from locations within the sandstone ore which do not see the main flow of pore fluid. This model is discussed in more detail in a subsequent section.

The data for arsenic and vanadium was not useful because concentrations of these elements were very low and near the detection limits of the available analytical equipment. Because of the similar nature of these elements compared with uranium, molybdenum, and selenium, it was assumed that the same diffusional mechanism applies to arsenic and vanadium.

During some of the preliminary runs the second elution showed slow increases of heavy elements with time. For these runs there was good

evidence that air entered the system either during the reservoir emptying and filling step or during the second elution when equipment suffered breakdown. It must be stated that the experimental procedure used is very difficult because of the many ways oxygen can get into the system and cause subsequent release of reduced heavy elements by oxidation. Also, because the release of heavy elements is very slow under the flow conditions studied, there is a high probability of mechanical failure in the pumping system and reactor appurtenances during the long runs.

#### Kinetics of Release

The kinetic model of heavy element release to flowing groundwater has been presented earlier. To summarize, the model is based on a rate of release proportional to a driving force given by a concentration difference between the bulk stream concentration,  $C$ , and an internal or shielded concentration,  $C^*$ . Thus, a plot of  $\ln(C^*/(C^* - C))$  vs time should give a straight line with a slope equal to  $k$ , the mass transfer coefficient.

All the data for the kinetic runs are tabulated in Appendix A. Runs C, D, and F used Wyoming ore while Runs J, N, and T used Texas ore. Appendix C discusses the manner in which mass balances were performed to obtain  $C^*$  as a function of time and then the subsequent calculation of the mass transfer coefficient,  $k$ .

Figure 14 shows the results of three runs for uranium using Wyoming ore. Correlation coefficients for the data range from 97 to 99 percent. Figure 14 is presented as an example. Values for  $\ln(C^*/(C^* - C))$  for all runs and elements are tabulated in Appendix A. Table IV shows the results of data analysis to obtain the mass transfer coefficient,  $k$ , for the various runs.

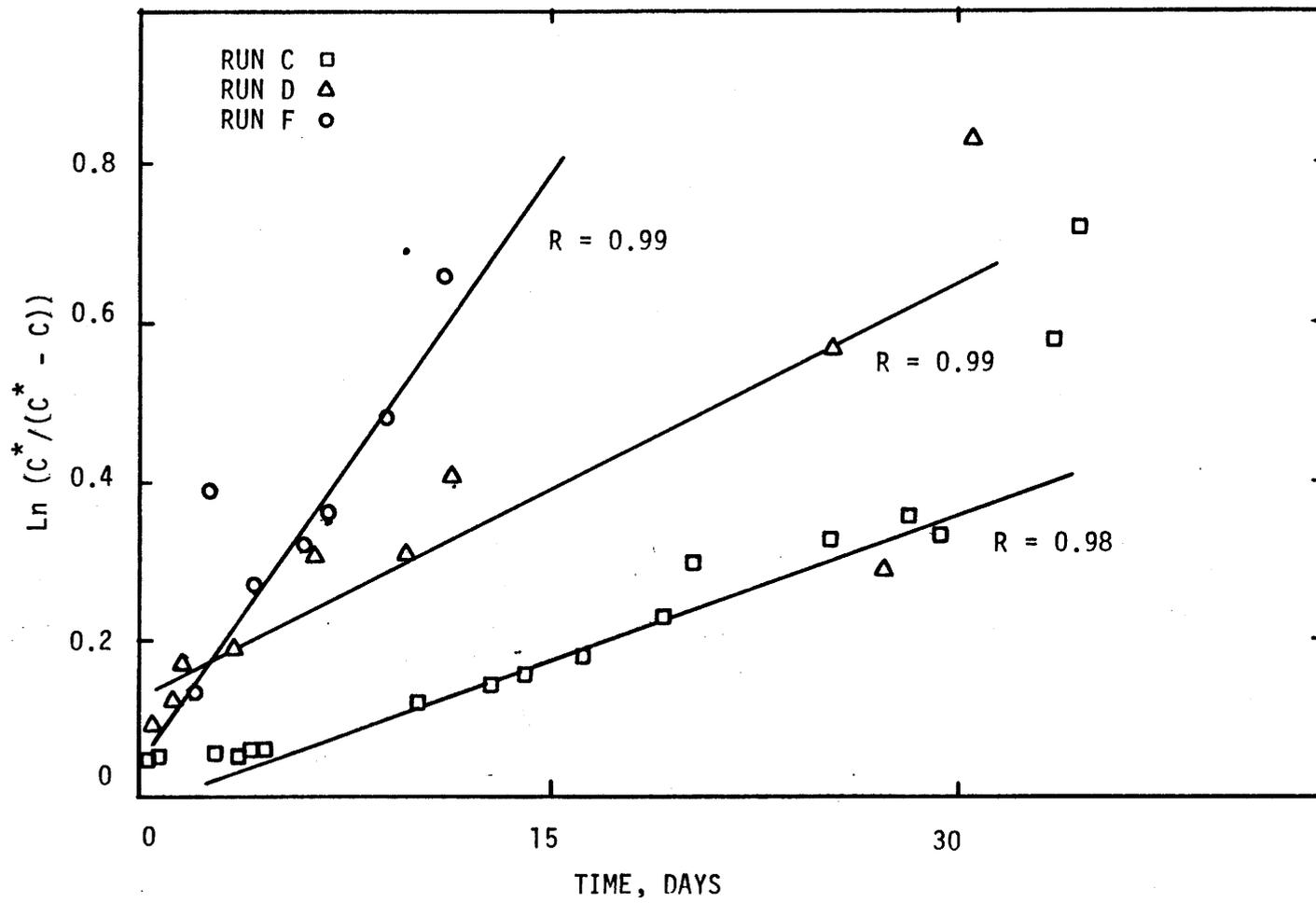


FIG. 14. DETERMINATION OF THE MASS TRANSFER COEFFICIENT FOR URANIUM.

TABLE IV

Determination of the Mass Transfer Coefficient, k

Run	Flow Rate		U	Mo	V	Se	As
	ml/min	m/day*					
C	10	28.4	0.010	-	0.012	-	0.053
D	10	28.4	0.017	-	-	0.012	-
F	5	14.2	0.048	-	0.089	0.043	0.118
J	2	5.7	0.031	0.047	0.016	0.009	0.010
N	10	28.4	0.089	0.128	0.010	0.032	0.072
T	50	142	0.86	0.110	-	0.30	-

Table IV indicates that k is a function of groundwater flow velocity. However, the pattern is not always consistent. Deviation from a consistent pattern is probably due to experimental and analytical errors, particularly when some concentrations of elements were near detection limits. Run F seemed particularly out of sequence. The mass transfer coefficients obtained for runs J, N, and T were seen to be roughly proportional to flow velocity as one would expect.

#### Available Heavy Element Release

The final information needed to use the kinetic data to simulate in-situ migration of heavy elements is the amount of heavy element available for transport. This term is called mass initial and its calculation is

described in Appendix C. Figures 15 and 16 show the amount of mass initial to be a function of the starting concentration of the heavy element in the bulk fluid at the start of the run. This value is given for our experiment as the final concentration of heavy element in the lixivient at the end of the leach step. Table V summarizes the results of these calculations by indicating the slope of the assumed straight line response. It can be seen that the slopes do not vary much with the exception of vanadium. The lines drawn on Figures 15 and 16 are assumed to go through the point zero-zero. Thus, the lines are drawn as a best estimate.

TABLE V  
Slope of Mass Initial vs Concentration

Element	Slope, mg/kg ORE/mg/l
Uranium	3.1
Molybdenum	2.4
Vanadium	10.0
Selenium	4.6
Arsenic	5.2

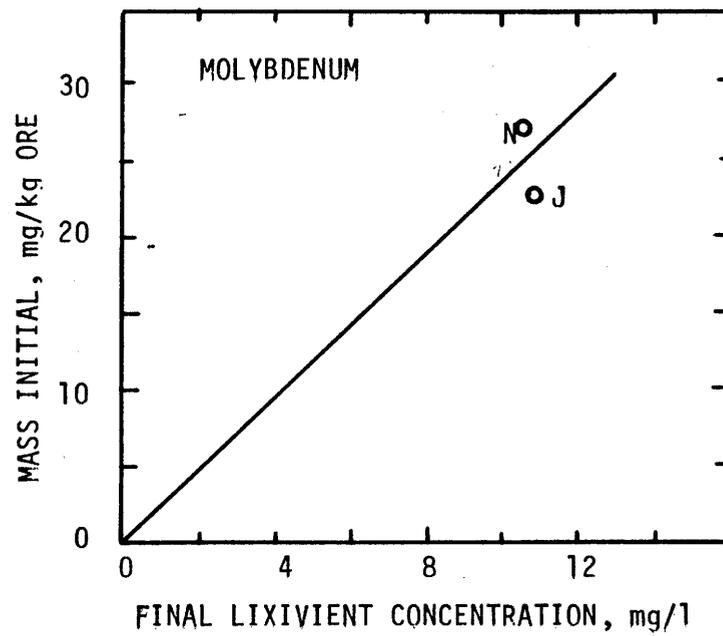
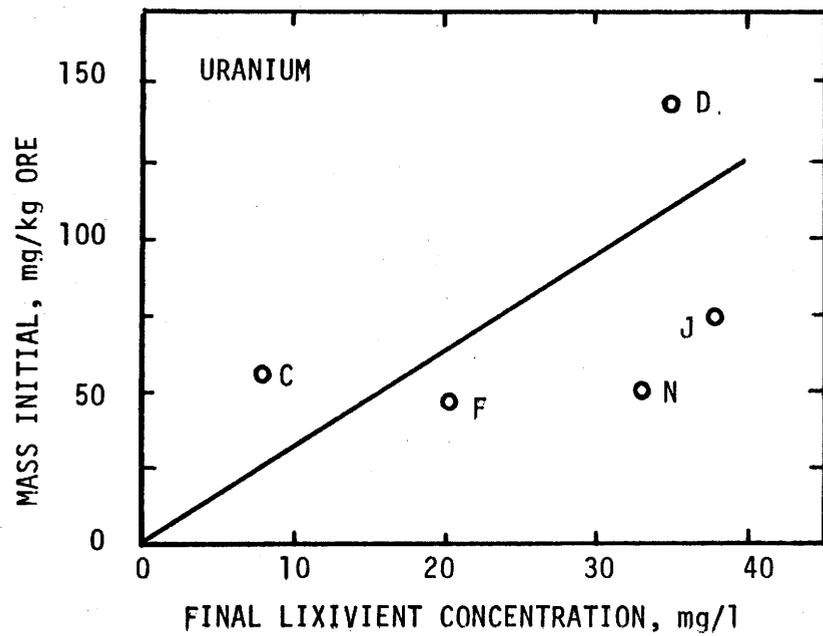


FIG. 15. MASS INITIAL VS FINAL LIXIVIENT CONCENTRATION. URANIUM AND MOLYBDENUM

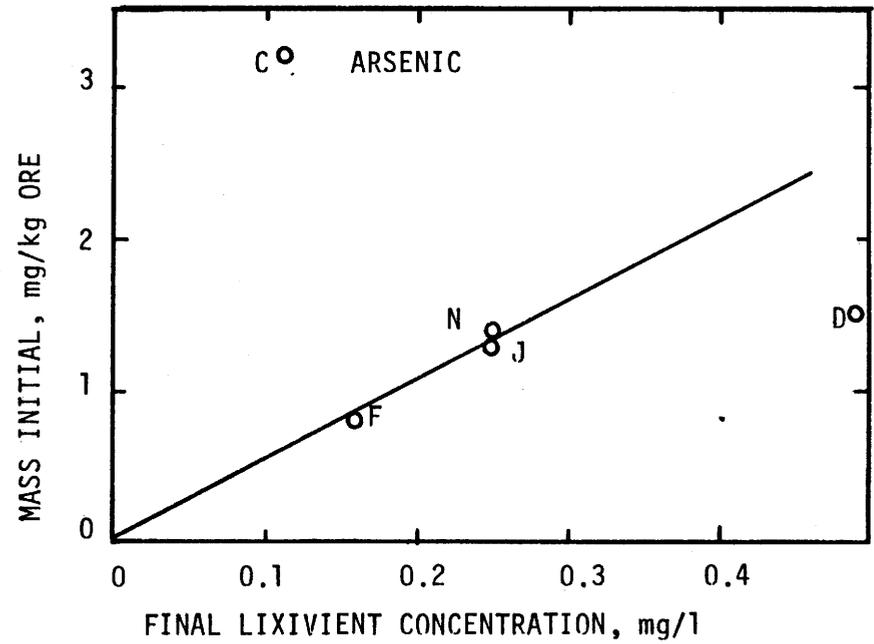
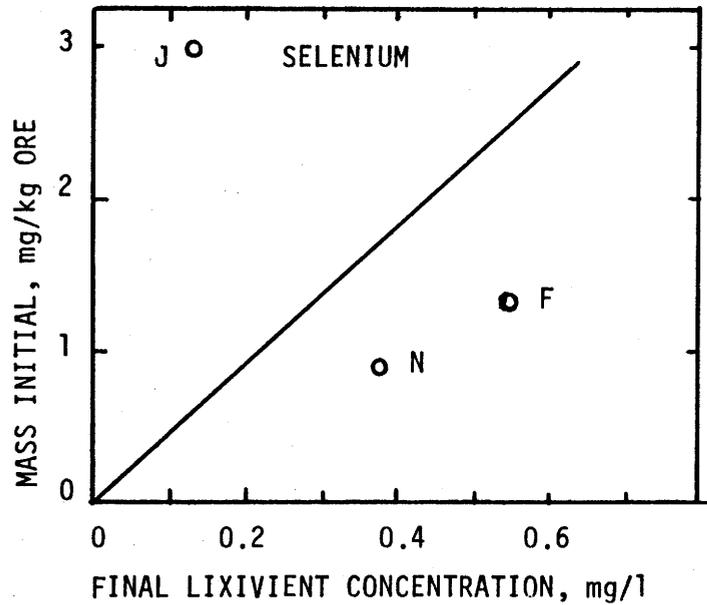
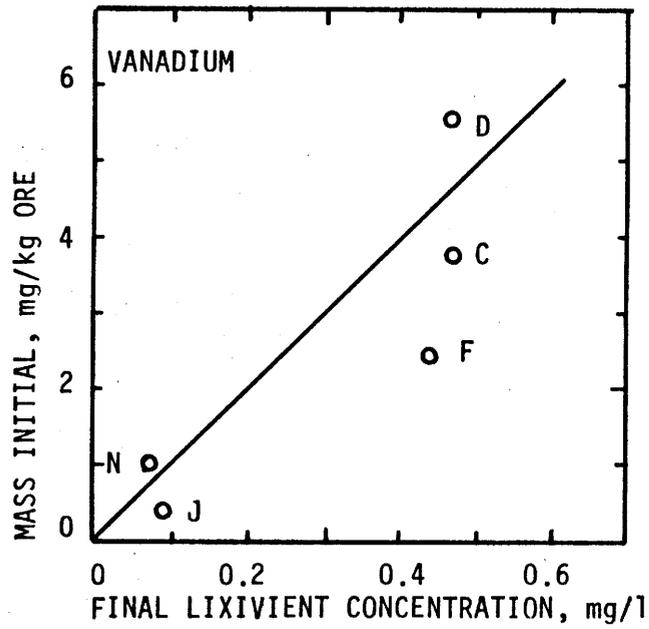


FIG. 16. MASS INITIAL VS FINAL LIXIVIANT CONCENTRATION. VANADIUM, SELENIUM, AND ARSENIC.

### Photomicrography

Scanning Electron Microscope (SEM) photomicrographs were taken for samples of the sandstones prior to experimental alteration. Plates 1 and 2 show representative photomicrographs of the Wyoming sand grains. Plate 1 is enlarged 220 times and Plate 2 is enlarged 2400 times. In Plate 1, two grains are shown on the left and right sides of the picture with typical pore space in between the grains. A rather large amount of debris including clay minerals can be seen between the grains. Plate 2 shows an enlargement of the contact of the grain on the left with the material in the pore from Plate 1. Plate 2 shows a large amount of material in between the grains and shows potential zones of higher permeability which are the dark areas on the photomicrograph. These zones of higher permeability occur at the contact with the grain and pore material and in between the fine-grained material that fills the pore space. In general, the grains themselves were found to be solid particles with no zones of permeability which could transmit water. Plate 2 shows that there are zones, such as between clay minerals, where water may be transmitted at a faster rate and zones where water may be trapped. SEM analysis tends to support the kinetic model that proposed the existence of large and small pore spaces which allow transmission of fluid at different rates.

### Speciation of Heavy Elements

The geochemical computer model, WATEQFC, was used to calculate the speciation of heavy elements in the experimental leach and groundwater solutions. Appendix B shows the experimental conditions and concentrations

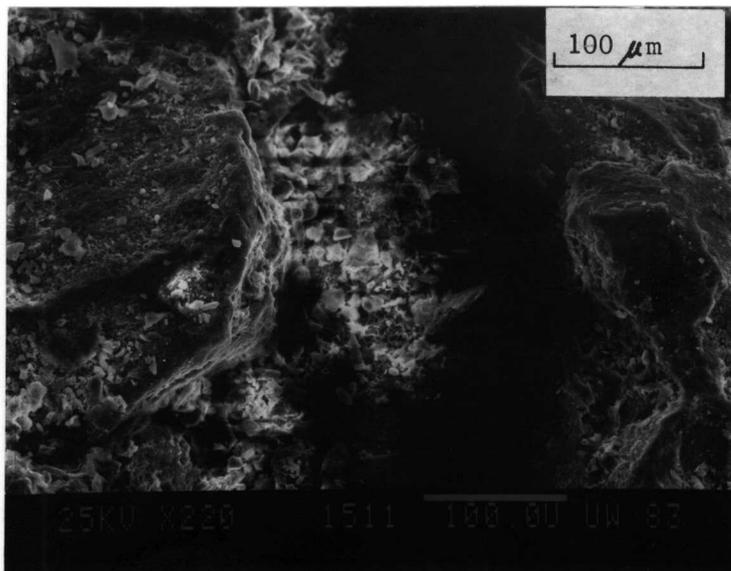


Plate 1. SEM Photomicrograph of Wyoming Sandstone showing two grains with abundant fine-grained material between the grains.

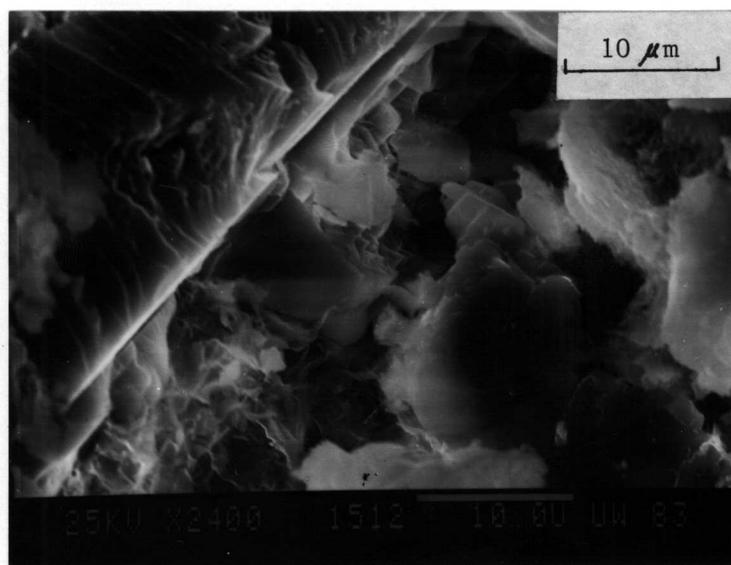


Plate 2. SEM Photomicrograph of Wyoming Sandstone showing boundary of a larger grain with fine-grained material and potential zones for higher permeability.

of the leach solution used in each run. For the leach solution input analyses consisted of the concentrations of ammonia (301 ppm), bicarbonate (309.9 ppm) and carbonate (249.6 ppm), baseline concentrations for the other anions and cations, and the metal concentrations which were analyzed in the leach solutions. PE was calculated from an assumed value of dissolved oxygen (1.0 ppm) which seemed to be a reasonable value at the end of the leaching stage in the experiments. The input pH of the leach solution was 8.5 and temperature was 25° C. Input values for groundwater calculations consisted of the metal concentrations determined from the groundwater analyses and baseline analyses for major ions. Dissolved oxygen concentrations for the groundwater calculations were varied between 1.0 and 0.01 ppm to examine the effects of changing the redox conditions on the speciation and saturation of the metals. Groundwater pH was 8.0 and the temperature was 25° C.

WATEQFC analysis showed that for water analyses from runs using both the Wyoming and Texas sandstones the metals occurred as anionic species. In the final leach solution the following species were predicted to be stable:  $\text{H}_2\text{AsO}_4^-$ ,  $\text{MoO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$ , and  $\text{HVO}_4^{2-}$ . Uranium was predicted to be speciated as  $\text{UO}_2(\text{CO}_3)_3^{4-}$  with much lower concentrations of  $\text{UO}_2(\text{CO}_3)_2^{2-}$  and  $\text{UO}_2(\text{HPO}_4)_2^{2-}$ . The computer model suggested that the metals in the experimental leach solutions were in the oxidized form. Supersaturation with respect to solid phases was calculated for uranium (and molybdenum in runs with the Texas sandstone). Uranium was slightly supersaturated with respect to uramphite  $((\text{NH}_4)_2(\text{UO}_2)_2(\text{PO}_4)_2$ . Supersaturated molybdenum phases include wulfenite ( $\text{PbMoO}_4$ ) and powellite ( $\text{CaMoO}_4$ ).

WATEQFC calculations of the groundwater solution shows that the metals may form the same species as in the leach solution and would be much lower in concentration. The concentration of vanadium in the experimental groundwater solutions appears to be high enough to precipitate uranium in the form of carnotite or tyuyamunite ( $\text{Ca}$  or  $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot n(\text{H}_2\text{O})$  respectively). Variations of the input dissolved oxygen concentration (and the calculated values for pE) did not appreciably change the results of WATEQFC. Even for very low residual concentrations of dissolved oxygen, the computer model predicted that the metals would be primarily in the oxidized form of the species.

The computer model also showed that iron oxides including hematite and  $\text{Fe}(\text{OH})_3$  (amorphous) could be expected to be stable phases in the leach and groundwater solutions in the experiments. The experimental conditions were not so highly reducing that iron would be reduced to  $\text{Fe}^{2+}$  in the solutions.

To summarize the result of the mobility of the heavy elements in groundwaters flowing through in-situ mine sites, the metals are likely to be oxidized, anionic species. Since strong oxidants are used to leach the uranium, other metals are oxidized and in their mobile forms. Iron and manganese oxides play a very large role in adsorption and precipitation processes of the metals. However, since the metals were typically in the anionic form and the surface charge on the iron oxides in an alkaline solution is negative, adsorption may tend to be minimized. Arsenate may be only slightly adsorbed in the alkaline groundwater (Frost and Griffin, 1977) and may coprecipitate with iron (Wilson and Hawkins, 1978). Molybdenum appears to be absent in many of the sandstone deposits in Wyoming. However, molybdenum may be mobile as the oxidized form where it

is present such as in the South Texas deposits. Selenium is most likely in the reduced selenite ( $\text{SeO}_3^{2-}$ ) form and its concentration in groundwater is expected to be low due to adsorption on iron oxides (Howard, 1977). Uranium is in the oxidized form as complexed carbonate species. Vanadium is probably limited in concentration in the groundwater due to formation of uranium-vanadium phases such as carnotite.

### CONCLUSIONS

The specific conclusions of the research are as follows:

1. The mechanism of release of heavy elements to groundwater under laboratory conditions using a typical Wyoming and Texas sandstone ore appears to be controlled by a diffusion process.

2. The rate of release of heavy elements studied in this work was seen to be readily modeled by an overall mass transfer model. The rate of mass transfer was proportional to the concentration difference between the bulk fluid and the internal fluid in the restricted flow passages.

3. The release of heavy elements was seen to be a slow process with overall mass transfer coefficients less than  $0.05 \text{ days}^{-1}$  at typical groundwater flow velocities.

4. The form of heavy elements were predicted to be anions such as  $\text{H}_2\text{AsO}_4^-$ ,  $\text{MoO}_4^{2-}$ ,  $\text{SeO}_3^{2-}$ ,  $\text{HVO}_4^{2-}$ , and  $\text{UO}_2(\text{CO}_3)_3^{4-}$ .

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(Using Wyoming Ore)

Groundwater Data in PPM When Appropriate

<u>Sample</u>	<u>As</u>	<u>U</u>	<u>V</u>	<u>Ln(C*/C*-C)</u>			<u>Days</u>	<u>Bed Volumes</u>
				<u>As</u>	<u>U</u>	<u>V</u>		
1	0.01	0.37	0.04	0.10	0.05	0.09	0.1	26
2	0.06	0.36	0.05	0.92	0.05	0.12	0.5	108
3	0.01	0.35	0.05	0.10	0.05	0.12	0.7	142
4	0.03	0.39	0.07	0.34	0.05	0.18	2.7	540
5	0.04	0.40	0.07	0.50	0.05	0.18	3.6	713
6	0.04	0.41	0.08	0.50	0.06	0.22	4.1	813
7	0.07	0.45	0.08	1.32	0.06	0.22	4.6	923
8	0.03	0.81	0.09	0.35	0.12	0.26	10.1	2018
9	0.04	0.93	0.09	0.53	0.14	0.27	12.8	2564
10	0.04	0.99	0.10	0.10	0.16	0.32	14.1	2827
11	0.05	1.09	0.10	0.77	0.18	0.34	16.2	3252
12	0.05	1.30	0.10	0.79	0.23	0.36	19.1	3825
13	0.06	1.55	0.11	1.16	0.29	0.44	20.2	4050
14	0.06	1.60	0.10	1.23	0.33	0.41	25.2	5053
15	0.06	1.65	0.10	1.33	0.36	0.44	28.2	5647
16	0.06	1.50	0.10	1.44	0.33	0.49	29.3	5864
17	0.06	2.05	0.11	1.60	0.58	0.65	33.4	6677
18	0.06	2.15	0.11	1.83	0.72	0.76	34.3	6865
19	0.05	2.30	0.11	1.27	1.00	0.95	37.2	7447
20	0.05	2.34	0.11	1.44	1.40	1.30	40.0	8007
21	0.06	2.47	0.11	0.00	0.00	0.00	42.8	8564

	<u>As</u>	<u>U</u>	<u>V</u>
Final Leach Solution (C*Initial)	.11	7.9	.47
Mass Initial	.32	6.0	.38

## APPENDIX "A"

RUN D

(Using Wyoming Ore)

Groundwater Data in PPM When Appropriate

<u>Sample</u>	<u>As</u>	<u>Se</u>	<u>U</u>	<u>V</u>	<u>LN(C*/C*-C)</u>				<u>Days</u>	<u>Bed Volumes</u>
					<u>As</u>	<u>Se</u>	<u>U</u>	<u>V</u>		
1	0.06	0.00	3.00	0.16	0.13	0.00	0.10	0.42	0.4	88
2	0.06	0.00	3.40	0.17	0.17	0.00	0.12	0.96	1.2	253
3	0.05	0.13	4.50	0.17	0.13	0.11	0.17	1.02	1.5	316
4	0.10	0.20	7.70	0.26	0.39	0.30	0.39	0.00	2.5	526
5	0.06	0.15	4.80	0.16	0.18	0.19	0.19	1.10	3.4	716
6	0.08	0.13	6.50	0.19	0.29	0.16	0.31	0.00	6.3	1326
7	0.07	0.12	6.20	0.16	0.25	0.15	0.31	1.95	9.7	2042
8	0.09	0.15	7.10	0.20	0.43	0.22	0.41	0.00	11.4	2400
9	0.11	0.14	7.90	0.20	0.83	0.21	0.57	0.00	25.3	5326
10	0.10	0.19	5.10	0.21	0.83	0.43	0.29	0.00	27.2	5726
11	0.20	0.25	8.10	0.25	0.00	1.82	0.84	0.00	30.4	6400
12	0.15	0.19	10.00	0.23	0.00	0.82	0.00	0.00	42.6	8968
13	0.14	0.20	8.40	0.21	0.00	0.00	0.00	0.00	45.2	9516

	<u>As</u>	<u>Se</u>	<u>U</u>	<u>V</u>
Final Leach Solution (C* Initial)	.50	1.3	35.1	.47
Mass Initial	.14	.25	13.1	.52

## APPENDIX "A"

RUN F

(Using Wyoming Ore)

Groundwater Data in PPM When Appropriate

<u>Sample</u>	<u>As</u>	<u>Se</u>	<u>U</u>	<u>V</u>	<u>LN(C*/C*-C)</u>				<u>Days</u>	<u>Bed Volume</u>
					<u>As</u>	<u>Se</u>	<u>U</u>	<u>V</u>		
1	0.05	0.08	2.80	0.17	0.38	0.16	0.13	0.49	2.0	196
2	0.06	0.06	3.20	0.18	0.99	0.16	0.27	1.12	4.2	412
3	0.05	0.06	3.40	0.17	0.66	0.16	0.32	1.00	6.0	588
4	0.04	0.11	3.50	0.18	0.45	0.50	0.36	1.29	6.8	666
5	0.05	0.09	3.80	0.17	0.75	0.35	0.48	1.22	9.0	882
6	0.06	0.11	4.00	0.17	1.47	0.61	0.66	1.45	11.1	1088
7	0.06	0.11	4.10	0.18	2.00	0.72	0.99	2.97	14.4	1411
8	0.06	0.13	4.30	0.18	0.00	0.00	0.00	0.00	16.5	1617
					<u>As</u>	<u>Se</u>	<u>U</u>	<u>V</u>		
Final Leach Solution (C* Initial)					.16	.54	22.3	.44		
Mass Initial					.07	.13	4.1	.23		

## APPENDIX "A"

RUN J

(Using Texas Ore)

Groundwater Data in PPM When Appropriate

Sample	<u>As</u>	<u>Mo</u>	<u>Se</u>	<u>U</u>	<u>V</u>	<u>LN(C*/C*-C)</u>					<u>Days</u>	<u>Bed Volume</u>
						<u>As</u>	<u>Mo</u>	<u>Se</u>	<u>U</u>	<u>V</u>		
1	0.03	2.00	0.05	4.90	0.02	0.13	0.20	0.18	0.14	0.25	0.7	32
2	0.05	2.50	0.05	6.60	0.02	0.30	0.69	0.23	0.38	0.44	7.9	359
3	0.05	2.60	0.06	7.40	0.02	0.30	0.85	0.31	0.53	0.46	13.0	591
4	0.05	2.50	0.09	7.40	0.02	0.31	0.85	0.65	0.58	0.49	15.0	682
5	0.05	2.50	0.06	7.80	0.03	0.31	1.06	0.33	0.81	2.77	18.0	818
6	0.12	2.80	0.13	9.20	0.03	0.00	0.00	0.00	0.00	0.00	25.0	1137
						<u>As</u>	<u>Mo</u>	<u>Se</u>	<u>U</u>	<u>V</u>		
Final Leach Solution (C* Initial)						.24	10.8	.03	37.8	.09		
Mass Initial						.12	2.4	.13	7.5	.03		

## APPENDIX "A"

RUN N

(Using Texas Ore)

Groundwater Data in PPM When Appropriate

<u>Sample</u>	<u>As</u>	<u>Mo</u>	<u>Se</u>	<u>U</u>	<u>V</u>	<u>LN(C*/C*-C)</u>					<u>Days</u>	<u>Bed Volume</u>
						<u>As</u>	<u>Mo</u>	<u>Se</u>	<u>U</u>	<u>V</u>		
1	0.04	1.80	0.05	3.00	0.02	0.17	0.19	0.14	0.09	0.34	0.8	175
2	0.04	2.30	0.06	3.90	0.02	0.21	0.48	0.27	0.21	0.38	2.0	437
3	0.05	2.40	0.06	4.40	0.02	0.29	0.56	0.28	0.28	0.39	3.0	656
4	0.07	2.40	0.07	4.70	0.02	0.50	0.60	0.39	0.35	0.39	4.0	874
5	0.06	2.50	0.06	4.90	0.02	0.40	0.76	0.31	0.47	0.40	5.0	1093
6	0.07	2.50	0.06	5.00	0.03	0.55	0.92	0.34	0.56	0.75	6.0	1312
7	0.07	2.40	0.06	5.20	0.02	0.59	1.05	0.38	0.91	0.41	7.0	1530
8	0.11	2.60	0.09	5.40	0.03	0.00	0.00	0.00	0.00	0.00	7.7	1683

	<u>As</u>	<u>Mo</u>	<u>Se</u>	<u>U</u>	<u>V</u>
Final Leach Solution (C* Initial)	.25	10.4	.38	33.7	.07
Mass Initial	.13	2.78	.09	5.0	.10

## APPENDIX "A"

Run T

(Using Texas Ore)

<u>Sample</u>	<u>Groundwater Data (PPM)</u>			<u>LN(C*/C*-C)</u>			<u>Days</u>	
	<u>Mo</u>	<u>Se</u>	<u>U</u>	<u>Mo</u>	<u>Se</u>	<u>U</u>		
1	0	0	0	0	0	0	0	
2	--	--	6	--	--	.55	0.1	
3	--	--	10	--	--	1.24	0.3	
4	2.9	20	--	.22	.21	--	1.0	
5	6.4	38	12.7	.57	.45	2.31	2.0	
6	8.9	7.4	13.9	.92	1.24	4.25	5.0	
7	--	--	14	--	--	4.95	7.0	
8	12	100	--	1.67	3.26	--	10.0	
9	12.5	103	--	1.86	4.64	--	15.0	
10	13.8	--	--	2.69	--	--	20.0	
11	12.6	--	--	1.91	--	--	26	
12	14.7	--	--	2.95	--	--	30	
Final Lixivient Concentration (C* Initial)						<u>Mo</u>	<u>Se</u>	<u>U</u>
						14.8	104	14.1

APPENDIX "B" - EXPERIMENTAL CONDITIONS

<u>Run</u>	<u>Ore Type</u>	<u>Ore Weight (g)</u>	<u>Ore Volume (cm<sup>3</sup>)</u>	<u>Leach Solution</u>	<u>Groundwater Flow Rate (ml/min)</u>	<u>Length of Run</u>
C	Wyoming	99.765	71.95	.03 ml H <sub>2</sub> O <sub>2</sub> .5 g/l NH <sub>4</sub> HCO <sub>3</sub> .5 g/l (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 1 l distilled H <sub>2</sub> O	10	43
C'	(Second Elution)			New 500 ml groundwater added	10	45
D	Wyoming	93	68.40	.03 ml H <sub>2</sub> O <sub>2</sub> .5 g/l NH <sub>4</sub> HCO <sub>3</sub> .5 g/l (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 1 l distilled H <sub>2</sub> O	10	45
D'	(Second Elution)			New 500 m groundwater added	10	50
F	Wyoming	97.943	73.47	.03 ml H <sub>2</sub> O <sub>2</sub> .5 g/l NH <sub>4</sub> HCO <sub>3</sub> .5 g/l (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 1 l artificial groundwater	5	16
J	Texas	100	63.34	.10 ml H <sub>2</sub> O <sub>2</sub> .5 g/l NH <sub>4</sub> HCO <sub>3</sub> .5 g/l (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 1 l distilled H <sub>2</sub> O	2	25

APPENDIX "B" - EXPERIMENTAL CONDITIONS (Cont'd.)

<u>Run</u>	<u>Ore Type</u>	<u>Ore Weight (g)</u>	<u>Ore Volume (cm<sup>3</sup>)</u>	<u>Leach Solution</u>	<u>Flow Rate (Ml/min)</u>	<u>Length of Run</u>
N	Texas	99.738	65.87	.10 ml H <sub>2</sub> O .5 g/l NH <sub>4</sub> HCO <sub>3</sub> .5 g/l (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 1 l distilled H <sub>2</sub> O	10	8
T	Texas	100 g		.25 g NH <sub>4</sub> HCO <sub>3</sub> .2 H <sub>2</sub> O <sub>2</sub> 1 l distilled H <sub>2</sub> O	50	40
T'	(Second Elution)				50	40

## APPENDIX C

## MASS BALANCE APPROACH TO CALCULATE C\*

The concentration of the fluid within the micropores of the rock (C\*) at the beginning of the groundwater stage was equal to the final concentration of the lixivient (C\*initial). At the end of the groundwater stage, C\* equaled the equilibrium concentration of the pore fluid (C\*end). To calculate the values of C\* at any time, equations 1 and 2 were used:

$$\text{mass released} = \Sigma(C_{\text{spls}})(V_{\text{spls}}) + (C_{\text{end}})(V_{\text{res}}) + (C_{\text{end}})(V_{\text{col}}) \quad (1)$$

$$C^* = C^*_{\text{initial}} ((\text{mass initial} - \text{mass released})/\text{mass initial}) \quad (2)$$

where:

C<sub>spls</sub> = Concentration in Samples, mg/ℓ

V<sub>spls</sub> - Volume of samples (ℓ)

C<sub>end</sub> = Concentration of groundwater at any time in the bulk fluid

V<sub>res</sub> = Fluid volume in reservoir (ℓ) at the end of run

V<sub>col</sub> = Volume of fluid in the column (measured at 0.06 ℓ)

C\*<sub>initial</sub> = Lixivient concentration (mg/ℓ) at the end of the leach step

C\* = Concentration associated with the micropore structure at any time, mg/ℓ

Equation 2 is solved first to obtain mass initial. This is achieved by running the experiments until no more heavy element is released to the circulating fluid. At that time, C = C\*. C\* initial is taken as the final lixivient concentration of heavy element. Thus, the only unknown is mass initial which can be determined.

Equation 2 is then used to calculate C\* at any time throughout the run. All other terms in the equation are known. Values for mass initial are given in Figures 15 and 16 for the heavy elements studied. The value was seen to be proportional to the final lixivient concentration.

## APPENDIX C (Cont'd.)

Values for mass initial are required for modeling and simulation of heavy element transport under field conditions.

Sample concentrations and volumes were summed, and the volume in the reservoir ( $V_{res}$ ) equaled the starting groundwater volume (0.5 l) less the total volume of samples less the fluid volume of the column. Values were known for  $C^*_{initial}$ ,  $C^*_{end}$  and the total mass released at the end (using equation 2), so that the mass initial (which is a constant for each run) was calculated as shown in equation 3.

$$\text{mass initial} = \frac{(C^*_{initial}) \cdot (\text{mass released})}{(C^*_{initial} - C^*_{end})} \quad (3)$$

From the calculated value for mass initial using equation 3, values for  $C^*$  were found using equation 2 for each sample. A FORTRAN V program was used to calculate values for mass released,  $C^*$  and  $\text{LN}(C^*/C^*-C)$  for each sample. Since the last value for  $C^*$  will equal the final groundwater equilibrium value ( $C$ ), the ratio of  $C^*/C^*-C$  will be undefined, so the program prints out the value of zero when this occurs.

```

PROGRAM CSTAR(INPUT,OUTPUT,TAPE5)

C
C
C THIS PROGRAM CALCULATES THE CONCENTRATIONS OF THE FLUID
C INSIDE THE MINERAL MICROPORES (C*) FOR EACH SAMPLE
C FOR EACH ELEMENT.
C
C INPUT VALUES ARE:
C
C THE FINAL LIXIVIENT CONCENTRATION (C*INITIAL)
C MASS INITIAL
C NUMBER OF SAMPLES IN THE RUN
C SAMPLE CONCENTRATIONS (MG/L)
C AND SAMPLE VOLUMES (L).
C
C**DATA TABLE**
C VSPL,VRES,VCOL : VOLUMES OF SAMPLES, RESERVOIR, AND COLUMN (L)
C C,CSTR,CLIX : CONCENTRATIONS OF SAMPLES, C*, AND LIXIVIENT
C*****
REAL C(29),C1(29),CLIX,CSTR,CLN,MI,MR
REAL VCOL,VRES,VSPL(29),VSPL1(29)
INTEGER N,I,J
PRINT*,'INPUT LIXIVIENT CONC.,MASS INITIAL, NUMBER OF SAMPLES'
READ*,CLIX,MI,N
DO 10 I=1,N
    PRINT*,'INPUT SAMPLE CONCENTRATION AND SAMPLE VOLUME'
    READ*,C(I),VSPL(I)
10 CONTINUE
WRITE(5,*) 'RUN N VANADIUM DATA'
WRITE(5,*) 'LIXIVIENT CONCENTRATION = ',CLIX
WRITE(5,*) 'MASS INITIAL=',MI
VCOL=0.060
VRES=0.440-VSPL(1)
C1(1)= C(1)
VSPL1(1)= VSPL(1)
DO 20 J=1,N
    MR=C1(J)*VSPL1(J)+C(J)*VRES+C(J)*VCOL
    CSTR=CLIX*((MI-MR)/(MI))
    IF(J.EQ.1) CSTR=CLIX
    IF(J.EQ.N) CSTR=C(N)
    IF ((CSTR-C(J)).GT.0) THEN
        CLN=ALOG(CSTR/(CSTR-C(J)))
    ELSE
        CLN=0
    ENDIF
    WRITE(5,*) '-----'
    WRITE(5,*) 'SAMPLE VOLUME=',VSPL(J)
    WRITE(5,*) 'SAMPLE CONCENTRATION =',C(J)
    WRITE(5,*) 'MASS RELEASED=',MR
    WRITE(5,*) 'C STAR =',CSTR
    WRITE(5,*) 'LN (C* / C* -C)=' ,CLN
    C1(J+1)=C1(J)+C(J+1)
    VSPL1(J+1)= VSPL1(J) + VSPL(J+1)
    VRES=VRES - VSPL(J+1)
20 CONTINUE
STOP
END

```

## APPENDIX D

HEAVY ELEMENT CONCENTRATIONS OF A URANIUM SANDSTONE DEPOSIT  
IN THE SOUTHERN POWDER RIVER BASIN, WYOMING (from Harris, 1982).

Core #	Elevation	U%	As%	Se%	V%
MXC-1	4884	ND	ND	ND	0.018
MXC-1	4881	0.178	0.003	0.005	0.010
MXC-1	4878	ND	0.002	0.004	0.015
MXC-1	4875	ND	0.005	0.021	0.009
MXC-2	4879	ND	0.004	0.001	0.056
MXC-2	4876	0.010	0.008	0.001	0.015
MXC-2	4873	0.286	0.007	0.008	0.026
MXC-2	4871	0.323	0.003	0.001	0.056
MXC-2	4869	ND	0.001	0.018	0.004
MXC-2	4858	ND	0.005	0.014	0.005
MXC-2	4853	ND	0.012	0.019	0.035
MXC-2	4851	0.052	0.010	0.086	0.047
MXC-2	4849	1.16	0.008	0.004	0.091
MXC-2	4847	0.443	0.005	0.002	0.026
MXC-2	4845	ND	0.009	0.008	0.041
MXC-3	4874	ND	ND	ND	0.038
MXC-3	4871	0.104	0.004	0.007	ND
MXC-3	4868	0.262	0.016	0.005	0.045
MXC-3	4866	ND	0.016	0.103	0.034
MXC-3	4862	ND	0.008	0.015	0.006
MXC-3	4860	0.114	0.004	0.007	0.010
MXC-3	4858	0.027	0.011	0.008	0.002
MXC-3	4856	0.233	0.007	0.010	0.014
MXC-3	4853	0.471	0.002	0.005	0.003
MXC-3	4850	0.263	0.003	0.002	0.018
MXC-4	4865	NE	0.010	0.002	ND
MXC-4	4862	0.092	0.002	0.002	ND
MXC-4	4860	0.305	0.010	0.006	ND
MXC-4	4858	0.198	0.003	ND	ND
MXC-4	4856	0.197	0.007	0.012	ND
MXC-4	4854	0.181	0.007	0.006	0.001
MXC-4	4852	0.047	0.005	0.008	0.003
MXC-4	4849	0.044	0.006	0.002	ND
MXC-5	4865	ND	0.008	0.005	0.004
MXD-5	4860	ND	0.010	0.006	ND
MXC-5	4855	ND	ND	ND	ND
MXC-5	4850	ND	ND	0.006	0.004
MXC-5	4846	ND	0.008	0.004	0.007

ND - Not detected

## APPENDIX E

 BASELINE GROUNDWATER ANALYSIS, IRIGARAY SITE  
 (In mg/l where appropriate)

<u>Date Collected</u>	<u>4/23/80</u>	<u>4/30/80</u>	<u>5/7/80</u>
Calcium	10.6	10.7	10.3
Magnesium	1.20	1.14	1.07
Sodium	143	144	142
Potassium	1.8	2.2	2.3
Ammonium	<0.5	<0.5	<0.5
Carbonate	20.04	23.4	13.2
Bicarbonate	72.47	68.2	85.8
Sulfate	234	228	233
Chloride	10.2	10.3	9.5
Total Nitrogen (NO <sub>2</sub> - HNO <sub>3</sub> )	<1.0	<1.0	<1.0
Fluoride	0.3	0.3	0.3
Silica (SiO <sub>2</sub> )	8.9	8.7	8.1
TDS	482.2	488.4	503.8
Conductance	722	775	769
Alkalinity (CaCO <sub>3</sub> )	92.8	95.6	92.3
pH	9.2	9.2	8.6
Aluminum	< .05	< .05	< .05
Arsenic	< .002	< .002	< .002
Barium	< .05	< .05	< .05
Boron	< .2	< .2	< .2
Cadmium	< .002	< .002	< .002
Chromium	.005	.005	.005
Copper	< .005	< .005	< .005
Iron	.21	.08	.02
Lead	< .005	< .005	< .005
Manganese	.009	.008	.005
Mercury	< .0002	< .0002	< .0002
Molybdenum	< .05	< .05	< .05
Nickel	< .01	< .01	< .01
Selenium	< .002	< .002	< .002

## APPENDIX E (Cont'd.)

<u>Date Collected</u>	<u>4/23/80</u>	<u>4/30/80</u>	<u>5/7/80</u>
Silver	< .002	< .002	< .002
Uranium (U <sub>3</sub> O <sub>8</sub> )	.02	.01	.09
Vanadium	< .05	< .05	< .05
Zinc	.03	.01	< .01