
Methods of Minimizing Ground-Water Contamination From In Situ Leach Uranium Mining

Final Report

Manuscript Completed: December 1984

Date Published: March 1985

Prepared by

W. J. Deutsch, W. J. Martin, L. E. Eary, R. J. Serne

Pacific Northwest Laboratory

Richland, WA 99352

Prepared for

Division of Radiation Programs and Earth Sciences

Office of Nuclear Regulatory Research

U.S. Nuclear Regulatory Commission

Washington, D.C. 20545

NRC File B2379

ABSTRACT

This is the final report of a research project designed to study methods of minimizing ground-water contamination from in situ leach uranium mining. Fieldwork and laboratory experiments were conducted to identify excursion indicators for monitoring purposes during mining, and to evaluate effective aquifer restoration techniques following mining. Many of the solution constituents were found to be too reactive with the aquifer sediments to reliably indicate excursion of leaching solution from the ore zone; however, in many cases, the concentrations of chloride and sulfate and the total dissolved solids level of the solution were found to be good excursion indicators.

Aquifer restoration by ground-water sweeping consumed large quantities of ground water and was not effective for the redox-sensitive contaminants often present in the ore zone. Surface treatment methods such as reverse osmosis and electrodialysis were effective in reducing the amount of water used, but also had the potential for creating conditions in the aquifer under which the redox-sensitive contaminants would be mobile. In situ restoration by chemical reduction, in which a reducing agent is added to the solution recirculated through the ore zone during restoration, can restore the ore-zone sediment as well as the ground water. This method could lead to a stable chemical condition in the aquifer similar to conditions before mining.

CONTENTS

ABSTRACT.....	iii
ACKNOWLEDGMENTS.....	xi
RELATED PUBLICATIONS.....	xiii
EXECUTIVE SUMMARY.....	xv
INTRODUCTION.....	1
CONCLUSIONS.....	3
RECOMMENDATIONS.....	5
LEACHING METHODS AND THE PRODUCTION/MOBILITY OF CONTAMINANTS.....	7
THE LEACHING PROCESS.....	7
THE PRODUCTION OF GROUND-WATER CONTAMINANTS DURING IN SITU LEACH MINING.....	11
GENERATION OF CONTAMINANTS BY THE PRODUCTION PLANT.....	12
SEDIMENT-DERIVED CONTAMINANTS.....	12
CONTAMINANT MOBILITY.....	15
EXCURSION DETECTION.....	17
AQUIFER RESTORATION.....	21
INDUCED-RESTORATION METHODS.....	21
Ground-Water Sweeping.....	21
Surface Treatment and Recirculation.....	22
In Situ Treatment Methods.....	24
EXPERIMENTAL STUDIES.....	30
Field Sampling Procedures.....	31
Analytical Methods.....	32
Experimental Procedures.....	34

EVALUATION OF NATURAL RESTORATION.....	39
Results of Static Batch Experiments Using Sediments from a Texas In Situ Leach Uranium Mine.....	40
Results of Static Batch Experiments Evaluating Natural Restoration at a Wyoming In Situ Leach Uranium Mine.....	46
Results of Column Experiments Evaluating Natural Restoration at a Texas In Situ Leach Uranium Mine.....	52
Results of Column Experiments Evaluating Natural Restoration at a Wyoming In Situ Leach Uranium Facility.....	54
EVALUATION OF APPLIED RESTORATION METHODS.....	62
Results of Ground-Water Sweeping Restoration Experiment.....	63
Results of Chemical Addition Batch Experiments.....	65
Results of Chemical Addition Column Experiments.....	76
SUMMARY OF EXPERIMENTAL RESULTS.....	81
REFERENCES.....	83
APPENDIX A - ANALYTICAL DATA FROM BATCH EXPERIMENTS WITH TEXAS SEDIMENTS.....	A-1
APPENDIX B - ANALYTICAL DATA FROM BATCH EXPERIMENTS WITH WYOMING SEDIMENTS.....	B-1
APPENDIX C - ANALYTICAL DATA FROM COLUMN EXPERIMENTS ON NATURAL RESTORATION.....	C-1
APPENDIX D - ANALYTICAL DATA FROM SULFIDE ADDITION EXPERIMENTS.....	D-1

FIGURES

1	Schematic of an In Situ Leaching Operation at a Roll-Front Uranium Deposit.....	8
2	Typical Well Configurations.....	9
3	Schematic Diagram of a Uranium Roll-Front Deposit.....	14
4	Aquifer Restoration Aided by Chemical Reduction.....	26
5	Dissolved Uranium Tricarbonate and HS^- Activities and pH in Equilibrium with Uraninite and Elemental Sulfur.....	27
6	Dissolved Uranium Tricarbonate, $\text{S}_2\text{O}_3^{2-}$, and HS^- Activities in Equilibrium with Uraninite and FeS	29
7	Activity of HS^- in Equilibrium with $\text{Fe}(\text{OH})_3$, S rhmb, and FeS or Pyrite.....	30
8	Flow Diagram of Ground-Water Monitoring System.....	31
9	Felmar Chamber and Gas Punging System.....	36
10	Laboratory Apparatus for Batch Sulfide Experiment.....	37
11	Column Design.....	39
12	Schematic of Column Test Apparatus.....	40
13	Calcium Solution Concentrations in Batch Experiments with Texas Sediments.....	41
14	Sulfate Solution Concentrations in Batch Experiments with Texas Sediments.....	41
15	Iron Concentrations in Batch Experiments with Texas Sediments.....	43
16	Dissolved Uranium Concentrations for the Batch Experiments with Texas Sediment.....	44
17	Dissolved Calcium Concentrations for Batch Experiments with Wyoming Sediments.....	48
18	Dissolved Sulfate Concentrations for Batch Experiments with Wyoming Sediments.....	48

19	Dissolved Iron Concentrations for the Batch Experiments with Wyoming Sediment.....	49
20	Eh Values for the Batch Experiments with Wyoming Sediments.....	49
21	pH Values for the Batch Experiments with Wyoming Sediments.....	50
22	Dissolved Uranium Concentrations for the Batch Experiments with Wyoming Sediments	51
23	Dissolved Uranium Concentration of Column Effluents as a Function of the Cumulative Amount of Solution Eluted from the Texas Natural Restoration Experiments.....	54
24	Dissolved Uranium Concentration in Effluent from Texas and Wyoming Natural Restoration Column Experiments.....	56
25	Effluent Concentrations of Calcium, Magnesium, and Sodium from the Wyoming Natural Restoration Experiments.....	58
26	Comparison of Predicted Major Cation Effluent Compositions with Analytical Values for the Wyoming Natural Restoration Column Experiment.....	61
27	Comparison of Predicted Major Anion Effluent Compositions with Analytical Values for the Wyoming Natural Restoration Column Experiment.....	61
28	Comparison of Predicted Uranium Effluent Composition with Observed Values for the Wyoming Natural Restoration Column Experiment.....	62
29	Uranium Effluent Concentrations from Ground-Water Sweeping Columns 1 and 2.....	63
30	Molybdenum Effluent Concentrations from Ground-Water Sweeping Columns 1 and 2.....	65
31	Plots Showing the Change in Eh and pH After Addition of Na_2S to Distilled, Deaerated Water and Distilled, Air-Saturated Water.....	67
32	Change in Eh and pH for Texas Lixiviant.....	68
33	Changes in Eh and pH of Mixtures of Texas Lixiviant and Iron-Oxide-Coated Sand.....	70
34	a) Change in Uranium Concentration in the Texas Lixiviant Caused by Adsorption onto the Iron-Oxide-Coated Sand for Duplicate Experiments, b) Change in Uranium Concentration in Texas Lixiviant and Iron-Oxide-Coated Sand After Adding 0.01 molar Na_2S at 23 h.....	72

35	Changes in Uranium Concentration in Mixtures of Lixiviant and Texas Leached Ore Showing the Effects of Na_2S Addition.....	74
36	Results from Four Experiments With Texas Lixiviant and Texas Leached Ore Showing Changes in a) pH after Na_2S Addition at 160 h, and b) Eh after Na_2S Addition at 164 h.....	75
37	Uranium Concentration in Column Effluents from Sulfide Addition Experiments.....	77
38	Calcium Concentration of Column Effluents from the Sulfide Addition Experiments.....	78
39	Sulfate Concentration of Column Effluents from the Sulfide Addition Experiments.....	78
40	pH of Influent and Effluents from Sulfide Addition Column Experiment.....	79
41	Eh of Column Effluents from Sulfide Addition Experiment.....	80

TABLES

1	Mean Concentration and Standard Deviation of Selected Constituents in Texas Ground Water and Lixiviant.....	18
2	Mean Composition of Ground-Water and Lixiviant Samples at a Wyoming In Situ Leach Uranium Mine.....	19
3	Thermodynamic Data for Computations.....	28
4	Sample Preservation Methods Used at the North Platte Mine.....	33
5	Solution/Sediment Mixtures Used in Batch System.....	36
6	Pyrite Content of Sediment.....	56
7	Results of Modeling Wyoming Natural Restoration Column Experiment: Sediment Storage Phase.....	59

ACKNOWLEDGMENTS

This research was supported by the Methods of Minimizing Ground-Water Contamination from In Situ Leach Uranium Mining Project conducted by Pacific Northwest Laboratory (PNL). The project was sponsored by the office of Nuclear Regulatory Research of the U.S. Nuclear Regulatory Commission (NRC). The support of our NRC project manager, Colleen Ostrowski, was greatly appreciated.

We also wish to acknowledge the management efforts of the PNL Uranium Mill Tailings Program Office, particularly Mike Foley. The following PNL staff contributed in the designated areas:

Andrew R. Felmy	Geochemical modeling and experimental design
Douglas R. Sherwood	Experimental studies and geochemical modeling
Bruce M. Sass	Theoretical calculations of sulfur stability
Stephanie B. McLaurine	Experimental studies and laboratory analyses
Tom R. Garland	Sample collection and field analyses
John W. Shade	X-ray diffractometry and mineralogy
Alan W. Lautensleger	Ion chromatography
Donald E. Rinehart	Inductively coupled plasma spectroscopy
Thomas G. Walker	Inductively coupled plasma spectroscopy
Lorraine P. White	Inductively coupled plasma spectroscopy
Michelle M. Messmer	Ion chromatography
Karl H. Pool	Supervision of analytical laboratory
Homer E. Kissinger	X-ray diffractometry
Ronald W. Sanders	X-ray fluorescence analysis
Laverne L. Baker	X-ray fluorescence analysis
Marvin J. Nason	Atomic absorption spectroscopy
Clark O. Harvey	Pulsed laser fluorescence analysis
Janelle L. Gowns-Berg	Technical editing
Glendon W. Gee	Technical review

We would also like to thank Ms. Deidre Berg and the Sigma V word processing team for their efforts in preparing this document.

We wish to express our appreciation to Uranium Resources Inc. for their cooperation in collecting samples at their mine sites in Texas and Wyoming. Bill McKnight, Steve Lampkins, Kelly Biddle, and Tony Olivas were especially helpful.

Finally, the efforts of our subcontractor, the Twin Cities Research Center of the U.S. Bureau of Mines are acknowledged. Daryl Tweeton was in charge of the Bureau of Mines work, which included operator surveys, laboratory experiments and computer model development. The assistance of Pamela Watson and Kent Peterson (formerly) at the Bureau of Mines is also greatly appreciated.

RELATED PUBLICATIONS

A number of other publications that provide background information and additional laboratory and field data have been published during this project.

- Bell, M. E., W. J. Deutsch and R. J. Serne. 1983. "Laboratory Studies on Natural Restoration of Ground Water After In Situ Leach Uranium Mining." In Proceedings of the Third National Symposium on Aquifer Restoration and Ground-Water Monitoring, ed. D. M. Nielson, National Water Well Association, Worthington, Ohio.
- Deutsch, W. J., R. J. Serne, N. E. Bell, and W. J. Martin. 1984. Aquifer Restoration at In Situ Leach Uranium Mines: Evidence for Natural Restoration Processes. NUREG/CR-3136, U.S. Nuclear Regulatory Commission, Washington, D.C.
- Deutsch, W. J., N. E. Bell, R. W. Mercer, R. J. Serne, J. W. Shade and D. R. Tweeton. 1984. Aquifer Restoration Techniques for In Situ Leach Uranium Mines. NUREG/CR-3104, U.S. Nuclear Regulatory Commission, Washington, D.C.
- Sherwood, D. R., C. J. Hostettler and W. J. Deutsch. 1984. "Identification of Chemical Processes Influencing Constituent Mobility During In Situ Uranium Leaching." PNL-SA-12173, Presented at the Symposium on Practical Applications of Ground Water Models, August 15-17, 1984, Columbus, Ohio.
- Deutsch, W. J., L. E. Eary, W. J. Martin and S. B. McLaurine. 1985. "The Use of Sodium Sulfide to Restore Aquifers Subjected to In Situ Leaching of Uranium Ore Deposits." To be presented at and published in the Proceedings of the National Water Well Assoc. Western Regional Ground Water Conference, held in Reno, Nevada, January 15-16, 1985.

EXECUTIVE SUMMARY

This is the final report of a 3-year research project conducted by Pacific Northwest Laboratory (PNL) for the U.S. Nuclear Regulatory Commission (NRC) to study methods of minimizing ground-water contamination at in situ leach uranium mining sites. This method of mining is used extensively in the western United States because it has low capital costs and impacts the environment less extensively than conventional mining techniques. The ore zones mined, however, are typically found in aquifers that contain ground water that is of suitable quality for many uses. Consequently, it is necessary to ensure that the mining operation does not contaminate this resource.

Our work was focused on the early detection of a loss of control of the leaching solution during mining (an excursion) and on aquifer restoration at the termination of mining. Samples of ground water, leaching solution, and aquifer sediments were collected at mine sites in Texas and Wyoming. These materials were used in laboratory experiments to identify practical indicators of an excursion and to evaluate restoration methods currently in use or considered for future use.

We found that the leaching process itself is very efficient and only affects a small quantity of the aquifer material. It is fairly selective for uranium minerals, although other minerals containing the redox-sensitive elements iron, sulfur, arsenic, selenium, and molybdenum are also dissolved by the oxidation process. Secondary reactions in the aquifer may also dissolve carbonate minerals. During surface treatment of the uranium-bearing leaching solution, sodium and chloride may be added to the leaching solution, which is then recirculated through the aquifer. The level of total dissolved solids in the leaching solution is typically four times that of the native ground water. The treatment of the leaching solution at the surface plant and the reactions between the leaching solution and the sediment produce many potential contaminants for the aquifer. However, these contaminants are also potential indicators of excursions from the leach field during mining. We evaluated the usefulness of many of these solution constituents as excursion indicators and found that, in most cases, the redox-sensitive elements and the major cations are too reactive with the sediments to be reliable indicators. The major anions (chloride and sulfate) were determined to be less reactive and may be effective indicators, providing that their concentrations in the leaching solution are significantly above that in the ground water. In addition, the level of the total dissolved solids in solution appears to be a relatively non-reactive parameter and may be a useful indicator.

Aquifer restoration at the termination of in situ leaching is required to ensure that residual leaching solution does not contaminate water supplies. We evaluated restoration methods that can be used to restore the water in the leach field and also studied the effect on solution composition of interactions of the leaching solution with sediments located down the hydrologic gradient from the leach field. It was determined that natural processes (such as mineral precipitation and adsorption) could remove a considerable amount of the contaminants from solution and could provide a good buffer between the mining

operation and other users of ground water in the vicinity of the mine. In fact, natural restoration appears to be a very effective method of lowering the dissolved concentration of redox-sensitive trace elements, especially uranium, which are frequently difficult contaminants to remove from the leaching solution using current restoration practices. However, natural restoration cannot be relied on to remove the major cations and anions from solution; therefore, the traditional applied restoration techniques, such as ground-water sweeping and surface treatment, must be used to lower the total dissolved solids level of the leaching solution remaining in the leach zone.

In the past, ground-water sweeping has been a very popular method of restoring the ore zone. However, this method involves long-term pumping of the well field and produces large quantities of ground water that must be treated as waste. Also, under certain circumstances, it appears that sweeping actually inhibits restoration for the redox-sensitive elements. Our laboratory experiments and the experiences of operators show that during ground-water sweeping, the concentration of redox-sensitive elements (particularly uranium, selenium, and molybdenum) does not decrease as might be expected if this method resulted in simple dilution and eventually total replacement of the water in the leached zone. Apparently, the new ground water introduced into the ore zone during sweeping results in the slow dissolution of minerals that contain redox-sensitive elements. In effect, the introduced water acts like a weak leaching solution and is not an effective restoration medium for some mine sites.

Several mine operators have used surface treatment methods, such as reverse osmosis and electrodialysis, to clean the solution pumped from the ore zone during restoration and then recirculate this treated solution through the leach field. These methods effectively decrease the amount of waste water generated during restoration, but they do not decrease the likelihood of continued slow dissolution of minerals containing redox-sensitive elements in the ore zone. In our laboratory experiments we added sodium sulfide to recirculated solution to create chemical conditions in the leached ore zone under which the redox-sensitive minerals would be stable. A sulfide-based reagent was selected because the original reducing conditions in the aquifers containing the ore zones are often a result of sulfide reduction processes. We found that adding relatively small amounts of sodium sulfide (5×10^{-3} molar) to the leaching solution and contacting it with the leached ore effectively lowered the uranium concentration of the leaching solution and produced sulfide compounds (probably FeS) in the sediment. Undesired side effects of the reaction (e.g., decreased permeability) were not observed during the experiments.

Based on the results of this project, we recommend that field studies be conducted to test the feasibility of using chemical reductants to enhance restoration at sites that potentially will be difficult to restore for the redox-sensitive elements. If the in situ chemical restoration method is shown to be viable at field sites, it could be used with surface treatment methods to restore both the ground water in the leach zone and to some extent the ore-zone sediment itself. Using a combination of these methods would lead to a more stable chemical condition for the restored zone than would be achieved by simple ground-water sweeping techniques. Furthermore, it appears that natural

restoration will also reduce the concentration of redox-sensitive contaminants that might migrate out of the restored zone. Natural restoration can be considered as an additional mechanism for removing contaminants from the ground water.

INTRODUCTION

In situ leach mining was first applied to uranium in the Shirley Basin of Wyoming in the early 1960s (Larson 1978). During the 1970s, a number of commercial operations were begun in Wyoming and Texas with pilot operations conducted in other western states. By 1979 it was estimated that in situ leach mining accounted for 9% of the uranium mined in the United States (Larson 1981). The in situ mining technique consists of injecting a leaching solution, termed a lixiviant, into a confined aquifer containing the uranium ore. The uranium minerals dissolve in the lixiviant, which is then pumped from the aquifer and treated at a surface plant to remove and concentrate the uranium. The lixiviant is refortified and reinjected into the ore zone to continue the leaching process. A particular leach field may be mined for a number of years before the ore supply is exhausted. During this time, the mine operators must monitor for excursions of the leaching solution by sampling a ring of monitor wells around the leach field. At the termination of mining, the operator must restore the quality of the ground water to a predetermined level established in the mining permit granted by the U.S. Nuclear Regulatory Commission (NRC) or the appropriate state regulatory agency. Monitoring during mining and aquifer restoration after mining are important to ensure that contaminants produced in the leach field during mining do not degrade the local ground-water supply.

This project was started during 1981 to study methods of minimizing ground-water contamination from in situ leach mining of uranium. It was sponsored by the Office of Nuclear Research of the NRC. The majority of the work was carried out at Pacific Northwest Laboratory (PNL) operated by Battelle Memorial Institute for the U.S. Department of Energy (DOE). Additional studies were performed at the Twin Cities Research Center of the U.S. Bureau of Mines. The primary issues addressed by this research dealt with establishing useful indicators to detect excursions and with evaluating currently used or suggested aquifer restoration methods. A number of types of lixiviants have been used at uranium leach mines; however, for this study the sodium carbonate-bicarbonate type was emphasized because it is commonly used at the present time and appears to be the preferred lixiviant for new plants. Mine sites in Texas and Wyoming were sampled and a series of laboratory experiments were conducted over a 3-year period to study monitoring and restoration methods.

This final report on the project includes a description of the chemistry of leaching of uranium minerals and the production and mobility of contaminants associated with the mining operation. This is followed by a section on the selection of excursion indicators based on the chemistry of the ground water and lixiviant, and the estimated mobility of dissolved species in the aquifer. The majority of the report discusses aquifer restoration methods and the results of experiments designed to evaluate these methods. Recommendations are made for developing a restoration scheme that couples some of the currently used techniques with the chemical reduction method to better re-establish the original chemical condition of the aquifer.

CONCLUSIONS

The presence of mine-generated contaminants in the ground water can be used to identify excursions during the leaching operation, but these contaminants must be removed from the ground water at the termination of mining or shown to be immobile in the natural aquifer system. During this project, field and laboratory studies were conducted to evaluate excursion indicators, aquifer restoration methods, and, in general, the mobility of contaminants in the aquifer environment. The following conclusions are drawn from these studies:

- Excursion Indicators--Dissolved chloride and sulfate should be good indicators of an excursion of lixiviant out of the leach field into the surrounding aquifer(s) if the concentration of these constituents in the lixiviant is significantly higher than that in the ground water. The total dissolved solids level of the solution should also be a good excursion indicator. The remaining solution constituents are either too reactive with the sediments, or generally, do not vary enough between the lixiviant and the ground water to make them good candidates for indicators.
- Natural Restoration--Natural restoration processes such as mineral precipitation and adsorption that occur between the residual lixiviant and the aquifer sediment will remove some contaminants from solution. Reducing conditions exist downgradient from the ore zone and under these conditions the redox-sensitive trace elements (uranium, arsenic, selenium, and molybdenum) will form relatively insoluble compounds. As a consequence, their solution concentrations will be lowered, perhaps to the restoration limit, after a period of contact with the aquifer sediment adjacent to the leached ore zone.
- Ground-Water Sweeping--Restoration by ground-water sweeping alone generates large volumes of waste water and is not generally effective for the redox-sensitive trace metals. Residual minerals containing these trace metals in their reduced valence forms continue to slowly dissolve during the sweeping process because of the flow of oxidizing ground water into the leached zone. The slow dissolution reactions maintain the concentration of these contaminants at relatively high levels during sweeping.
- Surface Treatment--Cleaning ground water at a surface treatment plant and recirculating it through the leached zone lowers the total dissolved solids level of the solution remaining in the ore zone, conserves ground water, and reduces the amount of waste solution that must be disposed of. An operator survey showed that both electro-dialysis and reverse osmosis techniques have been used successfully at in situ leach operations for at least partial restoration. As with ground-water sweeping, these methods can lead to continued mobility of the redox-sensitive trace elements.

- In Situ Restoration--The addition of sulfide to the ore zone during restoration can produce reducing conditions in the aquifer that will immobilize uranium, and, by analogy, other redox-sensitive elements. This technique reestablishes reducing conditions in the ore zone and may lead to long-term restoration of the aquifer system. However, the concentration of major cations and anions is not significantly affected by the reductant. Therefore, this technique should be used in conjunction with one of the other applied restoration techniques to take advantage of the superior qualities of each method.

RECOMMENDATIONS

The selection of an aquifer restoration technique to use at a particular site will depend on local conditions that include the characteristics of the ore zone aquifer and the method of leaching that was used. Both the Texas and Wyoming mine sites evaluated in this study used ground water amended with sodium carbonate/bicarbonate and oxygen as the leaching solution. These two sites are similar to other uranium ore deposits mined by in situ methods in the two states, and the type of lixiviant used is representative of that commonly used at this time. However, note that the following recommendations are based primarily on laboratory experiments and on a limited sampling of the mining industry.

- Excursion indicators should be selected based on differences in the chemistry of the ground water and the lixiviant and on the chemical reactivity of the indicator. Many potential indicators (such as uranium and pH) are not conservative, and their values will change rapidly as the lixiviant interacts with the sediment. In general, dissolved species that interact with the sediment do not travel as rapidly as the water and, thus, would not be useful as an early indicator of an excursion.
- Natural restoration can be an important factor in reducing the contaminant level of trace metals in solution and should be considered when restoration requirements are established. A conservative approach would be to ignore natural restoration, but this could lead to the requirement for unnecessary induced restoration that could waste ground-water resources and, in some cases, inhibit restoration by introducing oxidizing ground water into the leached ore.
- Practical, efficient aquifer restoration at a site should involve a combination of restoration methods that restores the aquifer sediment as well as the ground water. At the same time, the methods should not consume excessive amounts of ground water or produce large volumes of waste solution. The accepted practice of surface treatment and recirculation of ground water conserves water, but should be augmented by the addition of a reducing agent to immobilize redox-sensitive contaminants.
- Field studies should be carried out that incorporate this integrated approach to aquifer restoration. An actual test should be conducted so that comparisons can be made with other efforts that use individual restoration methods. A variety of reduced sulfur compounds must be evaluated on a field scale to fully demonstrate their advantages and disadvantages.

LEACHING METHODS AND THE PRODUCTION/MOBILITY OF CONTAMINANTS

During the past 30 years, methods of in situ leach mining have changed to improve production and minimize the generation of ground-water contaminants. This section describes efficient leaching methods and the by-products of leaching that must be dealt with during restoration of the ore-zone aquifer.

THE LEACHING PROCESS

In situ leach mining of uranium consists of the injection of a leaching solution (lixiviant) into an ore zone, oxidation and dissolution of the uranium minerals (typically uraninite and coffinite), complexation of dissolved uranium, and pumping of the uranium-bearing (pregnant) lixiviant to a surface treatment plant. The uranium is removed from the pregnant lixiviant by passing it through anion exchange columns that collect the complexed uranium. The spent lixiviant is fortified with an oxidizer and a complexing agent before being re injected into the ore zone to begin the cycle again. Figure 1 shows in schematic form the placement of a single injection well and a pair of production wells screened in a roll-front uranium deposit. This type of uranium deposit is the typical target of an in situ mining operation.

The deposit is found in sandstone aquifers that are confined above and below by less permeable aquitards. The monitor wells shown in Figure 1 are used to periodically sample the ground water to test for movement of lixiviant out of the controlled zone of the leach mining operation. Monitor wells are typically located in the ore-zone aquifer up and down the hydrologic gradient from the ore zone, and they may also be placed in the aquifers located stratigraphically above and below the ore-zone aquifer.

Several patterns of injection/production wells have been used in commercial in situ leaching. Well pattern design is based on experience gained in petroleum production and brine injection operations. The most common patterns are the five-spot, seven-spot, and the staggered pattern that is designed to match the ore body (Figure 2). Injection wells are usually placed on the outside of the pattern and production wells are placed on the inside. Production wells are pumped at a higher rate than injection wells so that the induced hydraulic gradient draws lixiviant to the center of the pattern. In this way, more solution is recovered than is injected, thus reducing lixiviant costs and decreasing the chance of lixiviant moving out of the controlled zone (an excursion).

The most widely used lixiviants are composed of ground water that has been amended with ammonium or sodium carbonate-bicarbonate. In addition, oxygen and/or hydrogen peroxide are added as oxidants. The lixiviant is designed to cause the oxidative dissolution of U(IV) minerals and results in the formation of aqueous U(VI) species. The added carbonate increases dissolved uranium concentrations by forming strong anionic complexes with U(VI) under neutral to

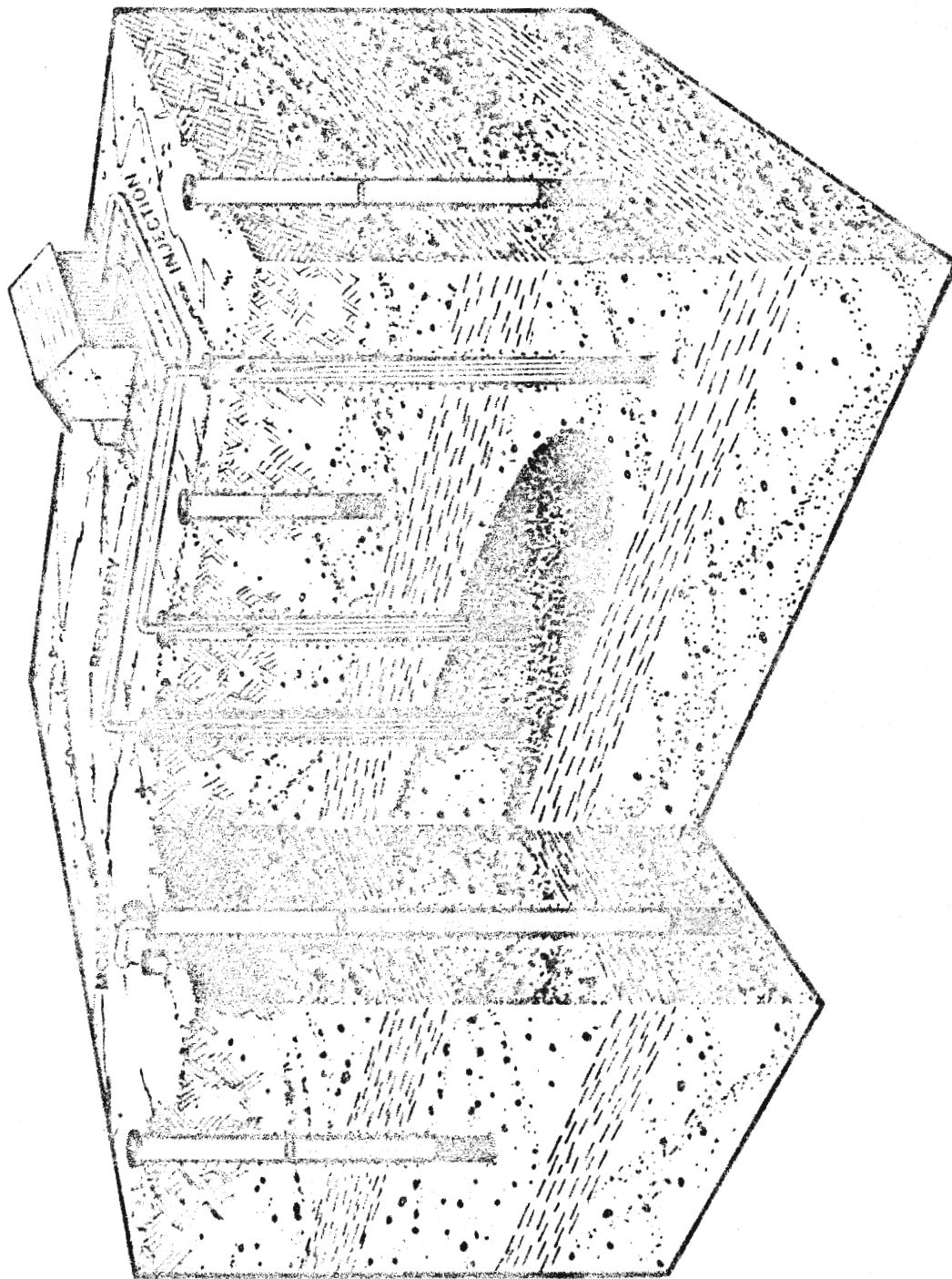


FIGURE 1. Schematic of In Situ Leaching Operation at a Roll-Front Uranium Deposit

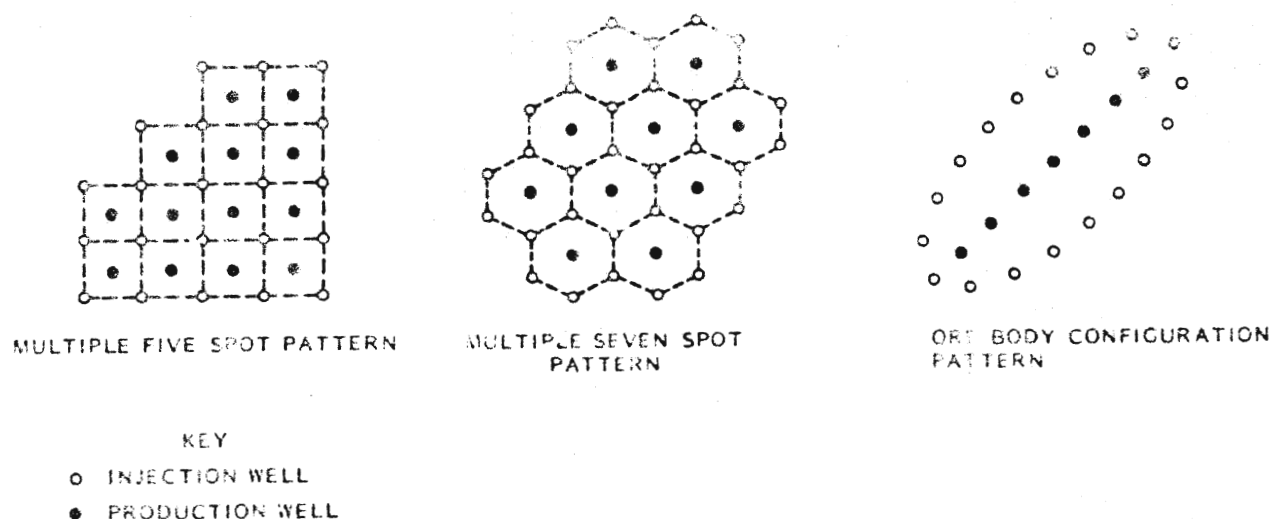
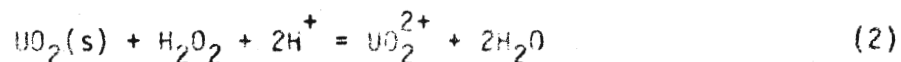
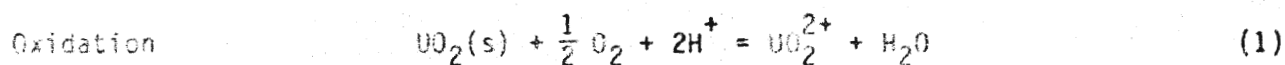
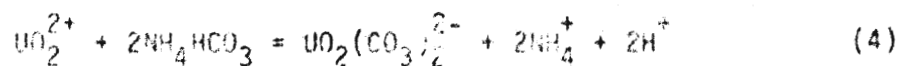
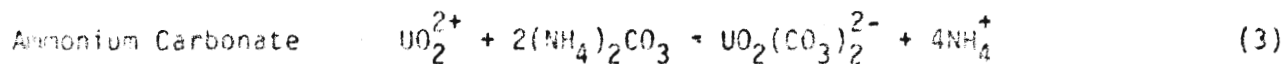


FIGURE 2. Typical Well Configurations (after Larson 1981)

alkaline conditions. Uranium concentrations greater than 200 ppm have been achieved in some leaching operations. Typical alkaline leach reactions would include the following (Tweeton and Peterson 1981):



Complexation



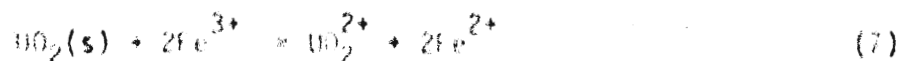
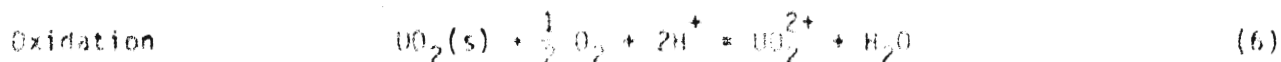
Many mining operations have used a variety of solvents because under certain conditions it is known that increasing the concentration of a solution

may cause clays to swell, which could affect the permeability of an aquifer. The major disadvantage of using an ammonium lixiviant is the great difficulty in removing the ammonium ion from the ore zone after mining is complete. Because ammonium is not a major constituent of the ground water, its concentration limit set for restoration is normally low, consequently ammonium's concentration in solution must be lowered by a large amount for restoration. However, ammonium in the lixiviant is adsorbed onto clays and zeolites in the aquifer and cannot be efficiently removed by simple flushing. Because of ammonium's high selectivity for clay and zeolite, ammonium desorbs very slowly and only with large quantities of water (many pore volumes). Tweeton (1981a) reports that of 11 field tests designed to restore ammonium to baseline concentrations, none reached targeted ammonium levels after 0.5 to 38 pore volumes of flushing. Complete restoration of ground water for ammonium may require 50 to 100 pore volumes, and, depending on pumping rate, this method of restoration could take many years.

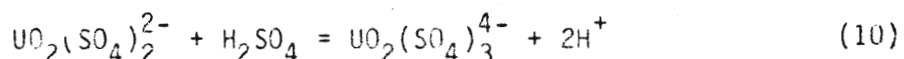
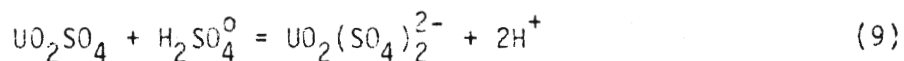
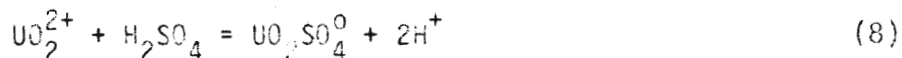
Because of these restoration problems with ammonium-based lixiviants, new mines have begun to use other types of alkaline lixiviants. Sodium carbonate-bicarbonate has been used in ore bodies where the clay content is low or where the sodium content of the natural ground water is high. In at least two mines, carbon dioxide has been added to natural ground water to give a carbonate/bicarbonate solution for leaching. This method is inexpensive, but not always effective (Tweeton and Peterson 1981).

Sulfuric acid lixiviants have been used successfully in some deposits. Uranium is generally dissolved more rapidly with strong acids than with alkaline reagents. Acids, however, tend to dissolve more heavy metal contaminants than do alkaline lixiviants. Also, the use of acid lixiviants is not practical in ore bodies containing relatively large concentrations of carbonate minerals, such as calcite, which neutralize the acid. Also, if calcium is present at even low concentrations in the ground water, calcium sulfate may precipitate when sulfuric acid is added. This precipitate may affect the permeability of the aquifer.

When an acid lixiviant is used, uranium may be oxidized by either ferric iron dissolved from minerals in the ore body or by oxygen added to the lixiviant (Amell and Langmuir 1979; Tatom, Schechter and Lake 1981). Typical sulfuric acid leach reactions include the following (Tweeton and Peterson 1981):



Acid Leaching



Because the alkaline leaching method is used predominantly at this time, the production of contaminants specific to the acid leach process has not been addressed by the research described in this report. However, many of the trace metal contaminants mobilized by acid leaching are also found to be present at higher-than-background levels in alkaline lixivants. Methods of reducing the contaminant level in acid and alkaline leached ore, however, may be different. Aquifer restoration of ore zones leached with ammonium-based lixivants has been discussed at great length in the literature (Humenick et al. 1978; Humenick et al. 1979; Walsh et al. 1979; Tweeton 1981a; Humenick and Garwacka 1982; Yan and Espenscheid 1982). Because ammonium-based alkaline lixivants are being replaced by sodium-based alkaline lixivants, this study has focused on the latter.

THE PRODUCTION OF GROUND-WATER CONTAMINANTS DURING IN SITU LEACH MINING

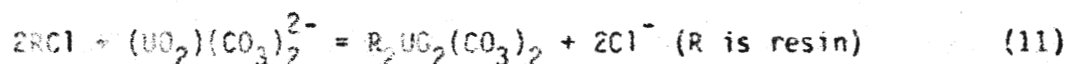
The contamination of ground water as a by-product of uranium leaching may arise from two sources. The addition of leaching chemicals to the ground water and the treatment of the pregnant lixiviant at the operating plant significantly increase the solution concentration of certain elements, creating a potential contamination problem. Also, chemical reactions between the lixiviant and the ore-zone sediment release some elements from the sediment that may reach contaminant concentrations in solution. A general discussion of the environmental geochemistry of the in situ leaching process is given by Kasper et al. (1979).

For the restoration of aquifers that have been mined by in situ leaching methods, a contaminant may be considered as any element in the residual aquifer pore solution that is above its allowed concentration at the completion of mining. The allowable concentrations for different elements are set by the competent state or federal regulatory agency. The concentration limit is generally chosen by considering the baseline water chemistry of the aquifer and the EPA or state water standards. Specific contaminants generally associated with in situ uranium mining with a sodium-based alkaline lixiviant are arsenic, selenium, molybdenum, chloride, sulfate, and uranium. In addition, the total dissolved solids (TDS) level of the lixiviant at the termination of mining is often several times larger than the original ground water. This is caused primarily by the addition of sodium carbonate/bicarbonate and chloride to the ground water during the onsite generation of the leaching solutions. Because

the origin of the contaminants will provide information on methods of minimizing them in the ground water, their sources are discussed in the following two sections.

GENERATION OF CONTAMINANTS BY THE PRODUCTION PLANT

As mentioned previously, lixiviant is made from ground water by adding an oxidizing agent, typically oxygen, and a compound containing a complexing agent. The oxygen is consumed by reactions within the aquifer during mining and is not considered a contaminant. However, the reagent containing the complexing agent is not completely consumed and is generally found at concentrations higher than those in ground water at the completion of leaching. In the cases studied for this research, the mine operators used sodium carbonate/bicarbonate as the reagent because carbonate forms strong anionic complexes with uranium. They found that adding sodium to the ground water did not cause clays in the sediment to swell and decrease the aquifer permeability. The anionic uranyl carbonate complex formed during leaching is removed from solution at the surface plant by strong base, anionic exchange resins as shown below (Thompson et al. 1978):



The reaction in Equation (11) shows that anion exchange process adds chloride to the solution. After removal of uranium from the leaching solution, the barren lixiviant is reforcified with sodium carbonate/bicarbonate and an oxidizer and then reinjected into the ore zone. The overall effect of the plant processing of the ground water and pregnant lixiviant is to generate sodium, carbonate/bicarbonate, and chloride levels in solution well above those of the original ground water. This processing often leaves the solution unfit for various human uses because the TDS is above the limits set by the EPA. These contaminants of the ground water are relatively easy to treat by several restoration techniques, which are described in this document. In contrast, the contaminants generated by the interaction of the lixiviant with the aquifer sediments are often more difficult to eliminate.

SEDIMENT-DERIVED CONTAMINANTS

The geochemistry of uranium roll-type deposits has been widely discussed in the literature (Zahl and Hagmafer 1974; Galloway and Kaiser 1980; Granger and Warren 1969; Granger and Warren 1974; Goldhaber and Reynolds 1977; Warren and Granger 1973). Aspects of roll-front geochemistry applicable to the generation of contaminants during leach mining are summarized in this section.

Uranium in roll-front deposits can occur as the minerals uraninite (UO_2) and coffinite ($USiO_4$) (Harshbarger 1972; Del, Riruno and Sakonaki 1975) or as an amorphous uranous silicate (Galloway and Kaiser 1980). The uranium solid phases occur as coatings on sand grains, matrix or grain-fracture fillings, or

as part of a clay cutan on the host sandstone. Epigenetic minerals that occur associated with the ore include pyrite (FeS_2), marcasite (FeS_2), native selenium, ferroselite (FeSe_2), hematite, and calcite. Figure 3 shows a schematic of a roll-front deposit and the location of several of these minerals relative to the ore. The uranium ore is located at the redox interface between oxidized sediment and unaltered reduced sediment. Pyrite and marcasite have a similar distribution in many ore zones and these minerals are often present in the unaltered and altered sections of the sandstone adjacent to the ore. Ferroselite and native selenium occur as clusters attached to clay or sand grains in the altered zone adjacent to the uranium ore. The presence of selenium in this zone suggests that it is less mobile than uranium when reducing conditions are established in the aquifer. Calcite occurs as a cementing material associated with some ore zones and the surrounding unaltered sands. Hematite and limonitic material, often associated with calcite, causes the red and yellow staining that is characteristic of the oxidized zone of the sandstone. In addition to these minerals, the elements molybdenum, arsenic, and vanadium are abundant locally in the sediments associated with certain roll fronts (Harshman 1974). Finally, carbonaceous material is often found in larger concentration in the unaltered zone of the aquifer compared to the altered zone.

Harshman (1972) suggests that the uranium roll-front deposits in the Shirley Basin of Wyoming were formed by a long-term migration and concentration of redox-sensitive elements in a confined sandstone aquifer. Uranium, and associated elements are mobilized in the source rock by ingressing alkaline, oxidizing ground water (depicted in Figure 3), which subsequently undergoes Eh and pH change in response to interactions with reductants (pyrite and organic matter) in the aquifer. The elements are distributed about the roll front as a function of their solubility in the changing chemistry of the ground water. The ore-forming process continues until the supply of uranium is exhausted, until the environment causing the deposition is destroyed, or until the ground-water flow pattern changes significantly. This theory of roll-front genesis has been expanded upon by a number of investigators (Granger and Warren 1974; Doi, Hirono and Sakamaki 1975; Galloway and Kaiser 1980) to fit particular situations, but the basic ideas have been preserved.

Uranium and the other redox-sensitive elements (arsenic, molybdenum, selenium, and vanadium) found associated with it in and around the ore zone, form stable solids in the near-neutral, low Eh environment of the roll front. The injection of oxidizing solution (lixiviant) into this zone may preferentially oxidize and dissolve the uranium minerals, but the other redox-sensitive minerals are also less stable under the new conditions, and they also dissolve to some extent. This releases the trace metals into the lixiviant and, especially in the case of arsenic, selenium, and molybdenum, the metals may reach contaminant levels.

In addition to the direct production of trace metal contaminants by oxidative leaching in the ore zone, calcium, magnesium, sodium, and potassium may have higher concentrations in the lixiviant than in the ground water because of secondary reactions associated with the oxidation of pyrite in the

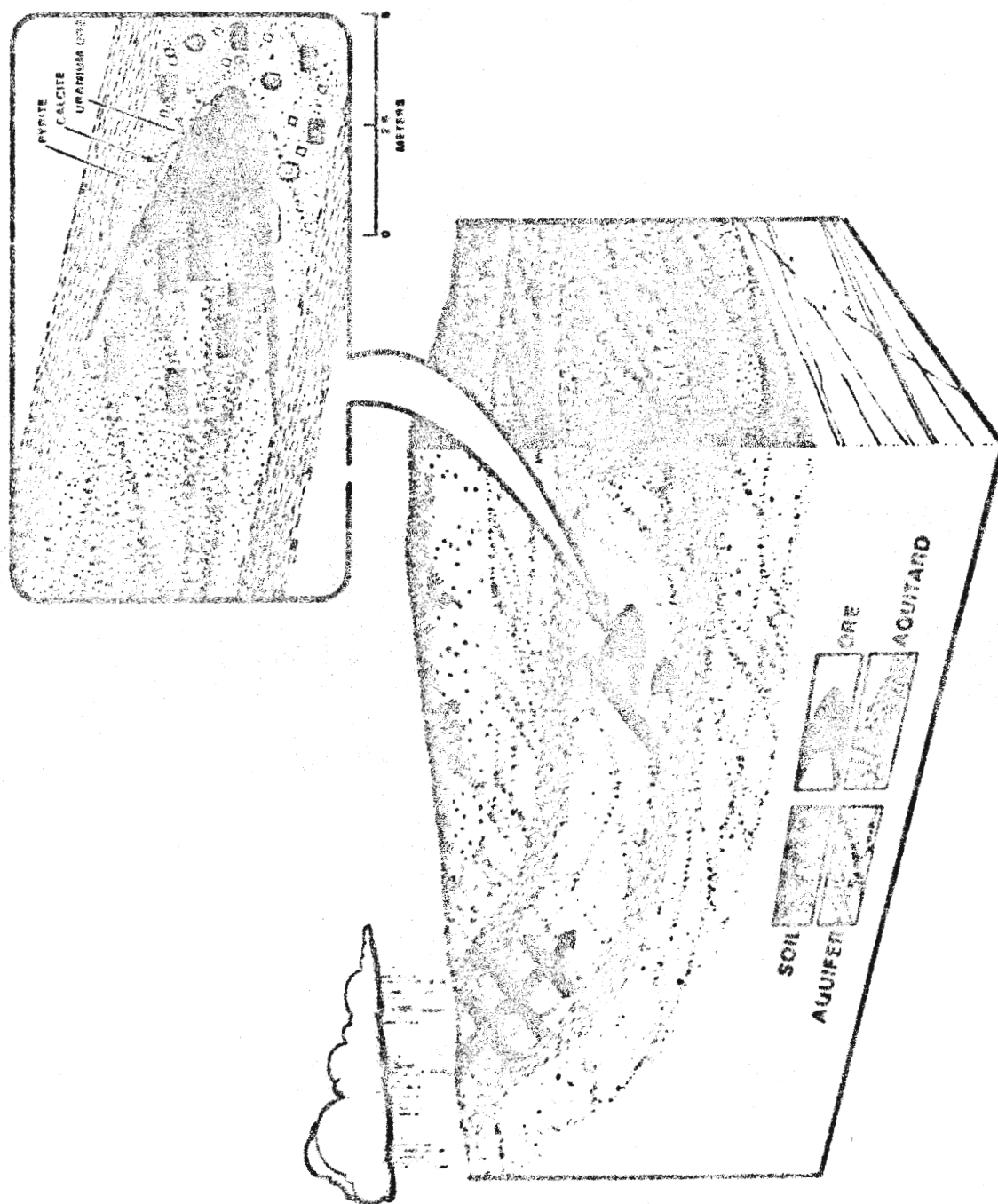
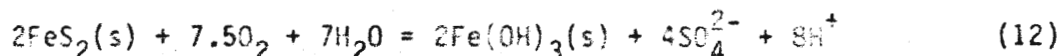
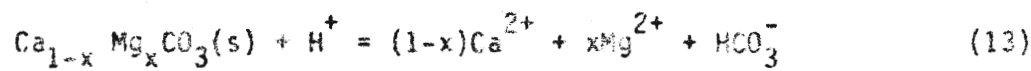


FIGURE 3. Schematic Diagram of a Uranium Roll-Front Deposit

ore zone. The oxidation of pyrite (FeS_2), which is a common constituent of the reduced zones of the ore-zone aquifer, produces sulfate (SO_4^{2-}) and adds hydrogen ions to the solution [Equation (12)]:



The hydrogen will react with magnesian calcite ($\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3$), which will buffer the pH of the solution and release Ca and Mg. An idealized reaction is shown in Equation (13):



In addition to dissolving carbonate minerals, hydrogen released by sulfide oxidation will hydrolyze silicate minerals present in the sediment. The primary silicates will alter to form clays and will add Na and K to the solution. These elements may also be added through ion exchange of Ca and Mg in the lixiviant for Na and K adsorbed onto the aquifer minerals. A steady-state condition will be established between dissolved oxygen, pyrite, magnesian calcite, clays, exchangeable cations, and the solution composition. During leaching the concentration of most of the dissolved constituents will be appreciably higher than their concentration in the original ground water.

CONTAMINANT MOBILITY

The contaminants that might be produced by sodium-based alkaline leaching of uranium include: sodium, chloride, carbonate/bicarbonate, sulfate, arsenic, selenium, molybdenum, and uranium. The chemical reactivity of these elements and compounds with the aquifer sediment and ground water will affect their mobility and, hence, the method of aquifer restoration necessary for the contaminant. Conservative elements, such as chloride, do not interact appreciably with the sediment, and they will essentially move at the speed of the ground water. Sodium and sulfate concentrations in solution will be affected by ion exchange between the solution and sediment. Also, sulfate and carbonate concentrations may be limited by the formation of secondary minerals such as gypsum and calcite.

Although the concentration of the major solution components (sodium, chloride, carbonate/bicarbonate, and sulfate) may be decreased by water/sediment interactions, it is doubtful that these reactions would lower concentrations to the original values in the ground water. Because of this, it would be best to remove the excess concentration of these elements from the solution while the solution is in the mine zone and not allow these contaminants to migrate with the ingressing ground water. On the other hand, redox-sensitive elements moving in the ground water will be affected by aquifer

conditions downgradient of the roll front, and their solution concentration may be rapidly reduced to below contaminant level as a result of adsorption onto the sediment or the formation of insoluble solids. This process is called natural restoration.

The concept of natural restoration (Buma et al. 1979; Riding and Rosswog 1979) was studied in the laboratory as part of this project. The results of the laboratory work are described in the section on aquifer restoration of this report. Those constituents of the leaching solution that do not interact with the sediment and that move at the speed of the water can be measured at the monitor wells that surround the leach field and can be used as first indicators that leaching solution has moved out of the controlled zone.

EXCURSION DETECTION

The early detection of a loss of fluid control during leaching (termed an excursion) is necessary to limit the spread of the lixiviant, and thus, to limit environmental impact. Although geophysical resistance measurements hold some promise as an excursion detection method (Kasper et al. 1978; Korman 1979; Tweeton 1981b), the primary technique employed at in situ leach mines is to sample the monitor wells for chemical parameters that have been determined to be good excursion indicators. Monitor well placement, construction, and sampling methods are very important parts of a monitoring program and have received much attention (Bishop 1980; Durler and Bishop 1980; Humenick, Turk and Colchin 1980). Data on the selection of excursion indicators were collected during this project and are the focus of this discussion.

The choice of parameters to measure will determine the likelihood of early detection and minimize the possibility of incorrectly identifying natural variations as excursions. Rothrock (1981) describes a statistical methodology for testing ground-water quality at in situ leach uranium mines. The measured value of the excursion indicator (e.g., solution pH or concentration of a dissolved constituent) should differ considerably between the lixiviant and the ground water, and the characteristic signature of the excursion indicator in the lixiviant should not be modified by interactions between the lixiviant and the aquifer sediment. As part of the field sampling work carried out for this project, ground-water samples were taken at two in situ mines: one in Texas and one in Wyoming. The composition of these ground-water samples can be compared with lixiviant used at the respective mines to determine effective excursion detection indicators for these sites as discussed below.

A description of the Texas site and the ground-water sampling methods may be found in Deutsch et al. (1983). The uranium ore at this site is found in a typical South Texas roll-front deposit at a depth of approximately 80 m in a confined sandstone aquifer. The field sampling procedures used at this site are summarized in the methods and materials section of this document. Table 1 lists the concentrations of selected constituents in the lixiviant used at this mine and an average composition of 10 wells sampled for ground water in the ore zone aquifer near the leach field. The concentrations of the solution constituents listed in Table 1 are appreciably higher in the lixiviant than in the ground water sampled; however the chloride concentration in the ground water is within two standard deviations of the lixiviant concentration, and for this reason chloride would probably not be a good indicator at this site. Calcium and magnesium concentrations are much greater in the lixiviant than in the ground water, and, based on this criterion alone, they would appear to be the best indicators. However, the transport of cations in the ground water will be affected by ion exchange reactions between the solution and the sediment. Consequently, the difference in concentration may not be preserved as the solution flows toward a monitoring well. Sulfate also shows a large difference in concentration between the lixiviant and ground water. Natural oxidation of pyrite by ground water could lead to large, localized variations in the sulfate concentration of the ground water and, therefore, the selection

TABLE 1. Mean Concentration and Standard Deviation of Selected Constituents in Texas Ground Water and Lixiviant (Deutsch et al. 1983)

	Ground Water		Lixiviant		Concentration Ratio Lixiviant/Ground Water
	\bar{x} , ppm	σ	\bar{x} , ppm	σ	
Ca	25.9	14.0	273.0	61	10.5
Mg	9.6	5.8	82.0	10	8.5
Na	436.0	90.0	1007.0	89	2.1
K	15.2	2.3	26.5	11	1.7
Cl	677.0	196.0	1009.0	33	1.5
SO ₄	71.1	15.0	1181.0	131	16.6
HCO ₃	173.0	36.0	579.0	79	3.3
U	0.17	0.21	28.6	35.4	168.0
pH (log units)	8.53	0.24	6.71	0.02	0.79
TDS	1458		4186		2.9

of sulfate as an excursion indicator should be made with caution. Based on the concentration ratios given in Table 1, uranium should be one of the best excursion indicators. Its concentration is generally orders of magnitude higher in the lixiviant, and U(VI) exists in solution as a mobile anionic carbonate complex. However, for the monitor wells located in the reduced zone of the ore-zone aquifer or the neighboring aquifers, uranium would not be a good excursion indicator because the U(VI) could be reduced to U(IV), which forms relatively insoluble compounds under reducing conditions. This would lower the dissolved uranium concentration, perhaps back to the original ground-water concentration.

The ion exchange reactions that retard the movement of several of the cations in the aquifer would have little effect on the TDS level (measured in equivalents per liter); consequently, monitoring TDS by measuring changes in specific conductivity of the fluid could indicate an excursion. Although precipitation of solids as the lixiviant reacts with the reduced sediment of the aquifer would reduce TDS somewhat, the TDS level should remain elevated for an appreciable distance away from the leach zone during an excursion. In general, for the Texas site studied, it appears that the TDS level of the monitored solution would be the best indicator of an excursion. Uranium would be a good indicator for the oxidized zones of the aquifers, and sulfate could be used if the natural variations of its concentration can be adequately described.

Six wells at an in situ leach mine in Wyoming were sampled to evaluate excursion indicators for that site. At this site, the operators conducted a pilot-scale leach operation of a roll-front deposit situated in a confined sandstone aquifer approximately 200 m below the surface. The dominant cation at both the Texas and Wyoming sites was sodium; however, chloride was the dominant anion at the Texas site and sulfate dominated in the ground water sampled in Wyoming. Table 2 lists the mean compositions and ratio of the ground water and the lixiviant used at the Wyoming mine. Uranium once again showed the largest variation between the lixiviant and ground water. Chloride

TABLE 2. Mean Composition of Ground-Water and Lixiviant Samples at a Wyoming In Situ Leach Uranium Mine. (All concentration units are ppm.)

	Ore-Zone Aquifer Ground Water ^(a)	α	Lixiviant Composition Well P-1 ^(b)	Ratio of Lixiviant to Mean Ore-Zone Ground-Water Composition
Ca	17	0.8	138	8.1
Mg	6.5	0.4	42	6.5
Na	89	3	365	4.1
K	4	0	12	3.0
Cl	6.1	0.8	140	.23
SO ₄	126	2	229	1.8
Alkalinity (as CaCO ₃)	152	7	620	4.1
Si	4.2	0.05	11.5	2.7
U	0.004	0.0001	18.2	4550
pH (log units)	8.47	0.1	6.7	0.8
TDS	539		1713	3.2

(a) Mean values computed for wells M-1 through M-6 at the North Platte, Wyoming mine site.

(b) Table 10, Uranium Resources Inc., North Platte Technical Report, Volume II: Restoration and Stage II Forecast, April 1983.

concentration in the lixiviant was 23 times that found for the ground water because chloride was added at the processing plant during uranium extraction. Because of this large concentration difference and the nonreactive nature of chloride, it would be a good excursion indicator at this site. The remaining solution constituents are either too reactive with the sediments or do not show a large enough variation between the solutions to make them good candidates for indicators. As in the Texas case, the TDS level is appreciably greater in the lixiviant and could be recommended as an excursion indicator.

AQUIFER RESTORATION

Restoration of an aquifer at the completion of leach mining of uranium is generally considered to be the process by which the chemical constituents of the ground water are returned to concentration levels similar to those of the original ground water in the aquifer. Restoration criteria for ground water are established for each mine by the appropriate regulatory agency. However, ground-water restoration is only a part of aquifer restoration. The sediment comprising the aquifer is also modified to some extent by the lixiviant. The ground-water composition can serve as an indicator of the state of the sediment after restoration; however, unless methods have been applied to reestablish reducing sediment conditions in the leached zone of the aquifer, the system may not be stable as new ground water flows into the leached ore zone. Complete restoration of the aquifer would include treatment to return the sediment to its original state. If the original state of the sediment can be achieved or at least approximated for the important constituents, then the ground-water/sediment system can be considered restored, and a good case can be made for long-term stability of the system. Restoration methods should be designed and implemented to obtain complete aquifer restoration.

The traditional methods of aquifer restoration are described in this section as well as the concept of natural restoration by which water/sediment interactions between the residual lixiviant and the aquifer sediment remove contaminants from the solution. Experimental studies and the results of geochemical modeling designed to evaluate natural restoration and induced restoration are discussed.

INDUCED-RESTORATION METHODS

This section describes the commonly used applied-restoration techniques of ground-water sweeping and various surface-treatment/recirculation methods. In addition, the in situ treatment method of chemical reduction by sulfide addition is discussed.

Ground-Water Sweeping

Displacement of residual lixiviant in the ore zone by replacement with ground water drawn in from the surrounding aquifer is termed ground-water sweeping. At the termination of mining, pumps in the wells are used to draw fresh ground water into the ore zone and the pumped water is disposed. The composition of the effluent from the wells is monitored to check on the progress of the restoration effort.

This method is the most popular one for restoration because it is uncomplicated, relatively inexpensive, and the operators and regulatory agencies are familiar with it. However, ground-water sweeping has a number of limitations that detract from its attractive features. Because of heterogeneities in an aquifer, the fresh ground water brought into the ore zone does not completely displace the residual lixiviant, and some portion of the solution pumped out of

the wells is the fresh ground water. Typically many pore volumes of water must be pumped from the ore zone before the solution concentration approaches that of the original ground water.

This could easily require millions of gallons of ground water for a typical 10-acre leach field. One of the reasons that so many pore volumes of solution must be pumped from the wells is that the lixiviant components (particularly ammonium) are adsorbed by clay minerals in the sediment, and their desorption rate is slow relative to the flow of ground water during sweeping. A second limitation of ground-sweeping is that large quantities of water must be disposed of. This may require expensive evaporation ponds or deep-well disposal where feasible. A final problem with ground-water sweeping is that it may actually defeat the purpose of aquifer restoration for certain ground-water constituents. Ground-water sweeping may bring into the leached ore zone oxidizing ground water from the zone up the hydrologic gradient from the ore zone. Any remaining uranium ore and sulfides of toxic trace metals (such as arsenic and molybdenum) would be susceptible to oxidation and dissolution by this ground water. In effect, the zone will continue to be mined with a weak lixiviant. This can cause a condition in which elevated levels of contaminants will be produced in solution for a long period of time. In many cases, these limitations to the ground-water sweeping method of restoration are so severe that additional methods must be used.

Surface Treatment and Recirculation

A number of surface treatment methods have been used at in situ mine sites to conserve ground water and to minimize the amount of waste solution. These methods involve treating the water pumped from the wells during restoration to produce a purified solution and a brine carrying most of the dissolved solids. The purified water is pumped down into the ore zone to displace more of the residual lixiviant. The surface treatment techniques that have been used are reverse osmosis (RO), electrodialysis (ED), and dual ion exchange (DIX). Both RO and ED allow recovery of 80% of the water recirculated for restoration. An informal survey conducted by the Bureau of Mines of 17 companies operating 27 leach operations revealed that surface treatment methods had been used at 14 sites. Reverse osmosis had been used at nine sites; electrodialysis at three sites; and ion exchange at two sites. General comments were made concerning these various methods:

- Reverse Osmosis--generally effective and dependable, some units subject to fouling, somewhat limited pH range.
- Electrodialysis--very effective, reliable, high initial capital cost.
- Dual Ion Exchange--effective and economical for selected contaminants.

The following sections describe these restoration methods. Additional information on surface treatment processes may be found in Riding and Rossing (1979) and Deutsch et al. (1984).

Reverse Osmosis

Reverse osmosis is a physical means of separating dissolved ions from an aqueous solution. An externally applied pressure in excess of the solution's osmotic pressure forces water through a semipermeable membrane while the dissolved ions are rejected. A typical operating pressure for RO used for in situ leach applications is several hundred psi. Applications of this technology to in situ uranium are described in Riding and Rosswog (1976) and in Bulletin 605 of the Trace Metal Data Institute (1981).

The three configurations of RO membranes are spiral wound, hollow fine fiber, and tubular. Riding and Rosswog (1976) recommend the spiral wound design. The tubular system has a high operating cost without the possibility of high water recovery. The hollow fine fiber is too susceptible to fouling and cannot be cleaned. The spiral wound design can be operated at high water recoveries (85%), can be easily cleaned, and is economical.

Concerning membrane material, Riding and Rosswog (1976) recommend cellulose acetate derivatives because the polyamide, polyfuran, polysulfone, polyethylene amine, and polybenzimidazolone types suffered from one or more of the following limitations: insufficient rejection of dissolved constituents, low water flux, little or no successful field operation, and incompatibility with oxidants present in the restoration fluid. The cellulosic type membranes have proved to be very successful.

Electrodialysis

Electrodialysis has been used successfully for in situ restoration applications, but has been used less often than RO. This restoration method for in situ mining has been evaluated by Garling (1981). Electrodialysis can be viewed as a combination of RO and ion exchange. Ions pass through semipermeable membranes under the influence of an electric field. In a typical design, membranes, spacers, and electrodes are stacked and held together by endplates much like a plate and frame filter. Spacing is usually 2.5 mm, and spacers are arranged to provide a tortuous path. Stacks range from 500 to 2500 m² of membrane area. A large stack can desalt 150 gpm at 20 to 50% salt removal. Practical systems use two to six stages.

Riding and Rosswog (1979) indicated that ED has some technical advantages over RO. Electrodialysis construction is simplified because of the lower feed pressure required: 60 psi for ED versus 400 to 800 psi for RO. Also, the pressure compaction that causes aging of RO membranes is alleviated. Electrodialysis membranes are of synthetic ion-exchange materials with a service life of up to 20 years, compared to 3 to 5 years for RO membranes. Electrodialysis membranes are stable over a pH range of 1 to 14. Cellulose acetate membranes for RO are most successfully operated in the limited pH range of 4 to 8. Thus, less pretreatment of the solution may be needed for ED than for RO.

Dual Ion Exchange

Although the report by Riding and Rosswog (1979) indicated that ion exchange costs more than RO for treating the high TDS restoration fluids, DIX may be cost-effective in certain cases. Dual ion exchange consists of replacing cations and anions in solution with hydrogen and bicarbonate ions using special resins. This procedure is known as the Desal process, and is described in Riding and Rosswog (1979).

The ion-exchange resins can provide greater selectivity than RO. An example of an application where this selectivity was advantageous occurred when a leaching company was required to significantly reduce sulfate but not chloride concentration levels. The selectivity for sulfate available with ion exchange resins allowed greater cost-effectiveness than would have been obtained with RO. It was also thought that RO would have been more susceptible to fouling in this case. However, in most cases selectivity is not unusually important, and thus RO will generally be more cost-effective than DIX.

In Situ Treatment Methods

This method of restoration involves the injection and circulation of chemicals into the aquifer in order to enhance the restoration process. In situ treatment explicitly recognizes the aquifer sediment as a continuing source of contaminants that must be considered along with simple displacement of residual lixiviant during restoration. The major advantages of in situ treatment are that 1) smaller volumes of waste water are produced, 2) it is more effective for certain contaminants (ammonium and redox-sensitive elements) than sweeping or clean-water circulation, and 3) it may be less expensive than surface treatment methods. Certain problems are also associated with in situ treatment: 1) uniform dispersal of treatment agents, 2) less positive control over the treatment process compared to surface methods, and 3) lack of sufficient experience in the use of some suggested chemical additives (sulfide compounds).

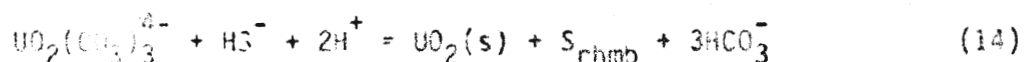
In situ treatment has been considered for treatment of ammonium, uranium, and the redox-sensitive trace metals. Proposed ammonium treatment methods include chemical and biological oxidation followed by surface treatment of nitrite/nitrate products and elution of ammonium from clays by means of high ionic strength solutions. These methods are described in Deutsch et al. (1984). Results of laboratory and pilot scale tests of cation elution of ammonium by concentrated solutions of calcium, magnesium, and sodium are summarized in Buma et al. (1981). In general, the cation elution method does reduce ammonium concentrations considerably in the restoration fluid; however, baseline levels have not been achieved in the three pilot tests reviewed. Because of the shift away from ammonium-based lixiviants in recent years, the primary emphasis of this project has been on restoration of aquifers leached with sodium-based lixiviants.

The primary contaminants that are produced by sodium-based lixiviants which can be treated by in situ restoration methods are the redox-sensitive elements (uranium, arsenic, selenium, and molybdenum). The addition of reduced

sulfur compounds (e.g., sulfide, sulfite, and sulfur dioxide) to a solution circulated through the leach zone for restoration has been suggested as a method of immobilizing the redox-sensitive elements. The conceptual basis for using reduced sulfur compounds during restoration is described in the following paragraphs, and laboratory studies of in situ restoration by sulfide addition are discussed in the experimental section.

The solid/solution system that is envisioned when sulfide is added as a chemical reductant to a leached ore zone is depicted in Figure 4. In this system, uranium (VI) tricarboxylate (UTC) is present in solution, and ferric hydroxide is present as a solid produced by the oxidation of pyrite during leaching. The bisulfide ion would be the dominant sulfide species in solution under alkaline conditions. It would lower oxygen and UTC concentrations in solution producing uraninite, dissolved carbonate, reduced sulfur species, and perhaps sulfate. The interaction of HS^- with ferric hydroxide, $\text{Fe}(\text{OH})_3$, produces FeS and elemental sulfur. The FeS and elemental sulfur may react slowly to produce the stable end product pyrite. The thermodynamics of these reactions are discussed below.

In the pH range under consideration, uranium exists primarily as the uranyl tricarboxylate species (UTC). Reduction of this species by HS^- and the formation of uraninite (or perhaps amorphous UO_2) can be represented by the following equation:



The free energy change for this reaction is -34.9 kcal and $\log K_{25^\circ\text{C}}$ is 25.6 if the UO_2 solid is uraninite.

Figure 5 is a plot of the activities of UTC, HS^- , and hydrogen ion in equilibrium with uraninite and elemental sulfur with the bicarbonate activity fixed at 300 ppm. (The thermodynamic data used for the calculations done in this section are listed in Table 3.) The plot shows that even low concentrations of HS^- will keep UTC at a very low level in solution. For instance, at a pH = 8, HS^- activity of 10^{-6} molar (= 30 ppb) and HCO_3^- activity of 300 ppm, the UTC activity is $10^{-10.5}$ molar (= 8 ppt). The highest UTC activity that is shown on the plot is $10^{-7.5}$ molar (= 0.8 ppb U). This UTC activity is attainable at equilibrium when the pH = 10, $[\text{HS}^-] = 10^{-7}$, and $[\text{HCO}_3^-] = 300$ ppm.

However, as depicted in Figure 4 the added sulfide will also be consumed by dissolved oxygen and ferric iron present as ferric hydroxides. Oxygen will be reduced by sulfide producing sulfate (if there is sufficient oxygen) according to



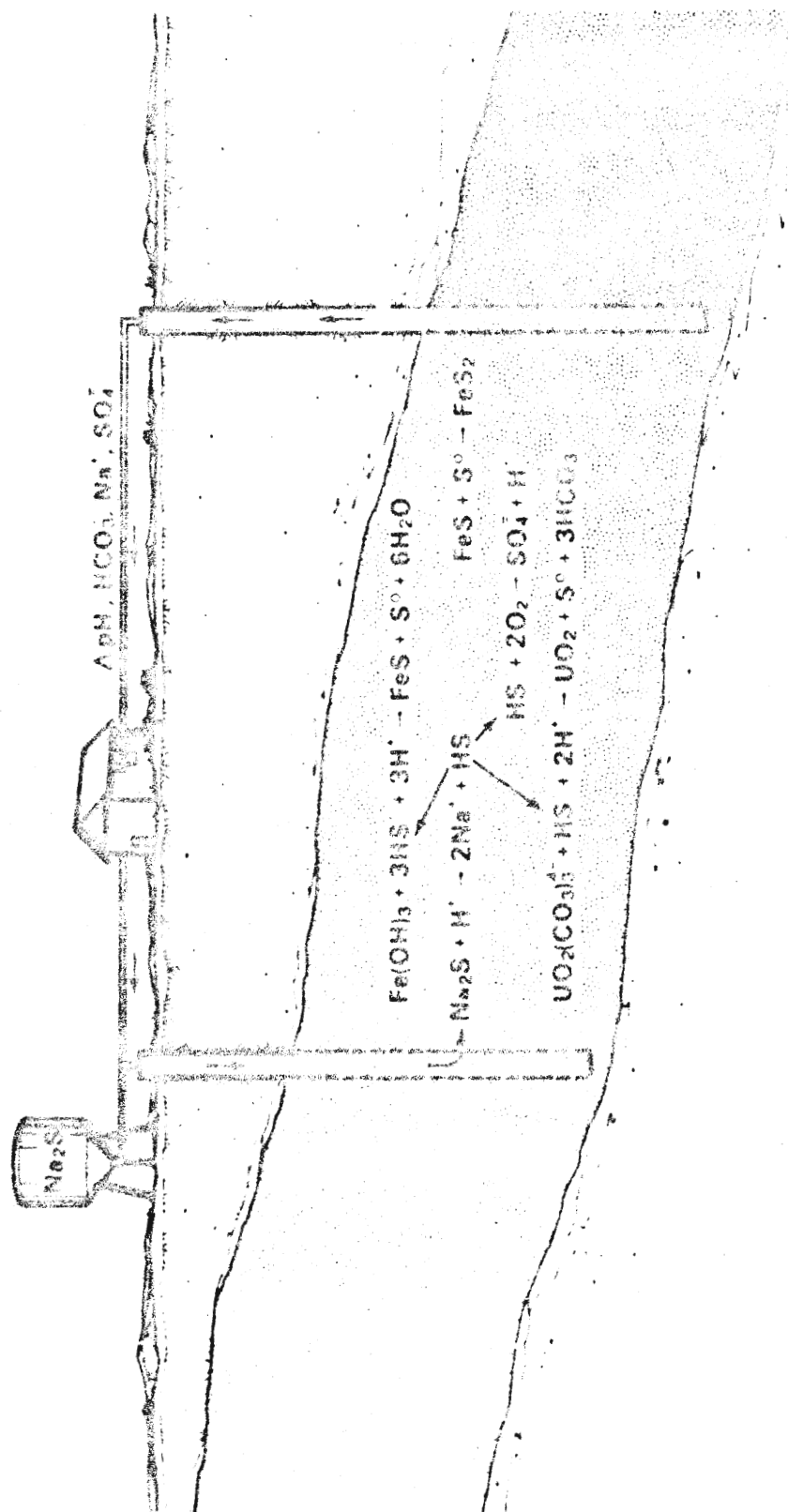


FIGURE 4. Aquifer Restoration Aided by Chemical Reduction

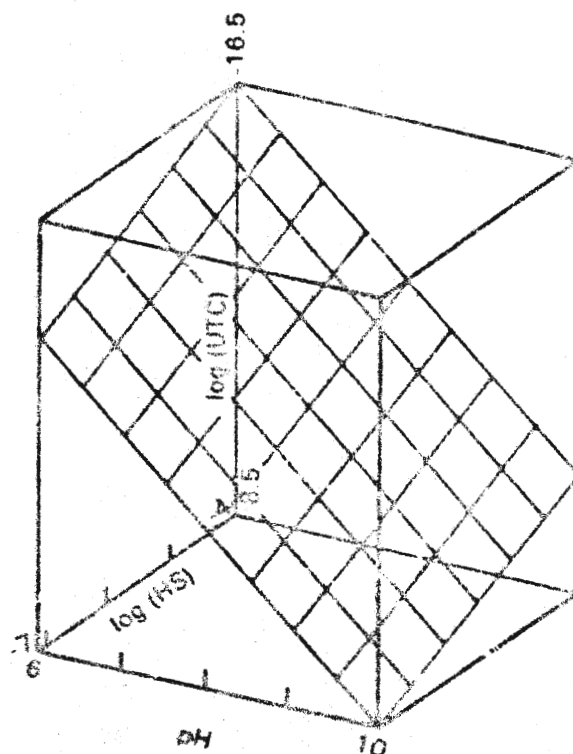
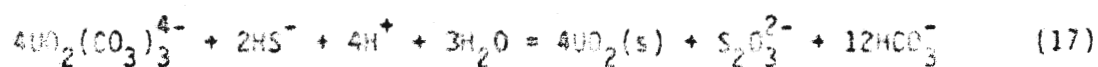
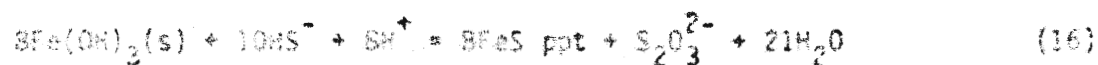


FIGURE 5. Dissolved Uranium Tricarbonate and HS^- Activities and pH in Equilibrium with Uraninite and Elemental Sulfur. Bicarbonate activity fixed at 300 ppm.

A possible set of reactions for the reduction of $\text{Fe}(\text{OH})_3$ and UTC might be the following:



Adding Equations (16) and (17) together and dividing by 2 gives

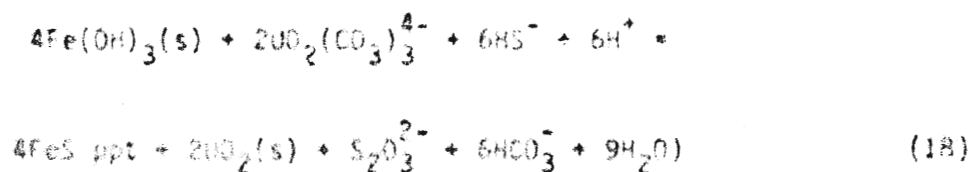


TABLE 3. Thermodynamic Data for Computations

Compound	G _f ^o , 298K	Reference
Fe(OH) ₃	-165.5 (kcal/mole)	Wagman et al. 1969
Pyrite	-39.9	Wagman et al. 1969
Mackinawite (tetragonal FeS)	-22.3	Berner 1967(b)
Greigite (cubic Fe ₃ S ₄)	-69.4	Berner 1967(b)
FeS ppt	-21.3	Berner 1967(b)
HS ⁻	+2.88	Wagman et al. 1968
S rhmb	0	Wagman et al. 1968
S ₂ O ₃ ²⁻	-127.2	Kaumov, Ryzhenko and Knodakovsky 1974
UO ₂ (c)	-246.6	Langmuir 1978
UO ₂ (CO ₃) ₃ ⁴⁻	-635.4	Langmuir 1978
UO ₂ (CO ₃) ₂ ²⁻	-503.2	Langmuir 1978
HCO ₃ ⁻	-140.26	Wagman et al. 1968
H ₂ O	-56.69	Wagman et al. 1968

The free energy change for this reaction is -138 kcal and log K_{25°C} is 101. Therefore,

$$\log[\text{UTC}] = 0.5 \log [\text{S}_2\text{O}_3^{2-}] + 3 \log [\text{HCO}_3^-] - 3 \log [\text{HS}^-] + 3 \text{ pH} - 50.5$$

Figure 6 is a plot of this equation with $[\text{HCO}_3^-] = 300$ ppm and reasonable ranges for the other variables. The plot shows that Fe(OH)₃, FeS, and UO₂ (uraninite) can coexist in the aquifer, and if the concentration of HS⁻ is greater than approximately 10⁻⁹ molar, the UTC activity will be small (0.03 ppm at $[\text{HS}^-] = 10^{-9}$ molar). From the stoichiometry of Equation (18), every six moles of HS⁻ added reduces 4 moles of Fe(OH)₃ and 2 moles of UTC at equilibrium. If more UTC than this is reduced relative to Fe(OH)₃ because of kinetic restraints on solid phase transformations (Fe(OH)₃ to FeS), then a disequilibrium may be generated that would force some UO₂ to dissolve when HS⁻ concentration becomes low. This redissolution of UO₂ is unlikely, however, because

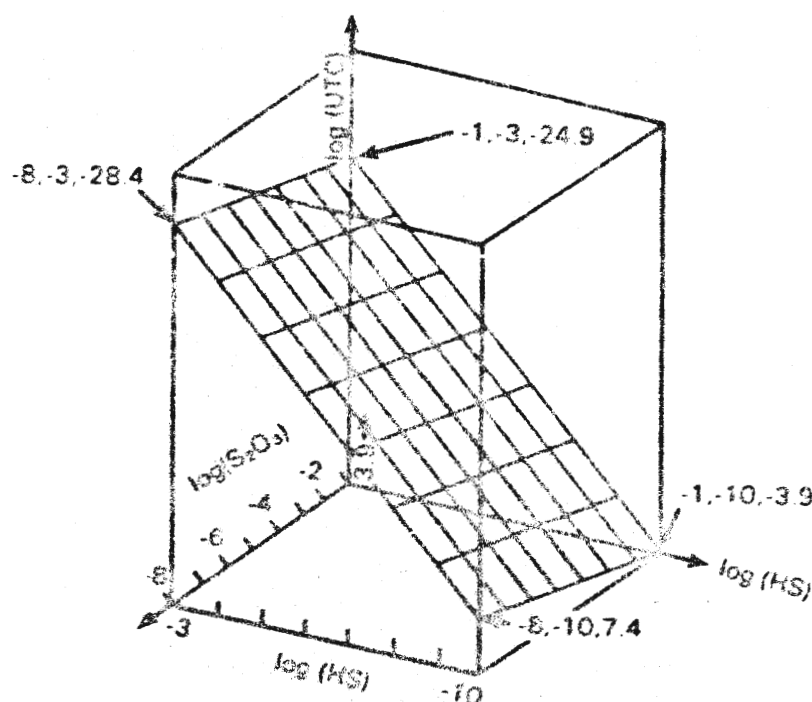


FIGURE 6. Dissolved Uranium Tricarbonate, $S_2O_3^{2-}$, and HS^- Activities in Equilibrium with Uraninite and FeS (ppt). HCO_3^- activity set at 300 ppm.

it is doubtful that $S_2O_3^{2-}$ would oxidize UO_2 . Under somewhat similar conditions, Goldhaber (1983) found that $S_2O_3^{2-}$ disproportionated to sulfate and sulfides generating highly reducing conditions.

Most pH-Eh diagrams of the sulfur system show elemental sulfur (S rhmb) as stable only up to a pH of approximately 5. Our system is expected to equilibrate in the range 7 to 9, therefore, there is some question as to whether elemental sulfur will be a stable solid in the system. It may be metastable in the system, and its presence would enhance the formation of pyrite from FeS (ppt) and mackinawite (FeS).

Figure 7 shows the stability of $Fe(OH)_3$ and FeS ppt, mackinawite, and pyrite in the presence of dissolved HS^- . In the pH range under consideration, the plot shows that very little HS^- needs to be in solution to establish an equilibrium between the two coexisting solids [$Fe(OH)_3$ /FeS pptd, $Fe(OH)_3$ /mackinawite, $Fe(OH)_3$ /pyrite]. If HS^- is added to solution, it will reduce $Fe(OH)_3$ to form the reduced sulfur solids until the HS^- level is very low.

Because of these findings, we decided that a laboratory test of the effectiveness of sulfide as a chemical restoring agent would be appropriate. From the calculations, it appears possible that adding sulfide to the system would

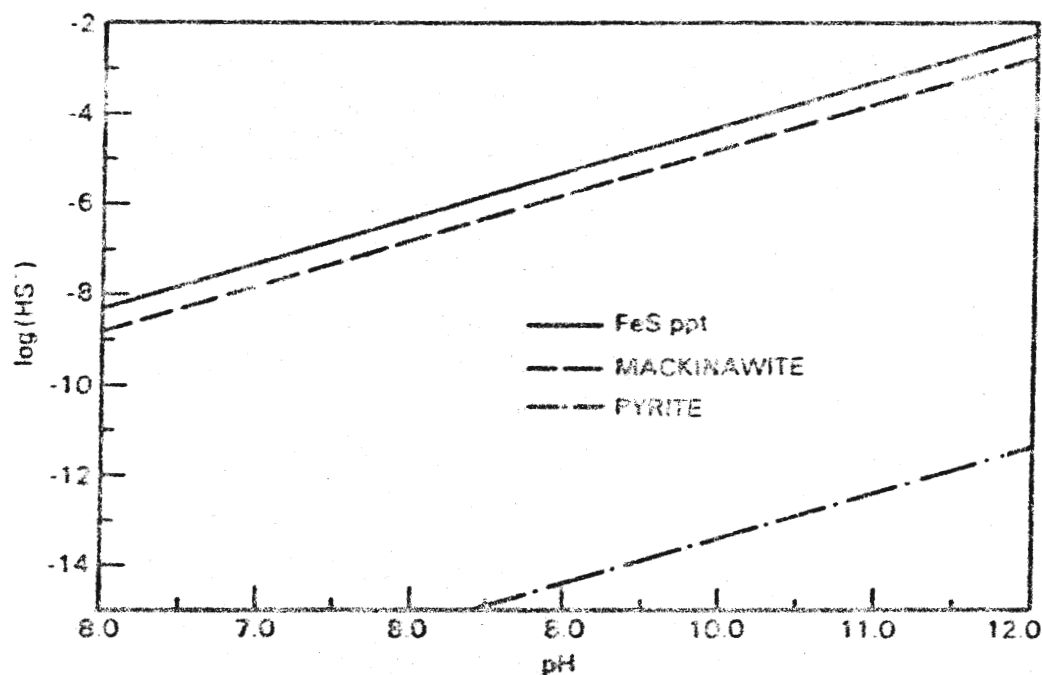


FIGURE 7. Activity of HS^- in Equilibrium with $\text{Fe}(\text{OH})_3$, S rhmb, and FeS or Pyrite. $[2\text{Fe}(\text{OH})_3 + 3\text{HS}^- = 2\text{FeS} + \text{S rhmb} + 6\text{H}_2\text{O}]$ or $2\text{Fe}(\text{OH})_3 + 3\text{HS}^- + 3\text{H}^+ + \text{S rhmb} = 2\text{FeS}_2 + 6\text{H}_2\text{O}]$

tend to reestablish reducing conditions in the aquifer because of the presence of newly formed secondary minerals and the removal of dissolved oxygen. The redox system would be similar to that of the original system before mining, and thus would theoretically have long-term stability and a lowered potential for releasing redox-sensitive contaminants to the ground water. The results of the experiments are described in the experimental section.

EXPERIMENTAL STUDIES

In this project, contaminant mobility and techniques for minimizing contaminant migration were evaluated primarily through laboratory experiments. We collected samples of sediment and ground water from aquifers that had been leached or contained ore zones that were amenable to in situ leaching, and we obtained samples of pregnant lixiviant for our experiments. This material was used in the laboratory to study natural restoration and the induced-restoration techniques of ground-water sweeping and chemical addition. Experimental and field sampling methods are described in this section as well as the results of the various laboratory studies.

Similar methods were used throughout the length of this project to collect field samples, analyze materials, and perform the laboratory experiments.

Field Sampling Procedures

The initial samples of ground water, aquifer sediment, and lixiviant were collected during March 1982 at the Benavides, Texas, in situ mine operated by Uranium Resources, Inc.^(a) Additional lixiviant was supplied from this mine by URI during April 1983. Samples of ground water and aquifer sediment were collected during August and October 1983 at the North Platte mine located near Douglas, Wyoming. This mine is also operated by Uranium Resources, Inc. Similar sampling procedures were used at both mine sites.

For ground-water and lixiviant sampling, a flow-through monitoring system was connected to the outlet line of a pump installed in the well. This allowed the measurement of certain solution parameters (pH, Eh, temperature, and electrical conductivity) that would indicate when ground water representative of the aquifer was being pumped from a well and a sample could be taken for analysis. Figure 8 is a schematic diagram of the monitoring system used at the Wyoming site. The system is composed of 1) a totalizer to measure the amount of water pumped from the well; 2) an electrode chamber that housed the pH, Eh, and temperature probes, as well as a standard mercury thermometer; 3) a water bath to allow temperature equilibration of the pH and Eh buffers with the ground water; and 4) an electrical conductivity cell. The system was air-tight

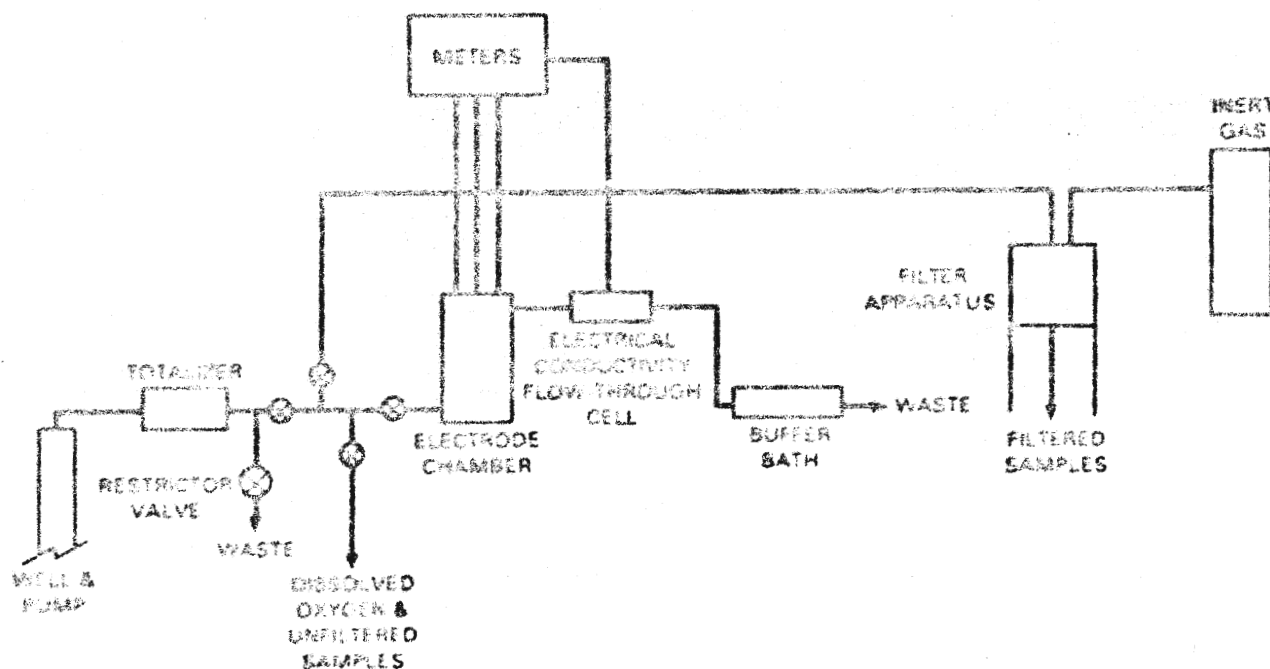


FIGURE 8. Flow Diagram of Ground-Water Monitoring System

(a) Uranium Resources Inc., Richardson, Texas.

to reduce contamination of the ground water with atmospheric oxygen. The pH, Eh, temperature, and conductivity were monitored continuously. When the reading on these parameters stabilized, filtered (0.22- μ m pore size) and unfiltered samples were taken for analyses that included onsite alkalinity and sulfide determinations. Subsamples were preserved by the methods listed in Table 4 for laboratory analysis at PNL as described in the following section.

To obtain sediment samples to use in laboratory experiments, four core-holes were drilled at both the Texas and Wyoming sites. The material collected represents unleached uranium ore, leached uranium ore (Texas site only), reduced sediment downgradient from the roll front, and sediments from the aquifers above the ore zones. The core material was photographed and described in the field, and then wrapped in plastic bags and placed in tight-fitting PVC tubes. The core material displaced most of the air from the tube, which was then capped and sealed with silicone rubber. For the Wyoming cores, the PVC tubes were fitted with a gas purging system to remove oxygen from the tube, thereby, inhibiting the oxidation of the sediment during storage. However, even for the Wyoming cores it became apparent during the laboratory experiments that the sediments had been at least partially oxidized during the storage period.

Analytical Methods

Chemical analyses were performed on ground water and lixiviant collected from the mine sites and on effluents from the flow-through column experiments and samples of supernatant from batch water/sediment interaction studies. A common set of methods were used to analyze these solutions. The concentration of most of the dissolved constituents, other than the major anions, were determined with an inductively coupled plasma (ICP) spectrometer. Several trace metals (Fe, Se, As, Al, V, and Mo) were also determined on a graphite-furnace atomic absorption (GFAA) spectrometer. Uranium was analyzed by the pulsed laser fluorescence method (Scintrex^(a) UA-3 operator's manual). For this method, aliquots of acidified samples are mixed with a solution containing a complexing agent that forms a long-lived fluorescent uranium complex. The fluorescence of the sample is measured and known addition techniques are used to correct for any matrix effects. This method is very sensitive, allowing measurements of uranium in the part-per-billion range.

The concentrations of major anions, other than carbonates, in solution were measured by ion chromatography on filtered samples. This procedure consists of chromatographically separating the anions in an exchange column followed by elution of the anions and measurement of conductivity at characteristic peak locations. A carbonate/bicarbonate carrier solution is used to elute the anions and maintain a known background conductivity level. Because the carrier eluant was a carbonate/bicarbonate solution, the inorganic carbon concentration of the solution could not be determined by ion chromatography. The classic standard acid titration procedure (ASTM D-1067, Part 31) was used to determine alkalinity from which the inorganic carbon

(a) Scintrex Limited, Concord, Ontario, Canada.

TABLE 4. Sample Preservation Methods Used at the North Platte Mine (from EPA 1979).

	<u>Total Amount</u>	<u>No. of Samples</u>	<u>Treatment</u>
As III and V	200 mL	2 - 100 mL	Filter and freeze
Fe II and III	200 mL	2 - 100 mL	Filter, acidify, and store at 4°C
TDS and Gamma Spectroscopy	4 L	4 - 1 L	Filter acidify and store at 4°C (duplicate untreated samples)
ICP Spectroscopy	200 mL	2 - 100 mL	Filter, acidify, store at 4°C
Ion Chromatography	200 mL	2 - 100 mL	Filter and store at 4°C
Dissolved Oxygen	600 mL	2 - 300 mL	None--analysis performed on site
S ²⁻ (total)	20 mL	2 - 10 mL	Add antioxidant buffer--analysis performed on site
S ²⁻ (filterable)	20 mL	2 - mL	Filter, add antioxidant buffer, analysis performed on site
Atomic Adsorption Spectrometry	50 mL	2 - 25 mL	Filter, acidify, and store at 4°C
U	50 mL	2 - 25 mL	Filter, acidify, and store at 4°C
Alkalinity (total)	20 mL	2 - 10 mL	Filter--analysis performed on site
Alkalinity (filtered)	20 mL	2 - 10 mL	None--analysis performed on site
Total Organic Carbon and Total Carbon	200 mL	4 - 50 mL	Filter and store at 4°C

concentration could be calculated. In most cases, the titrations were performed with an automatic titrator, and alkalinity was determined by measuring the amount of acid used to reach an inflection point in the pH curve.

The aquifer sediment samples were analyzed by a variety of techniques both before and after use in laboratory experiments. Samples were analyzed by x-ray diffraction to identify the major mineral phases. The most common minerals present in the sediments are quartz, feldspar, clay, and a calcite cement. Clay minerals were separated from some of the sediment for a more detailed analysis. The clay minerals were analyzed by standard procedures that involve saturation of the exchangeable sites with potassium and magnesium and treatment with ethylene glycol to cause expansion of any expandable clays. Also, the amount and identity of the exchangeable cations were determined on sediments used for the Wyoming column experiments.

Pyrite was present in some of the sediment collected from the Texas and Wyoming ore zones and from the sediments downgradient from the ore zone. Because pyrite can affect the redox state of the system, its concentration was measured in several sediment samples. A method developed and tested by Lord (1982) was used for pyrite determinations. This method consists of dissolution and removal of solids other than pyrite from the sediment followed by dissolution of pyrite and quantitative measurement of released iron. The detection limit for pyrite using this method is 0.004 wt% of the sediment.

Experimental Procedures

Two basic types of laboratory experiments were performed to investigate the production and mobility of contaminants associated with in situ leach uranium mining. Static batch experiments involved combining solution and sediment in a container to evaluate the effect of long-term water/sediment interactions on the chemistry of the solution and solid phases. Flow-through column experiments were conducted to study the influence on solution composition of the movement of lixiviant through aquifer sediment. The contact time of solution with sediment for the column experiments was 1 to 4 days; the batch experiments were run for up to 101 days. The combination of results from experiments over this time frame provided us with information that should be pertinent to actual field situations where the ground water moves at rates of tens of meters per year. The design of the two types of laboratory experiments is described in the following two sections. An evaluation of the results of the laboratory experiments follows these sections.

Batch Experiments

Static batch experiments were performed to evaluate the effect on solution and solid composition of long-term (months) contact between lixiviant and aquifer sediment. Solution and sediment samples were obtained from the Benavides in situ uranium leach mine near Bruni, Texas, and the North Platte mine near Douglas, Wyoming. The Texas lixiviant was obtained from a Benavides production well, and the Wyoming solution was a synthetic lixiviant made by adding the appropriate chemicals to ground water collected at the site. It was necessary to use synthetic lixiviant for the Wyoming site because the pilot plant was not leaching uranium at the time of sampling, so lixiviant was not available.

Three types of sediment were used for the batch experiments. Leached-ore sediment from the Texas site consisted of aquifer material from a uranium ore zone that had been leached during commercial operation of the plant. The area had been leached for approximately 2 years. The second sediment type used in the experiments was from the reduced side of the roll front in the Texas and Wyoming ore-zone aquifers. This sediment represents the material that the lixiviant would contact if the solution were allowed to leave the leach field and move down the hydrologic gradient. Finally, relatively fresh ore sediment from both Texas and Wyoming was used in some of the experiments.

The sediment samples were prepared for the experiment in an anoxic chamber to minimize oxidation of the sediment. Approximately 4 kg of each sediment type were disaggregated and placed into separate 4-L plastic containers, each containing 2-L of lixiviant. Pyrite from Ward's Natural Science Establishment,^(a) Inc. and FeS-coated sand prepared using a modification of Gent's (1977) method were added to some of the containers to determine how these solids affect reducing conditions in the system. Table 5 lists the variety of solution/sediment mixtures that were used in the experiment. Lids were placed on the containers, and they were agitated for approximately 15 min. After a settling period, two distinct layers were observed in the sediment as a result of separation of the fine and coarse particles. The solution contained some suspended particles. This solution was removed by suction, and 25-mL aliquots were filtered through 0.22- μ m filters for analysis.

The lids were replaced on the containers, and the slurries were shaken to ensure a homogeneous mixture. Once mixed, portions of the slurry were poured into 125-mL wide-mouth jars. A small amount of the original decant solution was added to the slurry so that when the lid was attached, no air was trapped in the containers. After all the samples had been prepared in this way, they were removed from the controlled atmosphere chamber and placed in the Felmar chamber. The Felmar chamber is a Plexiglas[®] box that is water tight and has two adjustable inlet/outlet valves to allow purging of gases from the chamber (Figure 9). The wide-mouth jars, which are water tight, were submerged under water in the chamber and the chamber was sealed. Upon closure of the chamber, nitrogen gas was used to purge the water of dissolved oxygen. An analysis of the water showed very little dissolved oxygen (<0.5 ppm) compared to air-saturated conditions (8 ppm).

By preparing our samples in a controlled atmosphere (argon) chamber, avoiding trapped air in the sample containers, and submerging the containers in deoxygenated water, we attempted to eliminate all external pathways for oxygen to diffuse into the enclosed environment of the sediment-lxiviant slurry. The only source of oxygen was that which was dissolved in the lixiviant (approximately 8 ppm) after its storage period. The samples were kept submerged for various lengths of time and then removed and sampled for analysis as described in the following paragraph.

(a) Ward's Natural Science Establishment, Monterey, California.

[®]Plexiglass is a registered trademark of the Rohm and Haas Co., Philadelphia, Pennsylvania.

TABLE 5. Solution/Sediment Mixtures Used in Batch Experiment

<u>Texas Lixiviant and Sediment from the Following Zones in the Texas Aquifer</u>	<u>Synthetic Wyoming Lixiviant and Sediment from the Following Zones in the Wyoming Aquifer</u>
1) reduced zone	1) reduced zone
2) oxidized zone	2) oxidized zone
3) ore zone	3) reduced zone plus 1% pyrite
4) ore zone plus 5% pyrite	4) reduced zone plus 5% pyrite
5) ore zone plus 20% FeS-coated sand	5) reduced zone plus 20% FeS-coated
6) leached ore	

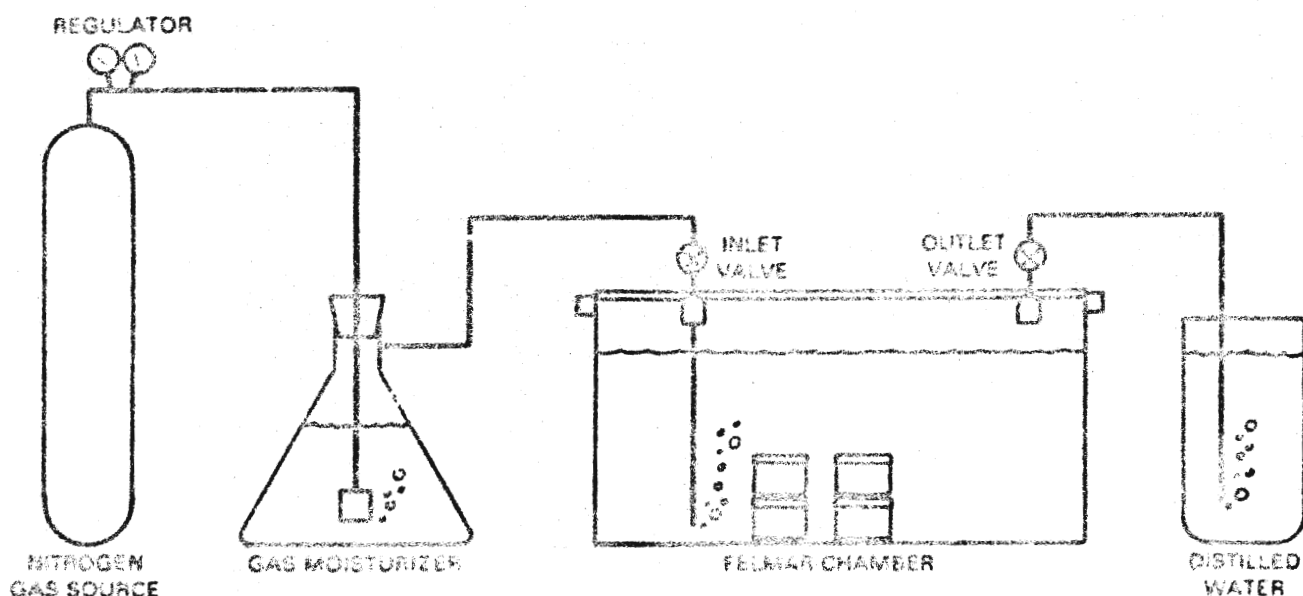


FIGURE 9. Felmar Chamber and Gas Purging System

Fourteen samples of each sediment type were submerged in the Felmar chamber. Duplicate samples were taken out of the chamber at 2, 4, 8, 16, 36, 75, and 101 days. After removal from the Felmar chamber, the samples were placed immediately in a controlled atmosphere chamber. In the chamber, the slurry samples were filtered through 0.45- μ m filters, and the pH and Eh of the solutions were measured. The solution samples were removed from the chamber, filtered through 0.22- μ m filters, and subsampled into five individual aliquots for chemical analysis. The methods used for solution analysis are described in a previous section.

The batch experimental method was also used to evaluate the effectiveness of sodium sulfide added to spent lixiviant as an aid to aquifer restoration. Sodium sulfide was added to solutions and solution-plus-solid mixtures to measure the effects on redox potential, dissolved oxygen content, pH, and solution composition. The solutions used in the experiments were distilled water and lixiviant from the Benavides (Texas) mine. For the solution/sediment systems, lixiviant was treated with sodium sulfide and allowed to interact with separate samples of iron-oxide-coated sand and leached ore.

The sodium sulfide batch experiments were conducted in 1-L reaction flasks fitted with pH and Eh electrodes, a sampling port, and gas inlet and outlet ports (Figure 10). Electric stirrers were placed under each flask and Teflon® stir bars were used to mix the solutions. Before experiments were begun and during sampling, nitrogen gas was flushed through the flasks to displace air and to minimize contamination with atmospheric oxygen. After flushing, the outlet gas lines were clamped. The flasks were not totally leakproof, and based on fluctuations in the Eh measurements, it is probable that air slowly leaked into the system. Temperature was allowed to fluctuate with room temperature, which was about 22 (±2)°C.

The sulfide-addition experiments with mixtures of solution and solids were started by adding 75 g of solid to 750 mL of solution. Solution samples for chemical analysis were withdrawn at measured time intervals to follow the

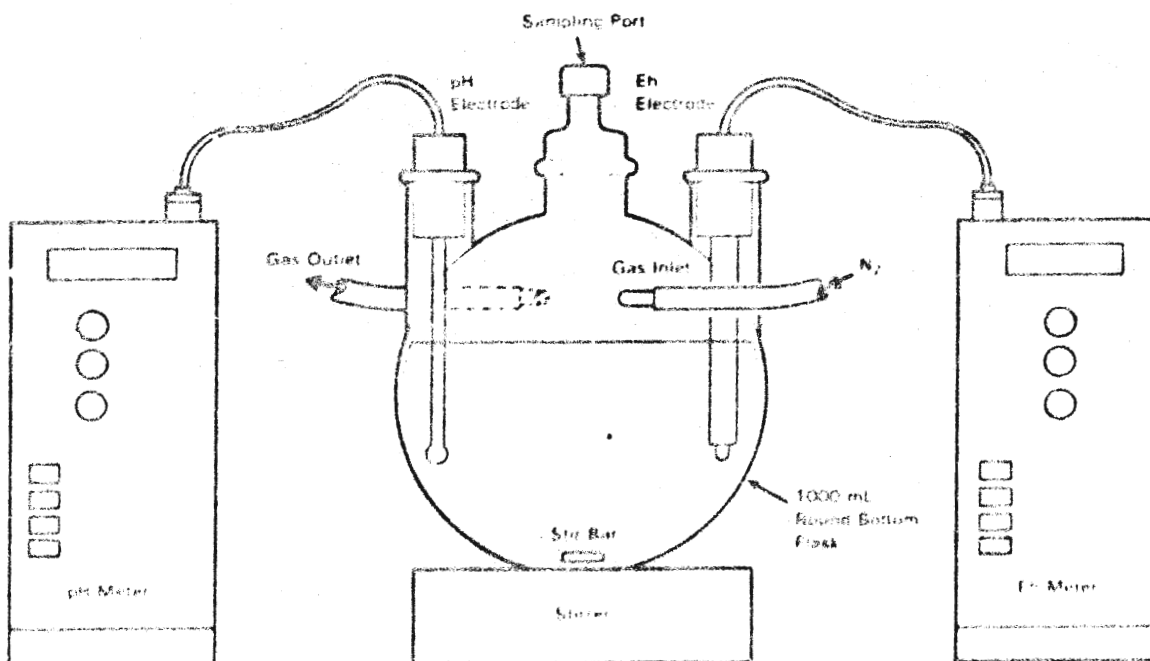


FIGURE 10. Laboratory Apparatus for Batch Sulfide Experiment

*Teflon is a registered trademark of the DuPont de Nemours, E.I., Co., Wilmington, Delaware

progress of any reactions. The pH and Eh were monitored continuously during each experiment. Solution samples were analyzed for the major cations, anions, sulfide, and dissolved oxygen. Analyses for cations and anions were performed as described previously. Samples for sulfide determination were preserved by adding sulfur antioxidant buffer. Concentrations of sulfide were then measured by Eh titration with lead perchlorate titrant and sulfide-specific ion and reference electrodes (Orion Research Inc. 1970). Dissolved oxygen was determined by Winkler titration (Franson 1981). As expected, the addition of relatively small amounts of sodium sulfide to the lixiviant had a major effect on Eh and dissolved uranium concentration.

Column Experiments

Flow-through column experiments were conducted to study natural restoration and restoration by induced methods. Natural restoration was evaluated by pumping lixiviant through columns packed with reduced sediment collected down-gradient from Texas and Wyoming roll-front uranium deposits. Leached ore and spent lixiviant from Texas were used to evaluate ground-water sweeping and restoration enhanced by the addition of sulfide to the system. The laboratory apparatus used for the column experiments was similar in all cases.

The sediment was packed in Lucite® columns that were sealed with Lucite® collars and endcaps as shown in Figure 11. Each endcap contained an O ring, which seated against the end of the cylinder, and was held by screws through the endcap and collar. Solution entered and exited through holes drilled in the endcaps of the columns. To prevent particle migration, each hole was covered with a nylon mesh filter (30- μ m pore size--21% open area) supported on a stainless steel screen and attached to the endcap with a silicone rubber compound. All columns had an inner diameter of 6.34 cm. Three different lengths of columns were used to give nominal pore volumes of 150, 300, and 600 cm³ when the sediment was packed to a bulk density of 1.5 g/cm³.

Each packed column was connected to a pump/collector system shown schematically in Figure 12. Lixiviant or ground water was pumped from a reservoir by either a syringe or a multistaltic pump. The solution flowed up the column (to enhance saturation of the column with the solution) and out to an automatic fraction collector. For some experiments, in-line Eh and pH measurements were made on the column effluents. The effluent samples were prepared and analyzed according to procedures described in the section on analytical methods. Several of the column experiments were conducted inside a controlled atmosphere chamber to minimize oxygen contamination from the atmosphere. The column experiments showed that natural restoration and restoration by chemical addition methods have advantages over the standard methods for restoration. Also, some of the limitations of ground-water sweeping were demonstrated. These results are described following the results of the batch experiments.

®Lucite is a registered trademark of the DuPont de Nemours, E.I., Co., Wilmington, Delaware.

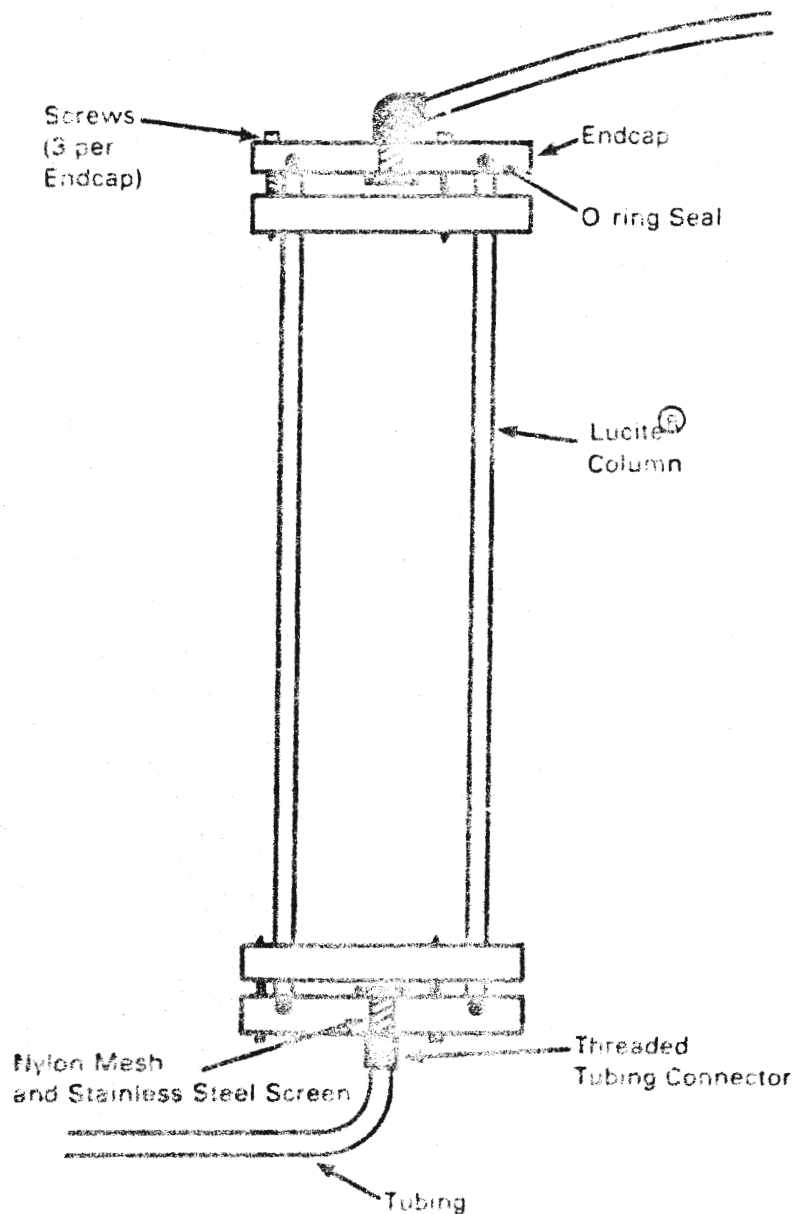


FIGURE 11. Column Design

EVALUATION OF NATURAL RESTORATION

This section contains a description of the results of batch and column experiments in which natural restoration processes were studied.

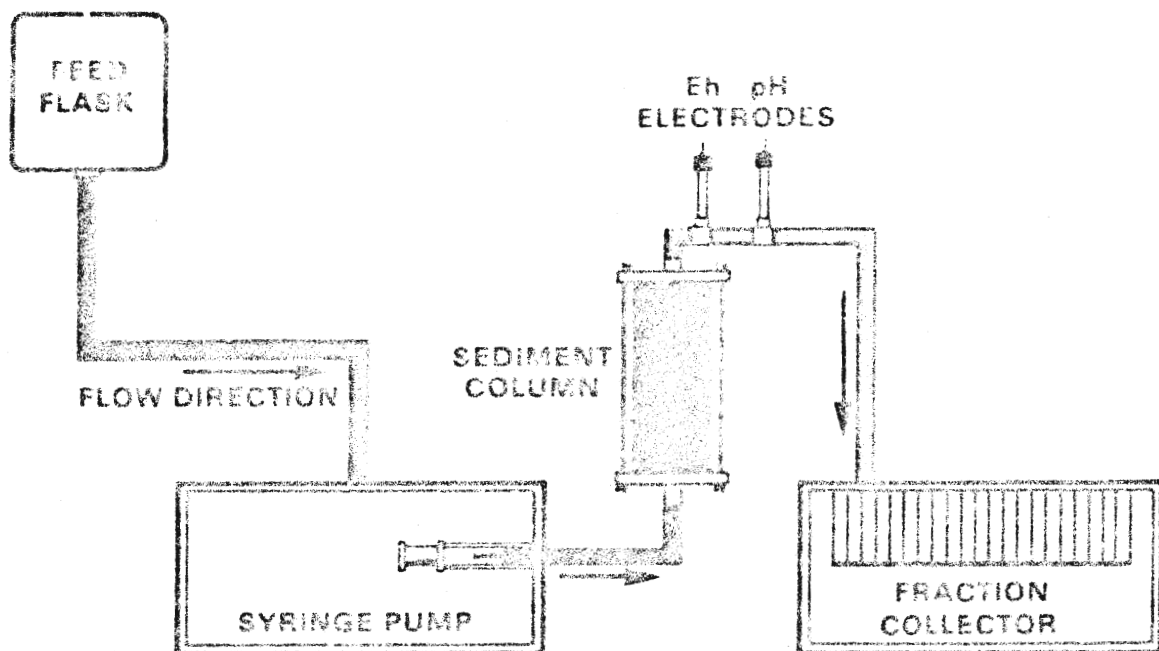


FIGURE 12. Schematic of Column Test Apparatus

Results of Static Batch Experiments Using Sediments from a Texas In Situ Leach Uranium Mine

Two sets of experiments each lasting 3-1/2 months were conducted. The first took place from February to May 1983 and the second from March to June 1984. Six types of sediment from the Texas mine site were used in the experiments:

1. reduced sediment from the zone downgradient of the ore zone
2. oxidized sediment from the zone upgradient of the ore zone
3. ore-zone sediment
4. ore-zone sediment with 5% pyrite added
5. ore-zone sediment with 20% FeS-coated sand added, and
6. leached ore.

These experiments were designed to study the effects on solution composition of long-term contact of lixiviant with the various types of aquifer sediments. The results of the experiments are described together.

Solution data from the batch experiments are given in Appendix A, Tables A.1 to A.6. The data show that dissolved calcium and sulfate concentrations increase significantly when lixiviant is initially mixed with all sediment types except oxidized sediment (Figures 13 and 14). High concentrations of calcium and sulfate were present in solution because the lixiviant mixed with pore fluids in the sediment that had high calcium and sulfate

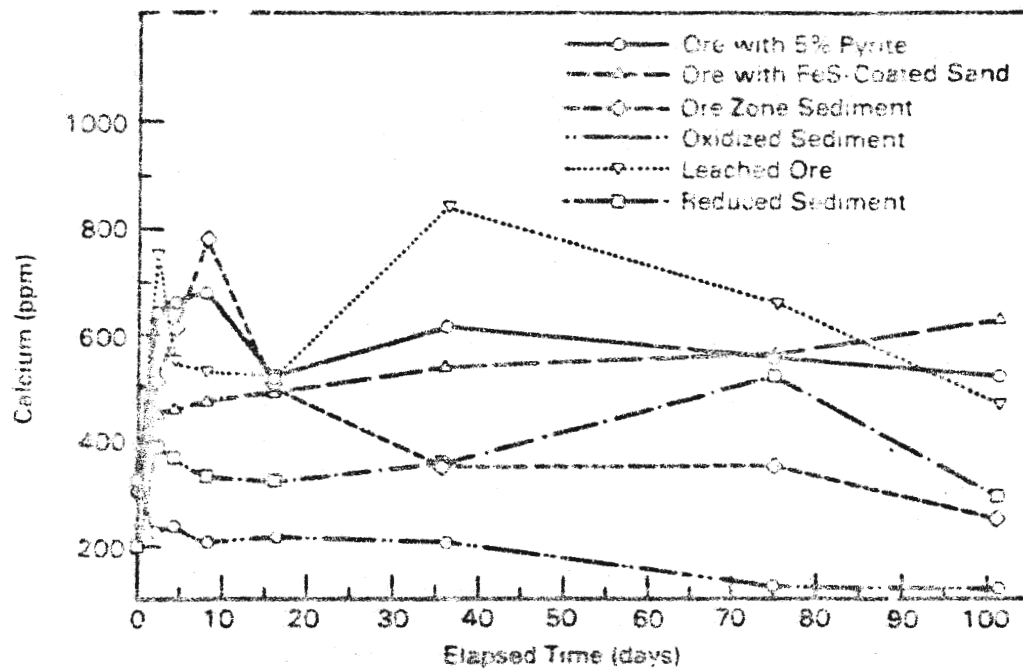


FIGURE 13. Calcium Solution Concentrations in Batch Experiments with Texas Sediments

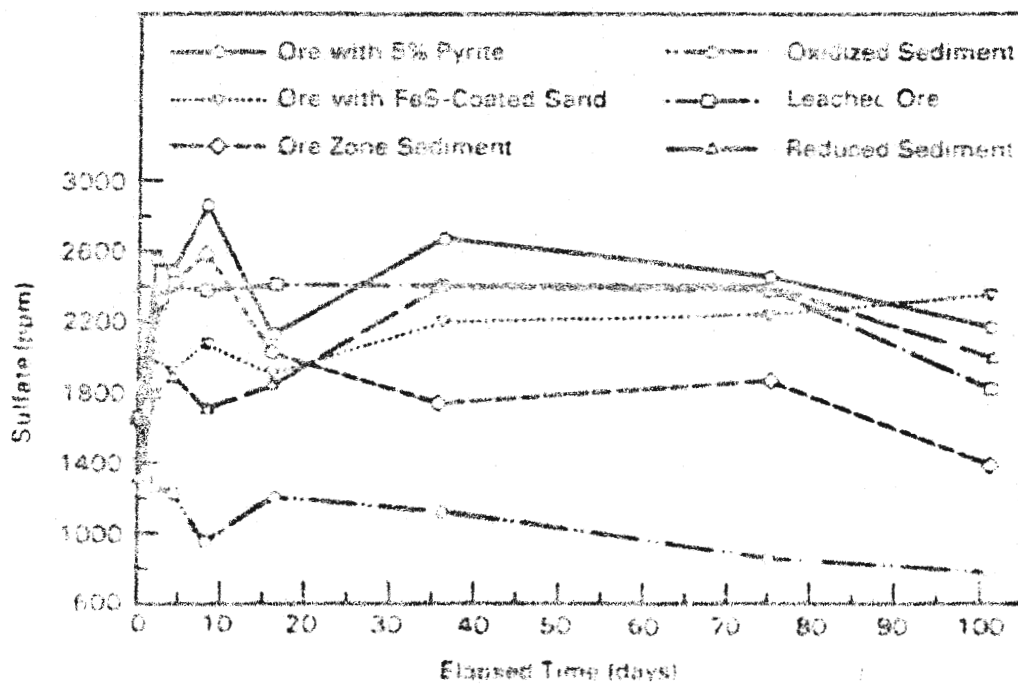
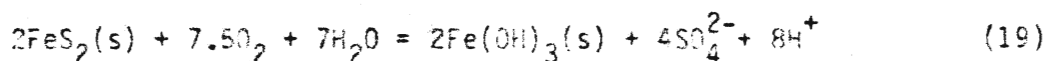
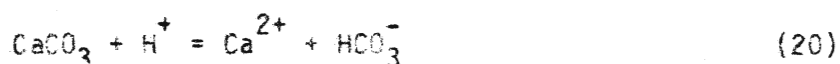


FIGURE 14. Sulfate Solution Concentrations in Batch Experiments with Texas Sediments

concentrations and possibly because soluble calcium sulfate minerals were dissolved from the sediment. The pore fluids had high calcium and sulfate concentrations as a result of reactions between the pore fluid and the sediment during storage of the core. The primary chemical process is the oxidation and dissolution of pyrite according to the reaction:



This reaction consumes oxygen and produces solid ferric hydroxide and dissolved sulfate and hydrogen ions. The increase in hydrogen ions increases the solubility of calcite in the sediment, and some of it dissolves:



This reaction will tend to buffer the pH of the solution near 8 if sufficient calcite is present, and it will also increase solution concentrations of calcium and carbonate. The calcium and sulfate solution concentrations in contact with the sediments are approximately those expected if gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) were dissolving and equilibrating with the solution. Calculation of the gypsum saturation index shows that the leached ore samples reach saturation with respect to gypsum and the reduced sediment solutions are slightly undersaturated. Pyrite was not present in the oxidized sediment from the aquifer; consequently, elevated calcium and sulfate concentrations were not found in the solutions contacting oxidized sediment samples.

The iron concentrations for the Texas leached-ore samples increased rapidly at the beginning of the experiment and leveled off between 16 and 36 days at approximately 27 ppm (Figure 15). The concentration of dissolved iron for the reduced sediment samples showed an increase after 16 days of the experiment with a maximum value of 3.9 ppm. At 75 and 101 days, the iron values decreased for both sediment types and reached lows in the range of 0.1 to 3 ppm with the leached-ore samples having the higher concentrations. Such high concentrations of dissolved iron were only possible at near neutral pH values if reducing conditions relative to the Fe(II)/Fe(III) couple existed in the system. A possible mechanism for producing such conditions is discussed at the end of this section. The fact that dissolved iron concentrations were not significantly elevated for the other sediments suggests that such highly reducing conditions were not present in these sediments. The experiments in which the ore-zone and oxidized-zone sediments were used were conducted 1 year after the experiments with reduced sediment and leached ore, and we believe that this additional storage time oxidized the sediments to such an extent that reducing conditions could not be produced in these solution/sediment mixtures. The iron

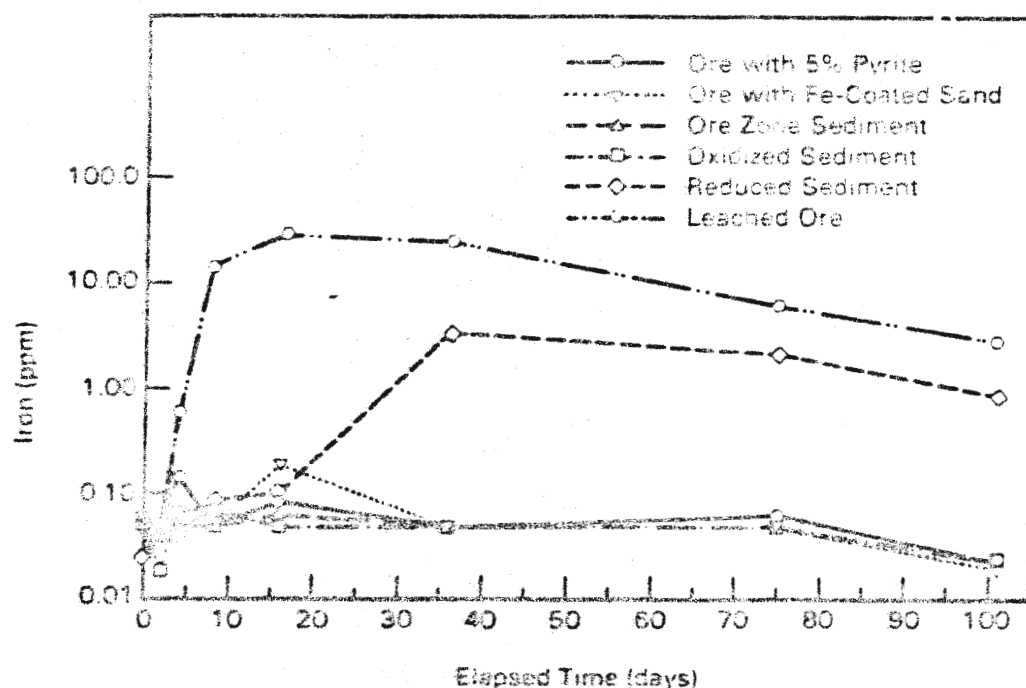


FIGURE 15. Iron Concentrations in Batch Experiments with Texas Sediments

concentrations in solution in contact with the ore-zone and oxidized-zone sediments were those expected if ferric hydroxide were forming and limiting iron concentrations in solution.

The dissolved uranium concentrations of the Texas batch experiments also show this difference in the redox state of the sediments. The uranium concentration in the original lixiviant used for the 1983 batch experiments with reduced sediment and leached ore was 52 mg/L. In the solution samples collected during the second day of the experiment, the uranium concentration for the reduced sediment samples had dropped to approximately 11 mg/L, and for the leached ore, the two analyses were 16 and 22 mg/L (Figure 16). The uranium concentration in the leached ore samples held steady at about 20 mg/L until the 15-day samples, which contained 3 and 5 mg/L for the duplicate samples. At 36 days, one of the leached-ore samples had 0.25 mg/L uranium, and the other had a much higher value of 13.8 mg/L. This high value falls well outside the established trend of decreasing uranium during the experiment. For the 75- and 101-day leached ore samples, the uranium concentration was in the range of 0.13 to 0.76 mg/L. The uranium concentrations in the reduced sediment samples followed a trend somewhat similar to that of the uranium in solution in contact with the leached-ore sediments. There was an initial large drop when the lixiviant was added to the sediment. The concentration of uranium in solution stayed between 10 and 18 mg/L through day 16 of the experiment. At day 36, the concentration dropped to about 1 mg/L. It was less than 1 mg/L for three of the 75- and 101-day samples and 3.3 mg/L for the fourth sample.

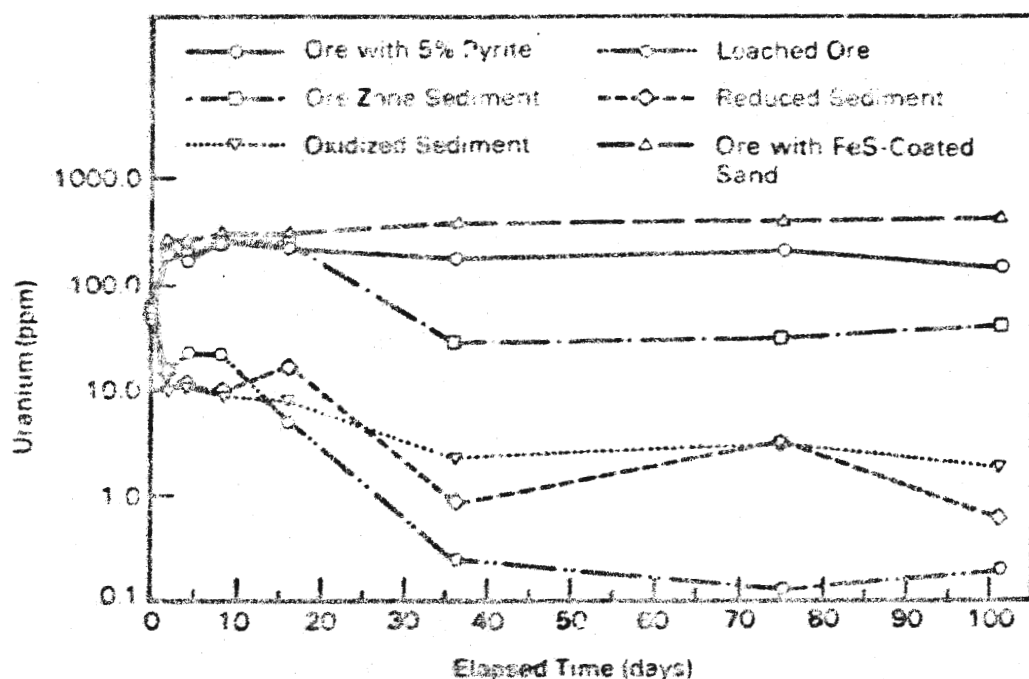


FIGURE 16. Dissolved Uranium Concentrations for the Batch Experiments with Texas Sediment

The lixiviant used in the 1984 batch experiments with ore-zone sediments and oxidized sediment had a uranium concentration of 44 ppm. As shown in Figure 16, the solution concentration of uranium increased to over 300 ppm for some sediments after contact with the ore-zone sediments. Oxidizing conditions were apparently well established in these sediments, and the uranium ore dissolved when the lixiviant was added. Even the addition of pyrite and FeS-coated sand to the sediment was apparently not enough to produce reducing conditions for the time scale of the experiment. Actually, the ore-zone sediment without reducing minerals added showed a greater reduction in dissolved uranium concentration. Assuming that this sediment had been oxidized during storage, it is reasonable to assume that the process lowering uranium concentration was adsorption on to ferric hydroxide, which is known to be a strong adsorber for uranium (Ames et al. 1983). For the sediment in which a reductant (pyrite or FeS-coated sand) was added, some of the original sediment was removed to allow for the volume of reductant, thereby lowering the amount of any ferric hydroxide that was present in the sediment. Also, if the reductant was working at all, it may have reduced the adsorption capacity of the remaining ferric hydroxide. The importance of ferric hydroxide in removing uranium from solution is suggested by the dissolved uranium concentrations for the oxidized sediment (Figure 16). Over the time period of the experiment, the uranium concentration decreased from 44 ppm to approximately 2 ppm. This was the lowest uranium concentration measured for the 1984 batch experiments and probably reflects the presence of ferric hydroxide in these oxidized sediments.

The experiments conducted show that a number of processes appear to be active in our batch system. These processes may include sorption, oxidation-reduction, and mineral dissolution/precipitation. The experiments conducted in 1984 did not adequately simulate natural restoration because of the oxidation of the cores during storage and the relatively large amount of uranium dissolved from the sediment during the experiment. However, information applicable to natural restoration was obtained from the 1983 experiments, and a discussion of these experimental results is emphasized here.

There is little doubt that the large increase in calcium and sulfate at the beginning of the experiments was caused by the dissolution of gypsum from the sediment. Gypsum is not a normal component of the aquifer sediments, and we believe that it was produced in the leached ore by oxidation of pyrite during the leaching process. Gypsum was probably produced in the ore-zone sediments and the reduced sediment by pyrite oxidation during collection and storage of the sediment.

The decrease in uranium concentration of the lixiviant from 53 to 21 mg/L on initial contact with both the leached ore and reduced sediment was probably caused by sorption of uranium by clays, oxyhydroxides, organic matter, or other solids present in the sediment. The concentration of dissolved uranium remained above 10 ppm for the majority of the 2-, 4-, 8-, and 16-day samples for these sediments, after which it decreased. The decrease in dissolved uranium concentration for the post-16-day samples may have resulted from the reduction of the uranium from the +6 to the +4 valence state and precipitation of uranium (possibly as UO_2). The identity of the reductant is of prime interest in this study. Pyrite was present in the sediment and could have served as a reductant for oxygen and U(VI), but the oxidation of pyrite would not lead to high iron values as were found in the experiment. Although the solution and sediments were not analyzed for bacteria, the most likely reducers in this system are bacteria, which use oxygen, iron, sulfate, and organic matter as their energy sources. Aerobic bacteria initially use oxygen dissolved in the lixiviant to oxidize available organic matter. The Eh of the solution is lowered by this process, but not enough to affect other redox-sensitive constituents in the solution. This could have been the situation in the 2- and 4-day samples in which iron and uranium concentrations remained close to the original value obtained for the slurry.

After the aerobic bacteria consume all of the oxygen, the next constituent to be reduced is iron (Champ, Gulens and Jackson 1979), which is present in the dissolved form and as ferric oxyhydroxide solids in the sediment. As Fe(III) is reduced to Fe(II) and the Eh is lowered, the Fe(III) solids become more soluble and iron concentration in solution increases markedly. There are probably more Fe(III) oxides to be dissolved in the leached ore than in the reduced sediment; consequently, dissolved iron concentrations are higher in the solutions from the leached-ore samples. The 36-day sample shows the maximum dissolved iron concentrations for both the leached ore and reduced sediment samples, and it is possible that at this point, iron-reducing bacteria had consumed all the available Fe(III). The Eh may be low enough that U(IV) minerals become supersaturated and begin to precipitate. This would lower the uranium concentration as was found in most of the post-36-day samples. As an

alternative to the process of uranium removal from solution by precipitation of U(IV) minerals, the surface exchange sites on the aquifer solids may be changing with time to a condition that would enhance adsorption of uranium and its removal from solution via a sorption process. However, this process seems less likely if the Fe(III) oxides are also being consumed during establishment of reducing conditions because these oxides are the solids most likely to adsorb uranium (Ames et al. 1983).

Sulfate-reducing bacteria may begin to influence the system as the iron-reducers begin to decline. This lowers the Eh even further and produces reduced sulfur species. This will have a significant effect on the iron concentration because ferrous sulfides (e.g., pyrite) are not very soluble under these conditions. The precipitation of ferrous sulfide minerals is reflected in the experimental results by the decrease in total dissolved iron concentrations from approximately 25 mg/L at day 36 to 2.8 and 6.2 mg/L at day 75 and 0.35 and 2.8 mg/L at day 101 for the leached-ore duplicate samples. Sulfate concentration (Figure 14) also dropped at the end of experiment, although it was not as dramatic as iron because dissolved sulfate concentration was much higher than dissolved iron. We noted at day 75 that the color of the sediment had changed from light gray to black with a metallic luster. This is a characteristic color for ferrous sulfide solids. The dissolved iron concentrations at day 101 for the reduced sediment are 0.1 and 0.8 mg/L while the peak values at day 36 were 3.4 and 3.9 mg/L. No significant color change was noted for the reduced sediments, which started out dark gray. The amount of ferrous sulfide precipitated in the reduced sediment samples that would be needed to account for the change in iron concentration was much less than in the case of the leached ore, and thus a color change may not have been noticeable. Similar changes in the iron content of sediments have been noted in experiments with lake bottom sediments in which bacterial action is known to be important (Mortimer 1941, 1942).

Results of Static Batch Experiments Evaluating Natural Restoration at a Wyoming In Situ Leach Uranium Mine

These experiments were conducted concurrently with the Texas batch experiments during March through June 1984. The Wyoming sediments that were used were collected during September 1983:

- 1) reduced sediment
- 2) reduced sediment with 1 wt% pyrite added
- 3) reduced sediment with 5 wt% pyrite added
- 4) reduced sediment with 20 wt% FeS-coated sand added
- 5) oxidized sediment.

Because we took added precautions in the field to keep the reduced sediments from being oxidized and because of the relatively short amount of time between sample collection and use of the sediments in these experiments, we feel that these experiments closely simulate the process of natural restoration for the Wyoming mine site.

The solution data for these batch experiments are contained in Appendix B, Tables B.1 to B.5. The lixiviant used in these experiments had a calcium concentration of 98 ppm and a sulfate concentration of 439 ppm. The supernatant of the lixiviant/reduced sediment mixture at the beginning of the experiments had much higher concentrations of these constituents: 247 ppm calcium and 850 ppm sulfate. A similar change in concentration for calcium and sulfate was noted for the Texas batch experiments. This occurrence is most likely a result of the formation of gypsum in the sediment from pyrite oxidation and calcite dissolution during storage of the sediment. Gypsum dissolved in the lixiviant when the solution was added to the sediment. The calcium and sulfate concentrations of the lixiviant did not change when it was added to oxidized Wyoming sediment collected upgradient from the ore zone where no pyrite is present. This is additional evidence that oxidation of pyrite in the reduced sediments produces the observed effect on calcium and sulfate concentrations.

Figures 17 and 18 show the response of the solution concentrations of calcium and sulfate to contact time with the various sediments. When no pyrite was added, the concentration of these constituents remained fairly stable. The greater the amount of pyrite added, the higher the resulting calcium and sulfate concentration in solution. In the case of the sediment with 5% pyrite added, the solution probably reached equilibrium with gypsum. The solutions in contact with sediment amended with FeS-coated sand did not show these large increases in calcium and sulfate concentration, and in fact they responded in a manner similar to the reduced sediment with nothing added to it. Although 20% of the sediment in the FeS-coated sand experiment consisted of the coated sand, the majority of the coated sand is quartz grains and probably much less than 1% of the total sediment weight is FeS. Apparently not enough FeS was in these sediment mixtures to affect solution concentrations of calcium and sulfate as was the case for the pyrite-amended sediments.

The concentration of dissolved iron for the various Wyoming sediments is shown in Figure 19. As was found for calcium and sulfate, dissolved iron did not show an appreciable change in concentration compared to the original lixiviant for the oxidized sediment and the FeS-coated sand sediment. Conditions probably remained oxidizing throughout these two experiments, and iron concentration was limited by relatively insoluble ferric hydroxide. The reduced sediments however show a very different response. At 8 and 16 days, there was a definite maximum in iron concentration. As in the case of the Texas sediments, these high dissolved iron concentrations are believed a result of the establishment of reducing conditions [for Fe(II)/Fe(III)] and the dissolution of ferric hydroxide in the sediment. Figure 20 shows that the Eh of the solutions were much lower than that of the original lixiviant (+397 mV), although there was not a direct correspondence between minimum Eh and maximum dissolved iron concentration. The pH values of the solutions were also affected by contact with reduced sediment. In most cases, the minimum pH was achieved at the end of the experiment after 101 days of contact time (Figure 21). The amount of pyrite present seemed to determine the amount that pH was lowered. For the original reduced sediment the minimum pH was 6.4; with 1% pyrite added, the lowest pH was 5.2; and with 5% pyrite added, it was 4.4. Apparently, there were not sufficient carbonate minerals present in this

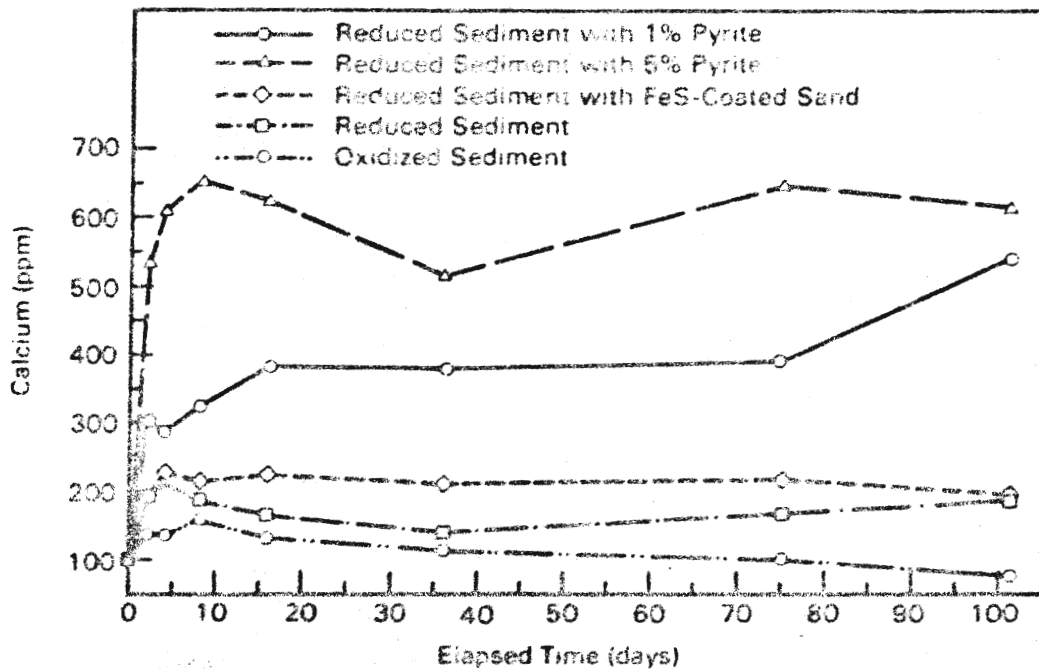


FIGURE 17. Dissolved Calcium Concentrations for Batch Experiments with Wyoming Sediments

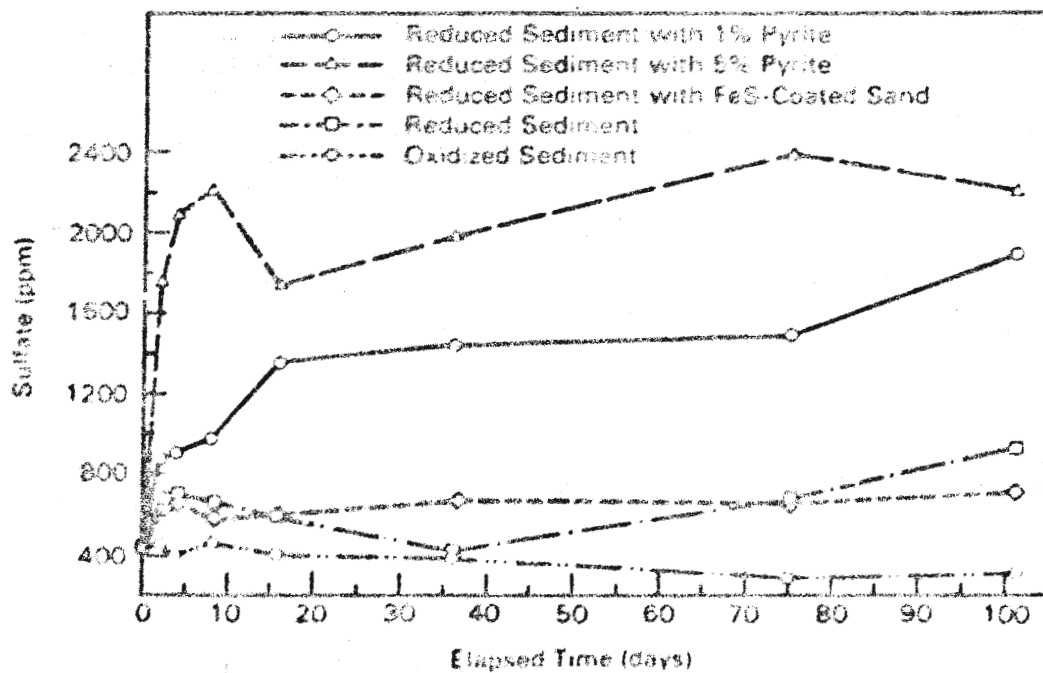


FIGURE 18. Dissolved Sulfate Concentrations for Batch Experiments with Wyoming Sediments

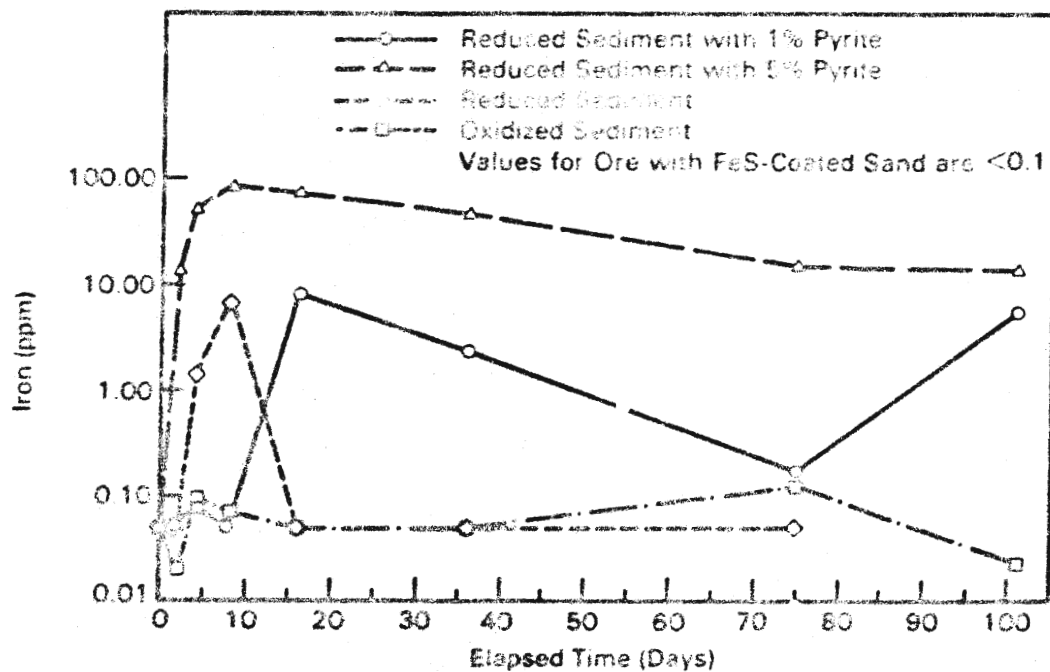


FIGURE 19. Dissolved Iron Concentrations for the Batch Experiments with Wyoming Sediment

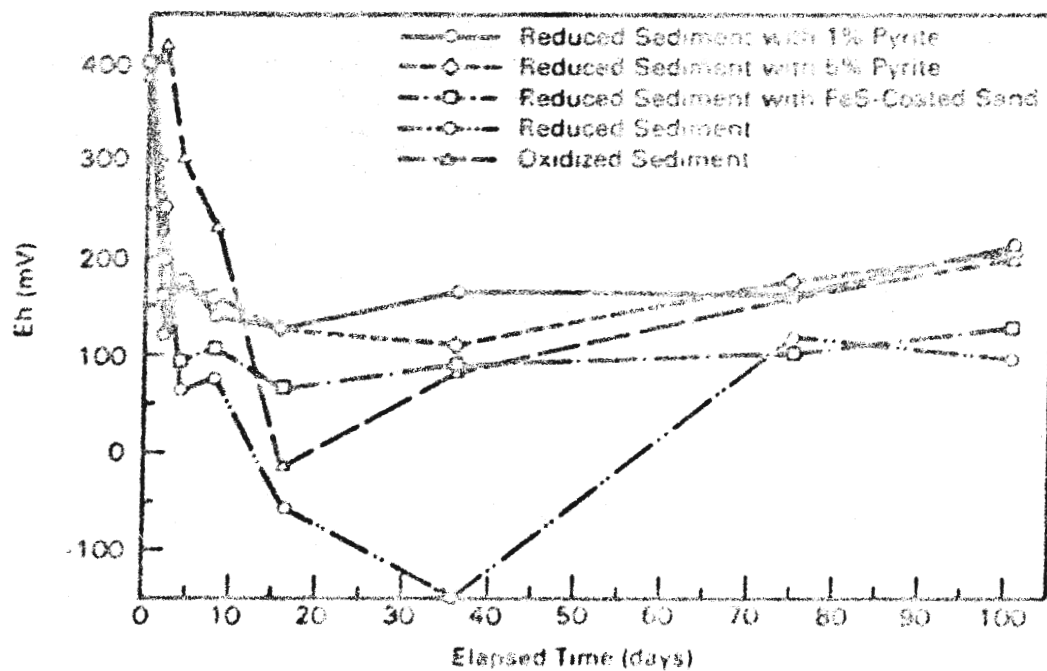


FIGURE 20. Eh Values for the Batch Experiments with Wyoming Sediments

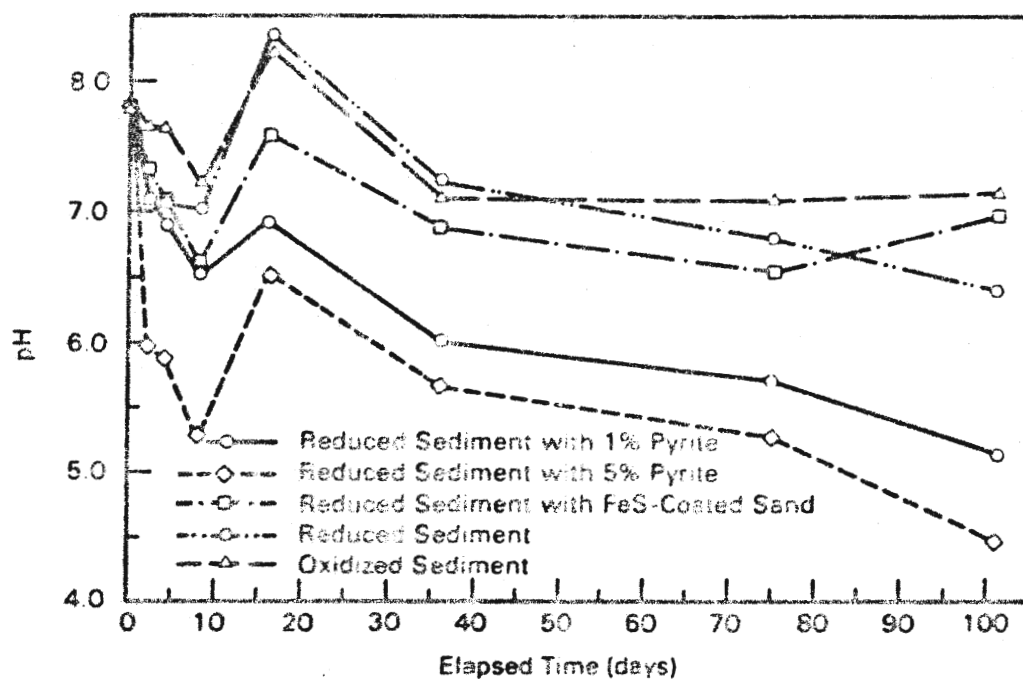


FIGURE 21. pH Values for the Batch Experiments with Wyoming Sediments

sediment to buffer the pH as well as the Texas sediments did. In the Texas sediment with 5% pyrite added, the minimum pH was 6.5. The low pH of the Wyoming sediments with pyrite added would also contribute to increases in dissolved iron concentration because the iron oxides are more soluble at lower pH values.

The dissolved uranium concentrations for the Wyoming batch experiments are shown in Figure 22. In all cases, the uranium concentration decreased throughout the experiment, and except for the oxidized sediment, it was less than 1 ppm at the 101-day sampling time. Because the solution chemistries of the experiments with reduced sediment and oxidized sediment were markedly different, we believe that the chemical process by which uranium is removed from solution may be different for the two sets of experiments. When pyrite was added to the reduced sediment, the redox state of the system was lowered as evidenced by the high dissolved iron concentrations. Because uranium minerals containing U(IV), are generally less soluble than those containing U(VI), the dissolved uranium concentration will decrease if conditions change such that the dominant uranium species shifts from U(VI) to U(IV).

Another factor to consider is the solubility of uranium minerals relative to the amount of carbonate in solution. Uranium (VI) forms strong carbonate

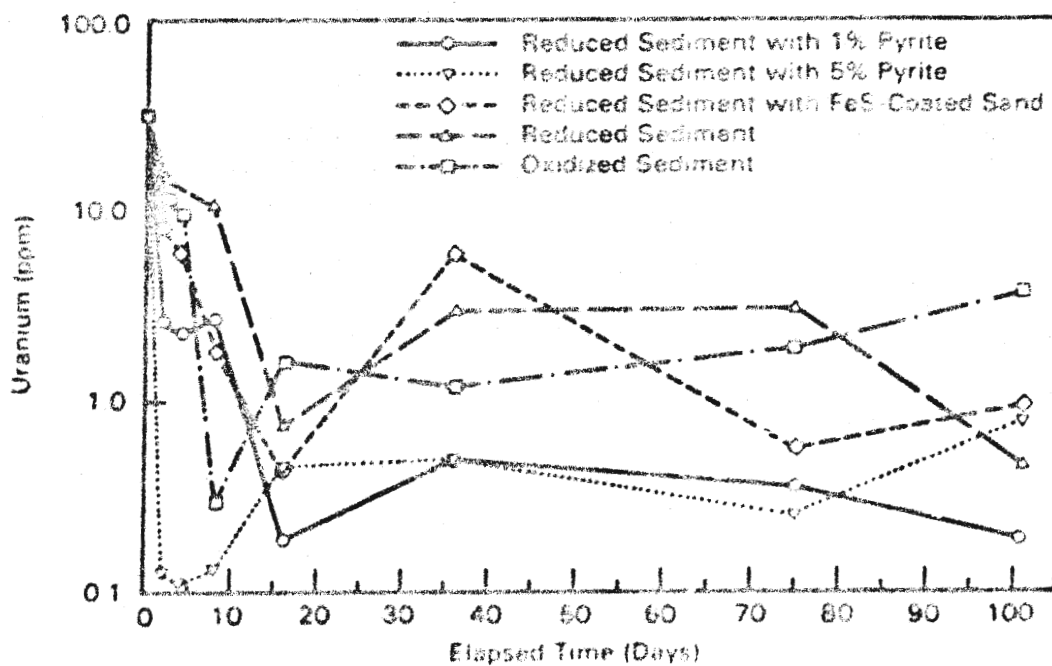


FIGURE 22. Dissolved Uranium Concentrations for the Batch Experiments with Wyoming Sediments

complexes (Langmuir 1978) that would be the dominant uranium complexes in the lixiviant used in these experiments. However, because the pH of the solution decreases from 7.8 to less than 5.2 for the reduced sediments with 1% and 5% pyrite added, the amount of dissolved carbonate drops precipitously, thereby decreasing the solubility of uranium minerals.

The formation of uranium minerals is not believed to cause the reduction in solution concentration of uranium in the oxidized sediment and FeS-coated sand experiments. In these experiments, it did not appear that reducing conditions were established because the iron concentration of the solutions did not increase. As discussed previously, the presence of ferric hydroxide in the sediment favors adsorption of uranium onto the sediment, and this is most likely the process that removes uranium from solution in contact with these sediments. It is interesting to note that the final dissolved uranium concentration for these two experiments is almost as low as that found for the reduced sediment with pyrite added. It appears that it does not matter whether the sediment is oxidizing or reducing; given sufficient time uranium will be immobilized by the sediment, and the concentration of dissolved uranium will be decreased accordingly. This is the main reason that we do not feel that uranium would be a good indicator of a lixiviant excursion from the leach field.

Results of Column Experiments Evaluating Natural Restoration at a Texas In Situ Leach Uranium Mine

These experiments were conducted during August 1982 and November through December 1982. They are described in detail in Deutsch et al. (1983). Here, we summarize the experimental results in order to compare them with the results of similar experiments carried out on Wyoming sediment and lixiviant.

The Texas column experiments showed that the redox potential and the concentrations of uranium and carbonate in the lixiviant that was pumped through the columns were greatly affected by contact with a small amount of sediment. The Eh of the solution changed from +300 mV to -300 mV; the dissolved uranium concentration dropped from 52 ppm to less than 1 ppm; and carbonate concentration decreased by half. The concentrations of most of the major cations (Na, Ca, Mg, and K) and anions (Cl and SO_4) in the column effluent were equal or close to those of the influent lixiviant. This suggests that most of the major ions of the lixiviant were not significantly retarded by chemical reactions as they passed through the column.

The chemical trends observed in effluent solution chemistry for the column experiments allow us to hypothesize on probable mechanisms at work in this water/sediment system. The initial effluent from the columns is composed chiefly of residual pore water in the sediment. It is distinctly different than the ground water that was collected at the site, and this variation is attributed to reactions occurring between the pore water and sediment during storage. The 10x to 40x increase in sulfate concentration of the initial effluent from all of the columns compared to the measured ground-water concentration of sulfate is a result of oxidation of pyrite (FeS_2) in the sediment by oxygen that entered the system during sample collection or storage. Pyrite oxidation produces sulfate and ferric iron. The sulfate concentration

increased in the solution, but iron concentration remained fairly stable because at the redox conditions of these solutions, it is precipitated as hydrous ferric oxyhydroxides.

The oxidation of pyrite also produces hydrogen ions that 1) compete with other dissolved cations for surface exchange sites, 2) hydrolyze silicate minerals, and 3) dissolve carbonates. These reactions all tend to increase the amount of Ca, Mg, Sr, Na, and K in the solution that is observed in the initial effluents. The only constituent of the initial effluent solutions that shows a lower concentration when compared to the ground-water composition is carbonate. Expressed as carbonate alkalinity, the concentration of this constituent decreased by half during the storage period of the core in response to the increasing concentration of Ca (and probably Mg and Sr to some extent) and the resulting precipitation of calcite (CaCO_3).

After the residual pore water was flushed from the cores, the effect of the lixiviant/sediment interaction was observed in the composition of the effluent solutions. Pyrite was stable in the low redox state of the system established by the reducing sediment and shown by the measured Eh values of the effluent. Because pyrite was stable, additional sulfate was not produced and the dissolution and ion exchange reactions accompanying an increase in hydrogen concentration did not occur. As a result, the concentrations of Ca, Mg, Sr, Na, K, and SO_4 decreased and approached the influent concentration as cumulative effluent volume increased. Most of these constituents did not quite drop to values as low as that of the influent (lixiviant) solution. At the low Ehs measured for the effluent, sulfide would be the expected sulfur specie rather than sulfate. Apparently, the rate of sulfate reduction was not adequate under the conditions of the column experiments to alter an appreciable amount of the influent sulfate to sulfide.

The chemical interaction of uranium with the sediment is of primary interest for its own sake and because from it, we may gain information about other redox-sensitive elements. The data from the November-December 1982 natural restoration column experiment (Figure 23) show that uranium concentration in solution was definitely affected by reactions between the lixiviant and sediment. Following an initial peaking of uranium concentration in the effluents from the three columns, the concentration decreased markedly and appeared to stabilize at the low ppm or ppb level. The previous report (Deutsch et al. 1983) discussed possible explanations for this phenomenon that include a lag time for the establishment of reducing conditions in the sediment-filled column and the formation of a concentration-limiting uranium solid with low solubility. Whatever the case, the movement of dissolved uranium is definitely inhibited by contact with the sediment used for these column experiments. Based on the occurrence of other redox-sensitive trace metals (e.g., As, Se, Mo) in the vicinity of typical uranium roll-front deposits, it is realistic to assume that the mobility of these elements would also be retarded by water/sediment interactions. Consequently, the results of these Texas column experiments showed that the movement of certain elements that have been identified as contaminants from in situ uranium mining will be retarded and that water/sediment interactions may possibly immobilize the contaminant.

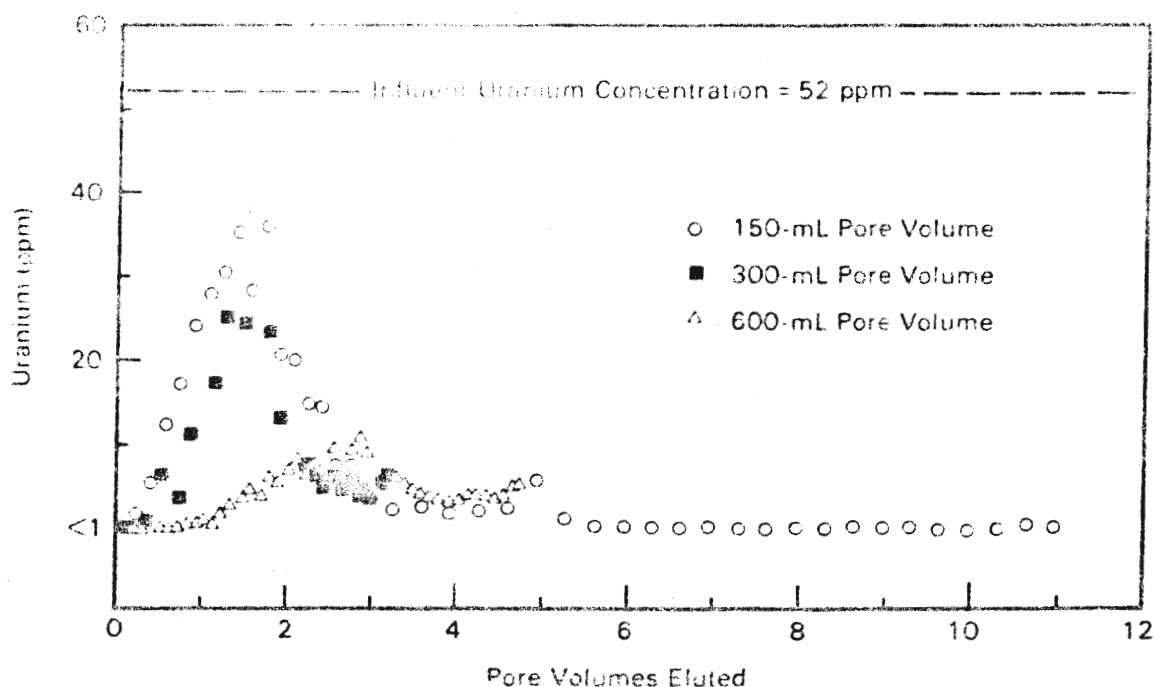


FIGURE 23. Dissolved Uranium Concentration of Column Effluents as a Function of the Cumulative Amount of Solution Eluted from the Texas Natural Restoration Experiments

Results of Column Experiments Evaluating Natural Restoration at a Wyoming In Situ Leach Uranium Facility

During December 1983, sediment from the North Platte (Wyoming) mine and a synthetic lixiviant similar in composition to the actual production leaching solution were used in a column experiment to evaluate the potential for natural restoration at this site. The results of this experiment have not been previously published and are presented in detail in this report.

The major minerals present in the sediment were determined by x-ray diffraction to be quartz, kaolinite, chlorite, and feldspar. This combination is similar to the mineralogy of the sediments used in the Texas natural restoration experiment. However, the Texas sediment also contained approximately 4 wt% pyrite, while the Wyoming sediment contained 3.05 wt% pyrite. Because pyrite contains elements in a reduced valence state, this mineral is potentially important in establishing the redox condition of a system.

The synthetic lixiviant was pumped through two separate sediment columns at a rate of approximately 6 ml/h, which equates to a pore water velocity 0.4 cm/h. The columns had a pore volume of 140 ml, and a residence time of about 1 day for the lixiviant in the columns. Twelve pore volumes of effluent

were collected from each column, and the chemical analyses of these samples are given in Appendix C. Changes in concentration of the major dissolved constituents provide information on the chemical processes occurring in the column and the potential efficiency of natural restoration for this site.

Figure 24 shows the concentration of uranium in the effluents from the duplicate Wyoming columns and for the Texas column that had the same dimension as the Wyoming columns. Uranium movement through the Wyoming columns was initially retarded by contact with the sediment, but influent concentration (14 ppm) was approached after 8 pore volumes flowed through the columns. This contrasts the Texas case in which effluent uranium concentration increased initially, but never reached the influent concentration of 52 ppm. Uranium in the Texas column effluents decreased rapidly after reaching its peak, and after a little over 5 pore volumes, the concentration was much less than 1 ppm for the subsequent 6 pore volumes of effluent. The difference in response of dissolved uranium for the Texas and Wyoming columns may be a result of the amount of pyrite in the sediments. If pyrite reacts sufficiently rapidly to affect the Eh of the solution flowing through the columns, it could establish conditions in which U(IV) minerals are stable. The relatively low solubility of these minerals would limit the amount of uranium in solution to values similar to those found in the Texas column effluents after 5 pore volumes of flow. The small amount of pyrite in the Wyoming sediments used in the column experiment may not have been enough to lower the Eh sufficiently to affect the amount of dissolved uranium. As shown in Table 6, not all of the reduced Wyoming sediment had such a low pyrite content as that selected for the column experiment, but, in general, there appeared to be less pyrite at the Wyoming site sampled than for the Texas site.

An alternative mechanism to the formation of U(IV) minerals that might explain the behavior of uranium during the column experiments, and which also involves the presence of pyrite, is the formation of ferric hydroxide minerals. When pyrite is oxidized, the Fe(III) produced forms ferric hydroxide minerals under oxidizing conditions. These solids have a strong affinity for dissolved uranium under the conditions of the experiment (Chatter, Maitly and Langmuir 1981). Consequently, adsorption of dissolved uranium may lower its solution concentration. Because the Texas sediment contains much more pyrite than the Wyoming sediment, more ferric hydroxide will be formed in the Texas sediment when oxidizing conditions are established during storage of the core and during passage of the oxidizing lixiviant through the column. The presence of relatively large amounts of ferric hydroxide in the Texas columns may effectively remove most of the uranium from the solution. In the case of the Wyoming sediment, which has much less pyrite and hence a smaller source of ferric hydroxide, dissolved uranium was not removed from solution after an initial loading of the surface sites on the ferric hydroxide with uranium species. At this time, we cannot determine which process, mineral precipitation or solute adsorption, is most important in removing uranium from solution. Undoubtedly, a combination of processes is involved.

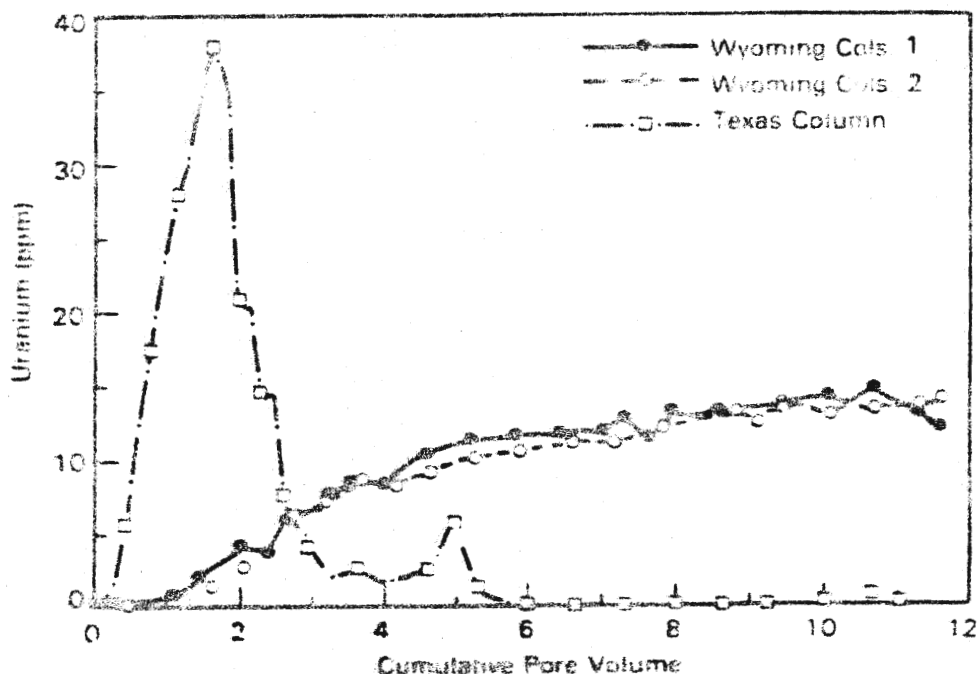


FIGURE 24. Dissolved Uranium Concentration in Effluent from Texas and Wyoming Natural Restoration Column Experiments

TABLE 6. Pyrite Content of Sediment

Source	Reduced Sediment		Ore-Zone Sediment		Oxidized Sediment		Leachon Ore	
	Sample	Pyrite (wt%)	Sample	Pyrite (wt%)	Sample	Pyrite (wt%)	Sample	Pyrite (wt%)
Texas	A27A	1.5	A17A	1.2	A18-215A	1.2	A1-225A	1.10
	A27B	1.1	A11B	1.2	A18-215B	1.2	A1-225B	0.95
	A36A	3.0	A38A	1.2	A18-216A	0.02	A1-226A	0.49
	A36B	2.9	A38B	1.2	A18-216B	0.02	A1-226B	0.40
Wyoming	B2A	0.05	B29A	0.46	B57A	0.01		
	B2B	0.05	B29B	0.42	B57B	0.014		
	B20A	1.0	B34A	0.32	B51A	0.02		
	B20B	1.0	B34B	0.30	B51B	0.005		

The x-ray fluorescence analytical method was used to determine the uranium concentration in the Wyoming sediments. The original sediment before contact with uranium-bearing lixiviant had a uranium concentration of less than 0.1 ppm. After 12 pore volumes (~1.7 L) of lixiviant with 15.6 ppm dissolved uranium had passed through the two columns, one column had an average uranium concentration of 15.1 ± 2.2 ppm uranium and the other had a concentration of 16.5 ± 2.8 ppm uranium. Because the x-ray fluorescence device was not

calibrated specifically for uranium, the results are somewhat suspect and can only be used for qualitative comparisons. The total amount of uranium that passed through each column was about 25 mg and the total amount eluted was about 17 mg. Therefore, 8 mg of uranium were deposited in each column that contained approximately 540 g of sediment. Based on the changes in the solution concentration of throughout the experiment, the sediment at the end of the experiment should have had a uranium concentration of about 15 ppm, which compares favorably with the x-ray fluorescence determinations of 15.1 ppm and 16.5 ppm for the two columns.

Distinctive trends in concentration were also noted for several of the other solution constituents. The initial effluent samples from the columns, representative of the sediment pore water, had much higher concentrations of calcium, sulfate, and magnesium and a lower pH than the ground water within the aquifer. As the synthetic lixiviant displaced the residual pore water in the column, the calcium, magnesium, and sulfate concentrations decreased and the sodium concentration and pH increased. However, concentrations of dissolved constituents similar to the lixiviant were not attained until many pore volumes of solution passed through the column. This suggests that chemical interactions between the solution and sediment, in addition to simple fluid movement, would be important in understanding the migration of the dissolved load.

As Figure 25 shows, the sodium value did not reach its influent concentration of 414 ppm until more than 7 pore volumes of solution flowed through the column. The calcium and magnesium concentrations showed a corresponding decrease to influent values of 79 and 44 ppm, respectively. This effect probably was caused by ion exchange between the solution and clays present in the sediment. To properly model such a system, we must know the cation exchange capacity of the sediment, and we must know the identity and concentration of ions initially present on the sediment at the beginning of the experiment.

The clays were characterized using standard soil chemical methods (Jackson 1956; Folk, 1984). We determined that the cation exchange capacity of the reduced sediment from one of the Wyoming cores was 2.5 meq/100 g. Calcium was the dominant exchangeable cation, occupying 63% of the exchange sites on the sediment. In order of decreasing abundance of exchangeable cations, magnesium was second (19%), potassium was third (14%), and sodium was fourth (4%). Using these values and the solution composition of the pore water, we calculated selectivity coefficients for the various cation pairs on the clays. From the selectivity coefficients and the ground-water composition of the aquifer sampled in Wyoming, we calculated the relative amounts of exchangeable cations that were present on the sediment in the aquifer. These amounts are different than those found for the core sediment because of reactions between the sediment and pore water during storage of the core. These reactions added considerable calcium to the solution, which then equilibrated with the sediment by displacing other cations. We calculated that the original sediment had 18% of their sites occupied by sodium, but reactions during storage of the sediments

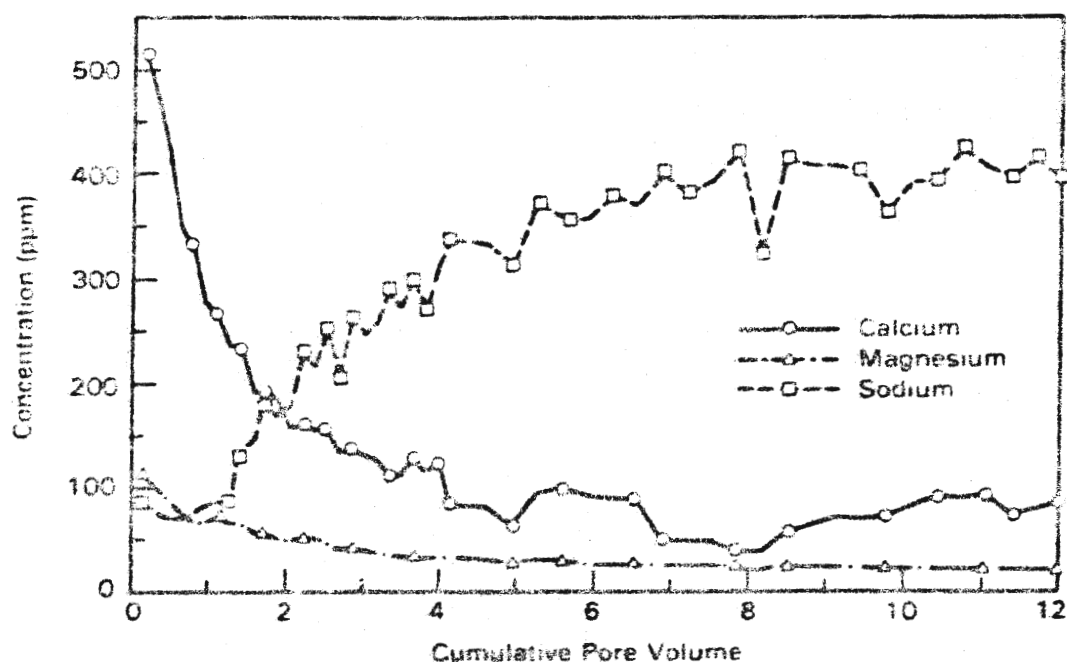


FIGURE 25. Effluent Concentrations of Calcium, Magnesium, and Sodium from the Wyoming Natural Restoration Experiments

reduced this amount to 4%. The calculated selectivity coefficients and observed solution compositions were used to model the Wyoming natural restoration column experiment as described below.

Modeling water/sediment interactions is a very useful method to identify and quantify the chemical processes occurring in the system. From the solution and sediment data, we have developed a conceptual chemical model of the system that incorporates the reactants and chemical processes that appear to be important. The model initially simulates storage of reduced sediment with ground water that has been oxidized during sampling and storage. This allows us to initialize the sediment and pore solution in the column as it exists at the commencement of the flow-through experiments. In the next phase, we modeled the interaction of lixiviant with the sediment during flow through the column. The chemical processes incorporated in the models include 1) oxidation of pyrite to produce ferric oxyhydroxide, sulfate, and hydrogen ions; 2) dissolution and equilibration with magnesian calcite; 3) equilibration of the solution with a gas phase having fixed partial pressures of oxygen and carbon dioxide; 4) ion exchange involving calcium, magnesium, sodium, and potassium; and 5) aqueous complexation of dissolved constituents. The MINTEQA computer code (Folmy, Girvin and Jenne 1984) was used to make the necessary speciation and mass transfer calculations. We compared the model results with observed effluent solution compositions from the natural restoration column experiment to determine how well we simulated the system.

Modeling the chemical interactions that occurred between the sediment and its pore water during collection and storage consisted of simulating the reaction of the ground water, which had been oxidized during sampling and storage, with reactive minerals in the sediment. Reactive minerals are those that can precipitate or dissolve over the time frame of interest (a few months in this case). Of the minerals present in the sediment, we considered magnesian calcite, pyrite, and ferric hydroxide to be reactive and quartz, feldspar, and the typical mafic minerals found in sediments to be nonreactive. We also allowed for ion exchange to occur between the solution and the sediment for the elements calcium, magnesium, sodium, and potassium.

The primary reactions that occurred during the simulation were oxidation and dissolution of pyrite, precipitation of ferric hydroxide, dissolution of magnesian calcite, and ion exchange. The resulting major ion composition of the pore water is shown in Table 7 along with the starting ground-water composition and the composition of the first effluent solution, which was the target solution. It can be seen that the oxidation of pyrite and precipitation of ferric hydroxide effectively lowered the pH of the solution, but that the pH was buffered by the dissolution of calcite to a value of 7.9, which is very close to that of the initial effluent pH (8.0). The amount of sulfate produced by the model was reasonably close to that of the effluent solution, although the carbonate concentration was about 40% too low. The simulated sodium concentration was over twice that which was actually present in the first effluent sample. This caused problems with the modeling of the flow-through experiment, which is described next.

The interactions of lixiviant with the sediment and its associated pore water were modeled by considering a simple mixing model to account for flow of solution through the column and a reaction model that allowed the solution to

TABLE 7. Results of Modeling Wyoming Natural Restoration Column Experiment: Sediment Storage Phase (concentration units are ppm unless otherwise noted)

	Starting Solution (Wyoming Ground Water)	Predicted Solution	Actual Solution (Pore water after storage)
pH (log units)	8.62	7.85	8.0
En (mV)	-64	+129	+175
Ca	17	459	515
Mg	6.4	90	113
Na	90	220	84
K	4	15	60
SO ₄	129	1847	1465
C _T (as CO ₃)	160	89	151

equilibrate with magnesian calcite and provided for ion exchange between the solution and the sediment. For the mixing model, a complementary amount of new lixiviant was added to the system as each solution sample was eluted. For instance, if a 20-mL sample of effluent was collected for analysis, we simulated this step in the experiment by adding 20 mL of lixiviant (the influent solution) to the pore solution. MINTEQA2 was used to equilibrate this new solution with the sediment, and a new solution concentration was calculated based on the reaction model imposed.

Initial modeling results show that we can adequately simulate the response of the major cations in the lixiviant to contact with the sediment by assuming that the solution is in equilibrium with magnesian calcite and ion exchange occurs between dissolved cations and exchangeable cations on clays in the sediment (Figure 26). The only cation that does not follow the predicted elution pattern throughout the simulation is sodium, which shows considerable divergence between the observed and predicted values for the initial pore volumes. This happened because the concentration of sodium in the pore solution of the stored sediment did not increase during storage, while that of calcium increased approximately 30 times. If calcium increased this much and ion exchange could occur, then some of the sodium should have been removed from the sediment, producing an increase in the dissolved sodium concentration. The model predicted that the dissolved sodium concentration should have been almost 0.01 molar, and the actual amount was only 0.004 molar. The reason for this discrepancy may be that the ground-water composition that we used to calibrate our model was not representative of the ground water from the aquifer where the core was taken. Because we had to use existing wells at the site to sample ground water, the water sample was taken a few miles from the coring site. If the actual sodium concentration in the ground water from the aquifer from which the core was taken was appreciably lower than that in the well sampled, then our initial amount of sodium on the exchange sites would have been lower. Then less sodium could be exchanged by the increased calcium and the simulated sodium concentrations would not have been as large for the early pore volumes and would have been closer to the observed values.

The chloride and sulfate concentration values from the simulation (Figure 27) show that we predicted the general trend of these conservative solution constituents using our basic mixing model. However, at the beginning of the experiment we calculated too much sulfate and not enough chloride. Apparently, the mixing model does not adequately account for hydrodynamic dispersion that would occur in the column. If a dispersion coefficient had been calculated using the chloride data and it could be used in a coupled hydrologic/chemical model, then the simulated sulfate data would be closer to the observed values. Modeling with dispersion would probably not significantly change the major cation values for the early pore volumes.

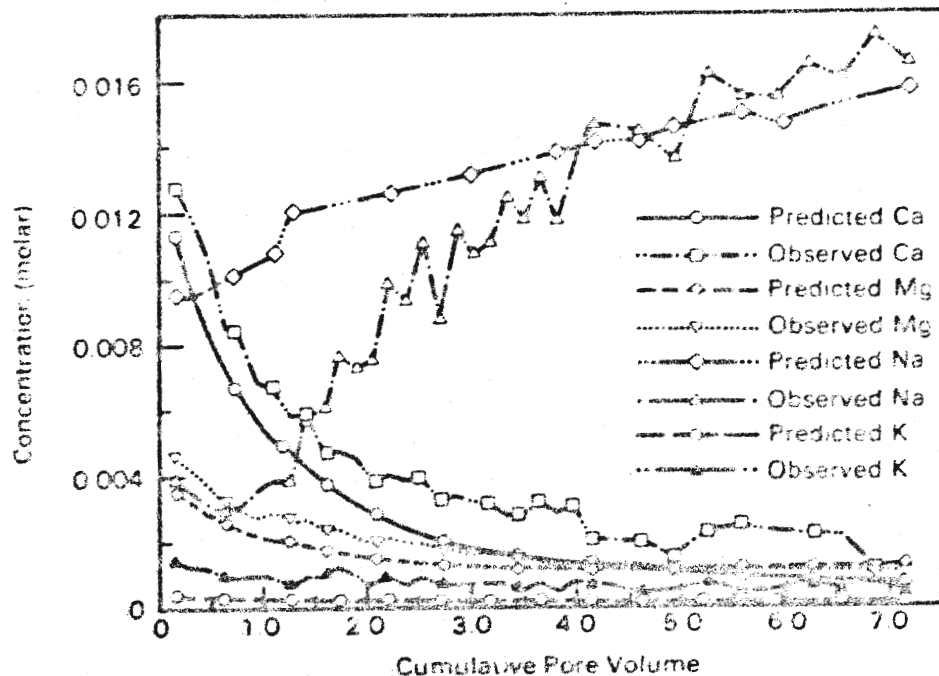


FIGURE 26. Comparison of Predicted Major Cation Effluent Compositions with Analytical Values for the Wyoming Natural Restoration Column Experiment

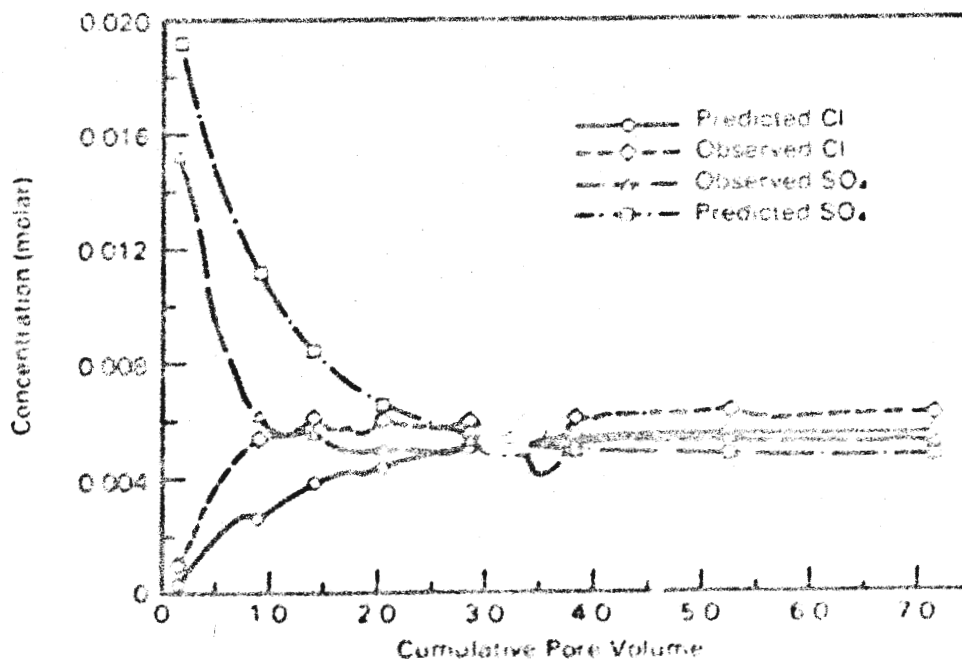


FIGURE 27. Comparison of Predicted Major Anion Effluent Compositions with Analytical Values for the Wyoming Natural Restoration Column Experiment

Although the mixing model worked fairly well for conservative elements, it did not work at all for uranium (Figure 28). The model predicted that the uranium effluent concentration will reach the influent value at 3 pore volumes of cumulative flow from the column, but the observed effluent samples showed that uranium did not reach influent concentration (6.3×10^{-5} molar) until over 11 pore volumes of solution were collected (analytical uranium data past 7.5 pore volumes are given in Appendix C, Table C.2). This behavior of dissolved uranium in contact with sediment probably resulted from adsorption onto the sediment minerals. At the present time, MINTEQA is not capable of simultaneously modeling ion exchange for the major cations and adsorption of uranium. Future versions of the code will include this capability, which will allow us to refine the model of this system.

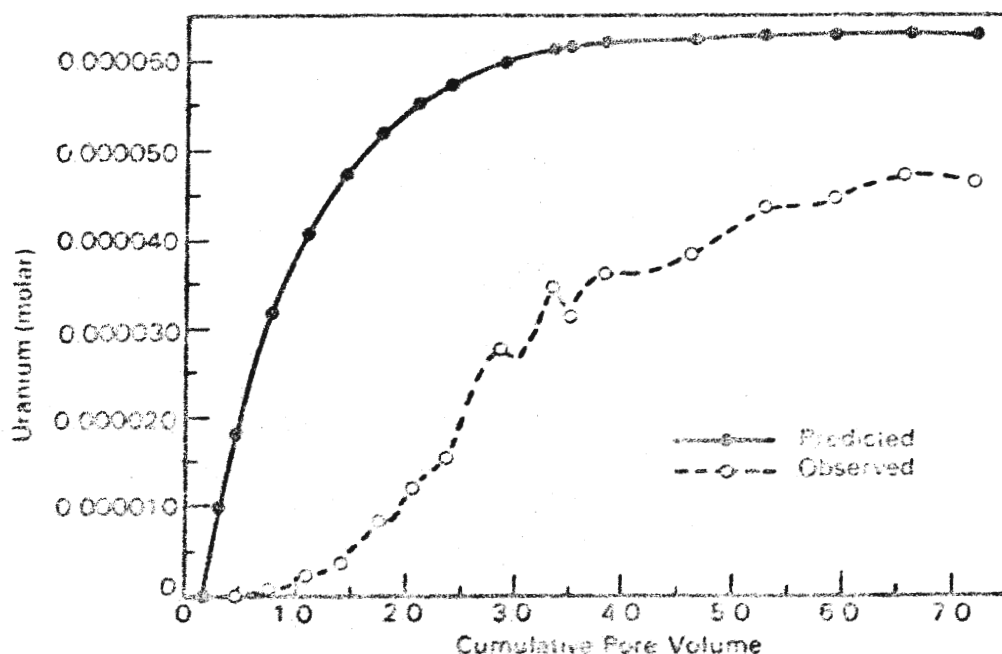


FIGURE 28. Comparison of Predicted Uranium Effluent Composition with Observed Values for the Wyoming Natural Restoration Column Experiment

EVALUATION OF APPLIED RESTORATION METHODS

This section discusses the results of experimental studies on aquifer restoration by ground-water sweeping and in situ restoration enhanced by the addition of a chemical reductant to the leached ore.

Results of Ground-Water Sweeping Restoration Experiment

In this experiment, columns of Texas leached ore were saturated with a lixiviant spiked with arsenic, selenium, and molybdenum. These elements were added to the lixiviant to test the effectiveness of ground-water sweeping for these contaminants, which are commonly mobilized during leaching of uranium. Lixiviant was pumped through each column until more than 2 pore volumes of solution had contacted the leached ore. The influent solution was then changed to native ground water. Ground water was pumped through the columns to simulate restoration by ground-water sweeping. The experiment was carried out in an anoxic chamber to approximate the reduced oxygen fugacities of the ore-zone environment. A complete description of the experiment may be found in Sherwood, Hostetler and Deutsch (1984). The results are summarized in the following paragraphs.

The uranium concentration of the lixiviant used to pre-equilibrate the columns at the beginning of the experiment was 3 ppm; the ground water used to simulate sweeping had a uranium concentration of 0.06 ppm. Figure 29 shows the uranium content of the column effluents. The initial uranium concentration peak was caused by pre-oxidation of uraninite in the ore during storage and its rapid dissolution on contact with the influent lixiviant solution. The fact that the uranium concentration remained elevated compared to the influent lixiviant or ground water for the duration of the experiment (over 16 pore volumes of solution) suggests that continued leaching of the ore may have

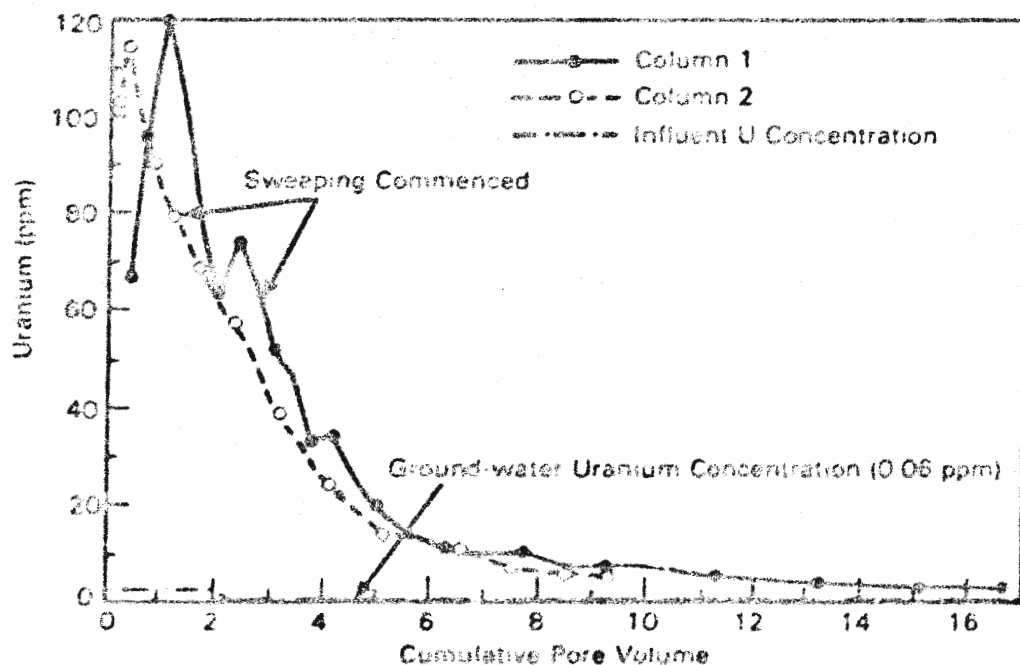


FIGURE 29. Uranium Effluent Concentrations from Ground-Water Sweeping Columns 1 and 2

occurred during sweeping. The ground water used in the experiment was similar to that which would be used during an actual sweeping operation at a mine site. The ground water would be oxidizing either because it was drawn primarily from the hydrologic zone upgradient from the ore zone or because it was recirculated through the plant equipment, which would probably allow atmospheric oxygen to dissolve in the solution. The oxygenated water would act as a weak lixiviant causing continued slow dissolution of uranium-bearing minerals and elevated uranium concentrations in solution. This would inhibit restoration for uranium at sites where residual uranium ore minerals are present.

Arsenic, selenium, and molybdenum were added to the spiked lixiviant at concentration levels of approximately 5 ppm. The ground water contained <0.015 ppm arsenic, <0.020 ppm selenium, and 0.16 ppm molybdenum. These elements exhibited markedly different mobilities on contact with the sediment. Arsenic concentrations in the column effluents remained below the analytical detection limit of 0.015 ppm. During lixiviant contact, selenium concentrations in the effluent were below the detection limit of 0.02 ppm. Selenium began to elute from the column when the influent was changed to ground water; however, its concentration in the effluent never rose above 0.2 ppm. Molybdenum was the most mobile of the elements added to the lixiviant. As shown in Figure 30, molybdenum concentrations peaked during the lixiviant contact portion of the experiment for each column and then slowly decreased to a level approximating that of the influent ground-water.

The column sediments were analyzed by x-ray fluorescence methods after the experiment to determine the location of the spiked elements in the core. In the first centimeter of the core (measured from the influent end of the column), the arsenic concentration was 10 ppm, which is four times the concentration of the original leached ore. Arsenic was not found at an elevated concentration at the effluent end of the core. Selenium was not detected in the original sediment (detection limit = 0.90 ppm); however, it had concentrations of 5.9, 2.3, and 1.8 ppm in the 0 to 1, 5 to 6, and 9.8 to 10.8 cm intervals of the core. The molybdenum concentration showed a slight increase in the last interval of the core, but was close to background for the rest of the core.

The sediment compositions and the effluent chemistries suggest that arsenic and selenium are not mobile under the conditions of the experiment, but that molybdenum would effectively move with the ground water. Arsenic and selenium are known to form solids in close proximity to uranium ore zones, while molybdenum is often found under more reducing conditions down the hydrologic gradient from the uranium deposit (Harshman 1974). This may partially explain the enhanced mobility of molybdenum compared to arsenic and selenium in the oxidizing ground water used during sweeping.

The ground-water sweeping experiment showed that uranium and molybdenum are potentially difficult elements to restore to baseline concentrations if they are present in residual ore minerals at the termination of leaching. A restoration method that does not introduce dissolved oxygen into the system should be used to keep these redox-sensitive elements immobile. The following

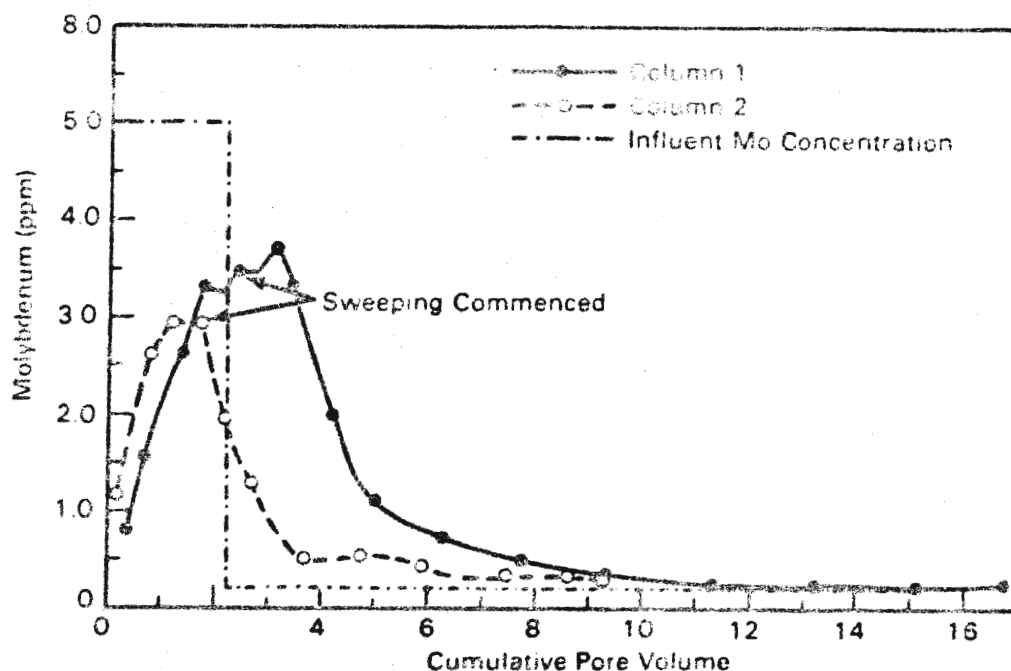


FIGURE 30. Molybdenum Effluent Concentrations from Ground-Water Sweeping Columns 1 and 2

section discusses in situ chemical restoration, which appears to be capable of producing the desired results without producing unwanted by-products.

Results of Chemical Addition Batch Experiments

As mentioned previously, long-term pumping of well fields to restore the aquifer may complicate efforts to lower dissolved uranium concentrations. The ore zone in a typical sandstone uranium deposit is generally located in a confined aquifer along an oxidation-reduction interface (DeVoto, 1978; Warren, 1972). Oxidizing conditions usually lie in the direction of higher hydrostatic gradient and reducing conditions generally exist in the downgradient direction. Consequently, the pumping of the leach field with or without reinjection may result in the flow of relatively more oxidizing solutions into the ore zone. Because the common ore-forming minerals such as uraninite and coffinite are more soluble in oxidizing solutions (Langmuir 1978), this type of restoration method may inhibit efforts to lower dissolved uranium to baseline levels. However, the injection of a chemical reductant such as sodium sulfide during the recirculation of treated ground waters could theoretically reestablish reducing conditions in the ore zone. Uranium is much less mobile in reducing conditions because of the low solubility of the U(IV) minerals. Also, the generation of reducing conditions in the ore zone is expected to enhance restoration of the aquifer to its original state and should promote long-term chemical stabilization of the aquifer.

A series of experiments are described here in which sodium sulfide was added to solutions and solution plus solid mixtures to measure the effects on oxidation potential, dissolved oxygen, and uranium concentrations. The first experiments were kept simple; sodium sulfide was added to distilled water. Next, sodium sulfide was added to a leaching solution that was obtained from the Benavides in situ leaching operation in Texas. After completion of these initial experiments, the effects of adding sodium sulfide to mixtures of the Texas lixiviant and iron-oxide coated sand, and Texas lixiviant plus leached uranium ore were measured. The results of each experiment are described separately.

Sodium Sulfide with Water

In the initial set of experiments, sodium sulfide was added to distilled, deaerated water and to distilled, air-saturated water to measure the changes in Eh, pH, and the concentration of dissolved oxygen. The air-saturated water initially had dissolved oxygen concentrations of approximately 8 ppm. The deaerated water contained less than 0.1 ppm dissolved oxygen. Adding sodium sulfide to these solutions lowered the Eh as shown in Figure 31. Higher sodium sulfide concentrations resulted in lower Eh values. Also, the Eh of the air-saturated water was lowered less than that of the deaerated water for similar concentrations of sodium sulfide. It is reasonable to expect that some of the sulfide added to the air-saturated water was oxidized by dissolved oxygen, and this process resulted in the somewhat higher Eh values relative to the deaerated water. Concentrations of dissolved oxygen at the end of the experiments were determined to be less than 0.1 ppm. In a few samples, oxygen levels were higher, but this was probably caused by the introduction of air during the filtration of these samples before the analysis of dissolved oxygen.

In Figure 31, the change in pH caused by adding sodium sulfide is shown for the distilled, deaerated water and the distilled, air-saturated water. The addition of sodium sulfide sharply increased the pH to a value between 10.2 and 12.0, depending on the Na_2S concentration, for both the aerated and deaerated water. After the initial increase, the pH values remained steady. The increase in pH was caused by the reaction between sulfide and hydrogen ion (Robie, Hemingway and Fisher 1978):



The final pH in the air-saturated water was slightly lower than in the deaerated water. This difference was probably caused by the slight buffering effect of dissolved CO_2 in the air-saturated water.

Sodium Sulfide + Texas Lixiviant

In a similar set of three experiments, Na_2S was added to the Texas lixiviant to monitor the changes in Eh, pH, and uranium concentration. After the addition of Na_2S , the Eh of the lixiviant dropped to a value between -50 and -320 mV (Figure 32). Solutions with the highest Na_2S concentrations

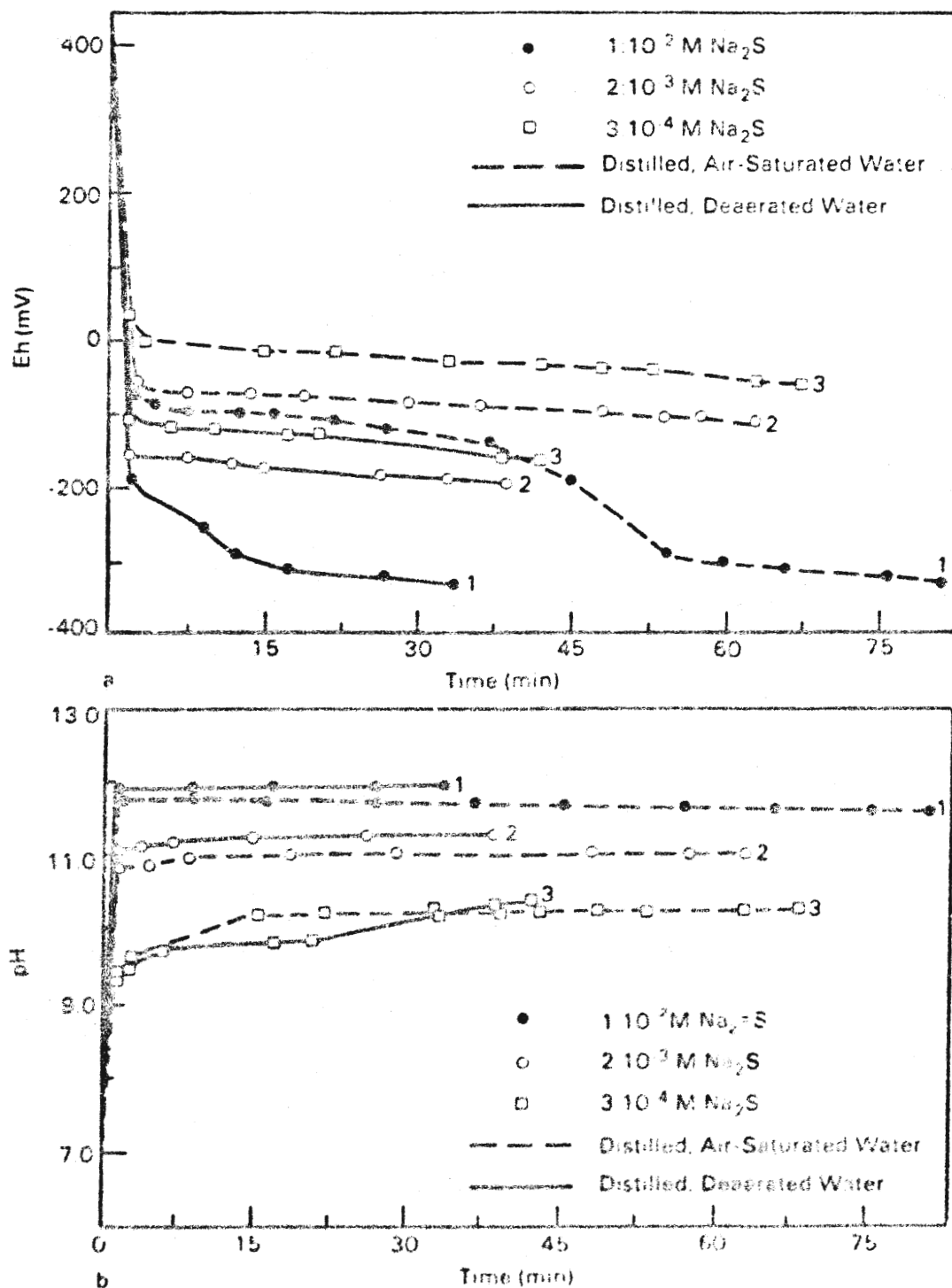


FIGURE 31. Plots Showing the Change in Eh (a) and pH (b) After Addition of Na₂S to Distilled, Deaerated Water (solid lines) and Distilled, Air-Saturated Water (dashed lines)

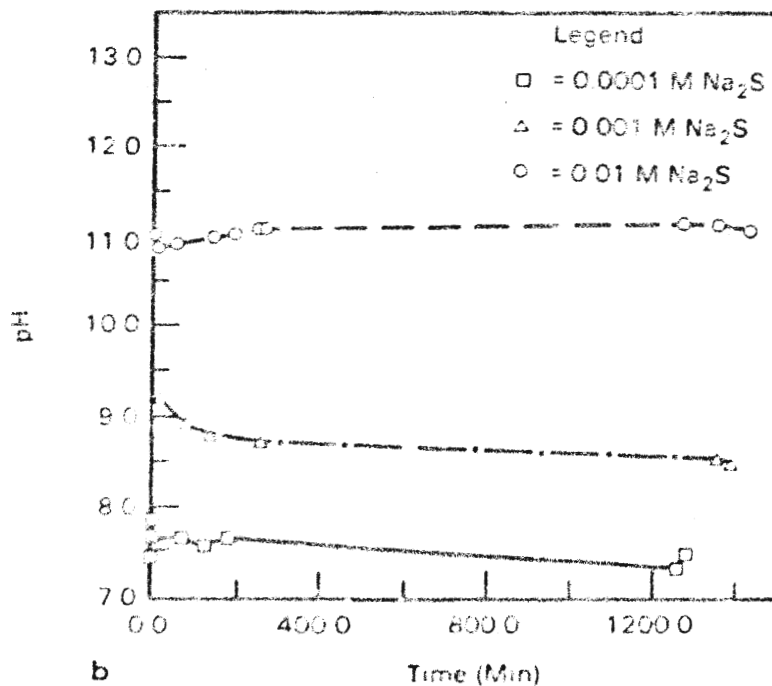
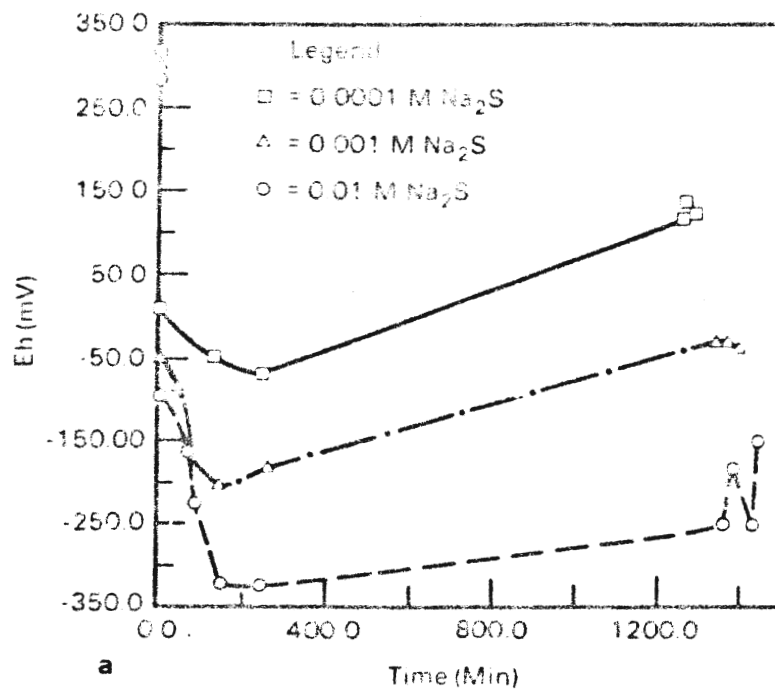


FIGURE 32. Change in the Eh (a) and pH (b) for Texas Lixiviant. Sodium sulfide added 1 min after start.

dropped to the lowest Eh values. After the initial decrease, the Eh remained steady for a short period before slowly rising for the remainder of the experiment. This slow rise was probably caused by the leakage of air into the flasks and subsequent oxidation of the sulfide.

The change in pH is shown in Figure 32. For the 10^{-4} molar Na_2S solution, the pH remained essentially unchanged, whereas for the 10^{-3} and 10^{-2} molar Na_2S solutions the pH rose to a steady value after a few hours. Both the pH and Eh responses to the addition of Na_2S to the lixiviant were slower than those observed in the experiments with water (Figure 31). Also, the Eh did not reach values quite as low nor did the pH reach values quite as high in the lixiviant as in the water. The lixiviant had some buffering capacity, which affected its response to changes in Eh and pH caused by the addition of Na_2S . Uranium was determined at the end of each of the three experiments with lixiviant, but only in the 10^{-4} molar Na_2S solution did the uranium concentration decrease significantly. Dissolved uranium dropped from 44 to 1.7 ppm at the end of this experiment. Dissolved uranium concentrations in the 10^{-3} and 10^{-2} molar Na_2S solutions remained unchanged at the starting value of 44 ppm.

Sodium Sulfide with Texas Lixiviant and Iron-Oxide-Coated Sand

The effects of adding Na_2S to a strongly oxidized system were tested by adding this reductant to a mixture of the Texas lixiviant and iron-oxide-coated sand. The iron oxide coating on the quartz sand grains used in these experiments consisted of mostly hematite, Fe_2O_3 , and goethite, HFeO_2 . It was produced by neutralizing a solution of ferric chloride in the presence of the sand (Bent 1977). In general, the Eh dropped sharply after the addition of the Na_2S to this mixture (Figure 33). After the initial decrease, the Eh in the 10^{-3} and 10^{-2} molar Na_2S solutions slowly rose for the remainder of the experiments, and less than 1% of the added sulfide was still present in these solutions after about 17 hours. In both the 10^{-3} and 10^{-2} molar Na_2S solutions, the Eh did not reach values as low as those observed in the lixiviant-only experiments shown in Figure 32. In contrast, the Eh in the 10^{-4} molar Na_2S solution remained at low values that were similar to those measured in the lixiviant-only experiments. Approximately 90% of the added sulfide was still present in the 10^{-4} molar Na_2S solution after 23 hours. However, the possibility that the sulfide would be oxidized after a longer period of time resulting in an increase in the Eh cannot be discounted on the basis of these short-term experiments.

The change in pH after adding the Na_2S is shown in Figure 33. The pH in the 10^{-3} and 10^{-2} molar Na_2S solutions rose only slightly before reaching steady values. The effect of adding Na_2S was more noticeable for the 10^{-4} molar solution where the pH increased to a value of about 10.3. The pH values measured in these solutions were significantly lower than those observed in the previous experiments (Figures 31 and 32).

Uranium concentrations in the lixiviant were also measured. The measured concentrations, only in the 10^{-4} molar Na_2S solution, were not different from 44 ppm. In the 10^{-3} molar Na_2S solution, uranium decreased to only 7 ppm. In the 10^{-2} molar Na_2S solution, the uranium concentration was not measured.

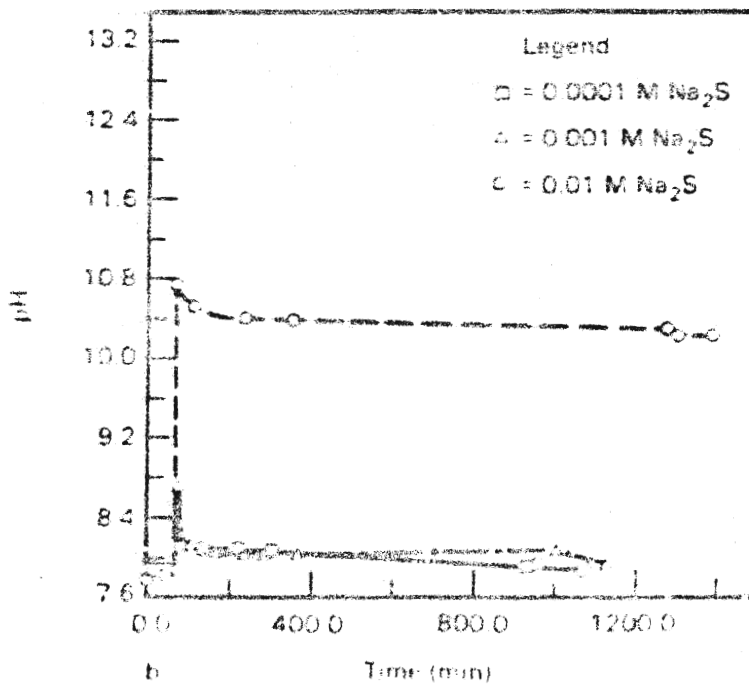
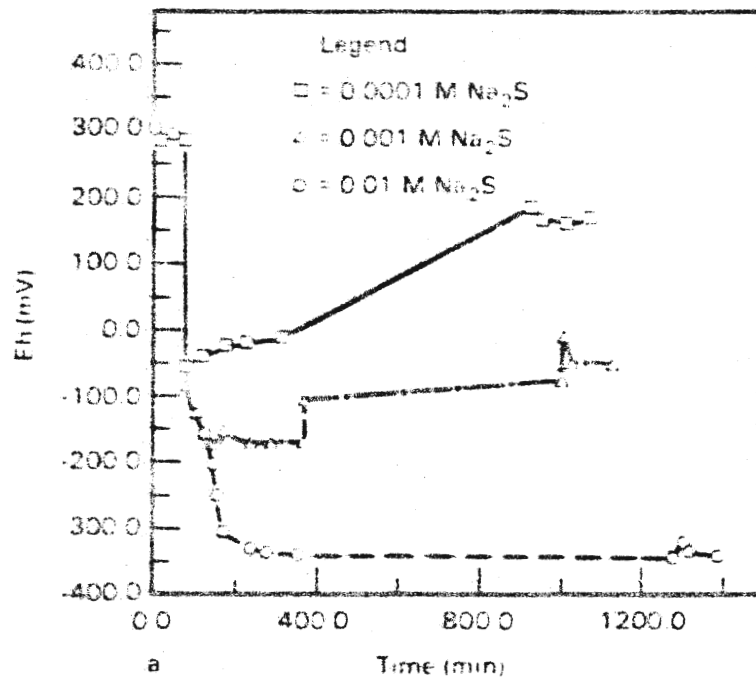
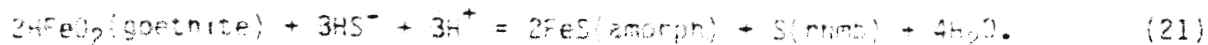


FIGURE 23. Changes in the Eh (a) and pH (b) of Mixtures of Texa Lixiviant and Iron-Oxide-Coated Sand. Sodium sulfide added 75 min after start.

for the 10^{-4} molar Na_2S solution. This result seems anomalous, but may be an indication that uranium is adsorbing onto the iron oxides. In the solutions with lower sulfide concentrations, uranium adsorption may be relatively more important.

During the experiments with 10^{-3} and 10^{-2} molar Na_2S solutions, it was noted that the iron-oxide-coated sand slowly changed from reddish-brown to dark brown or black. This suggests that amorphous iron sulfides were forming in these experiments. It has been shown by Rickard (1974) and Pyzik and Sommer (1981) that iron sulfides are formed upon the addition of Na_2S to mixtures of goethite and water between pH 6.5 and 8.0. The likely reaction for FeS formation is



At a pH above about 7.7 to 8.2, elemental sulfur is unstable, depending on the total sulfur activity (Rickard 1974), and may react with dissolved sulfide to form polysulfides (Berner 1964). Further reaction between FeS and elemental sulfur may occur given sufficient time and amounts of these reactants to produce crystalline ferrous sulfides, such as mackinawite (Berner 1967a). However, for the brief experiments conducted here, amorphous FeS and FeS(amorph) are expected to be the dominant products.

In the above experiments with iron-oxide-coated sand and Texas lixiviant, it was not clear whether the adsorption of uranium onto the iron oxides appreciably lowered the uranium concentrations. Adsorption of uranium has been shown to be significant between pHs of 4 and 8 (Van Der Weijden, Arthur and Langmuir 1976), and uranium adsorption onto colloidal ferric oxides has been suggested as a possible mechanism for concentrating uranium during the formation of some hydrothermal uranium deposits (Giblin, Batts and Swaine 1981). The effects of uranium adsorption were measured by adding the iron-oxide-coated sand to the Texas lixiviant, and then measuring the change in dissolved uranium with time. In these experiments, the uranium concentration was determined to have decreased by about 40% from the starting values after about 13 to 14 days (Figure 34). It was apparent that adsorption onto the iron oxides did lower the concentration of uranium by a measurable amount in these experiments.

In two more experiments, uranium concentrations were measured for about 24 hours before Na_2S was added to the lixiviant plus iron-coated-sand mixtures to compare the decrease in uranium concentrations. Adding the Na_2S to give an initial concentration of 0.01 molar sulfide resulted in a decrease of almost two orders of magnitude (from 44 to 0.6 ppm) in the uranium concentration in 48 hours (Figure 34).

Sodium Sulfide with Texas Lixiviant and Texas Leached Ore

Another set of experiments was conducted to test whether adding Na_2S would reduce the dissolved uranium concentrations in mixtures of the Texas lixiviant and Texas leached ore. A total of four experiments were conducted simultaneously

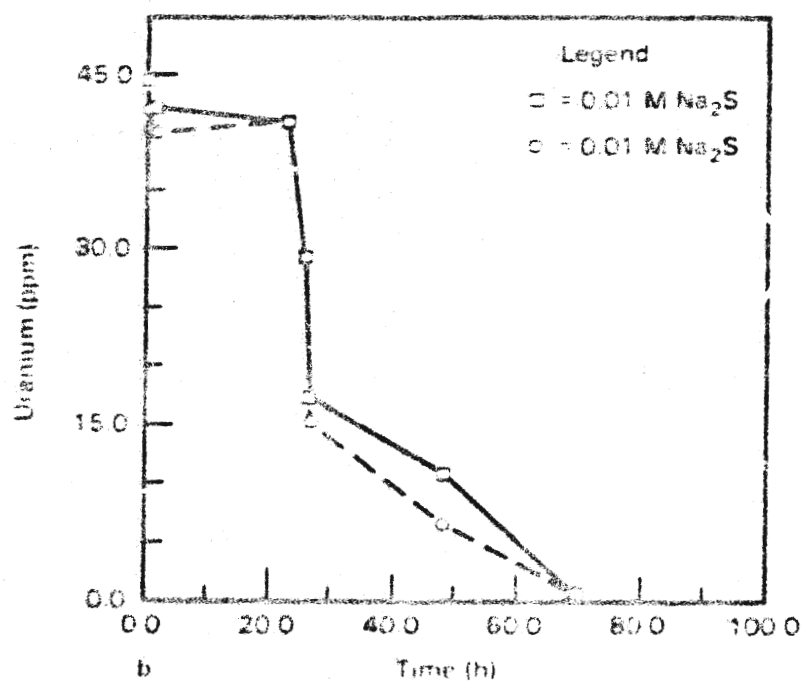
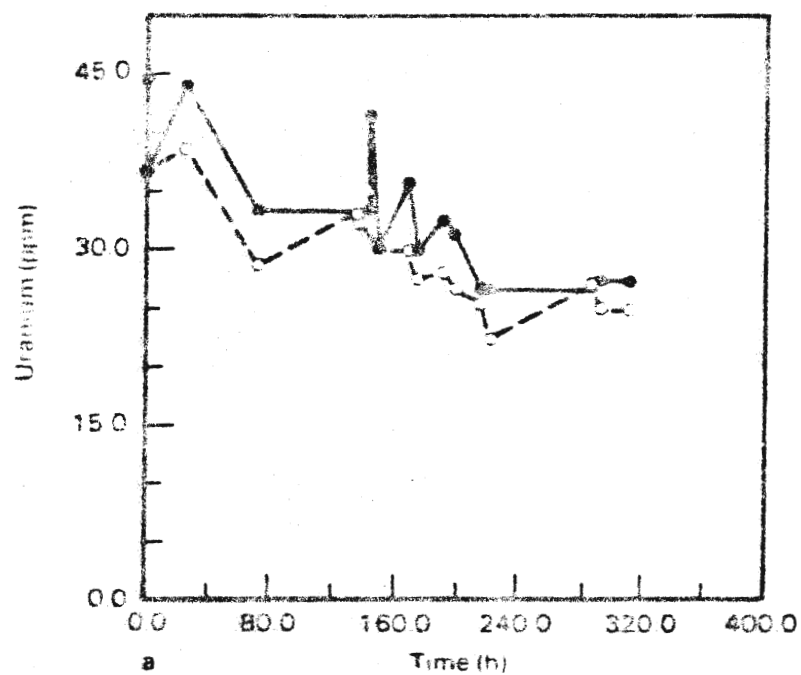


FIGURE 24. a) Change in Uranium Concentration in the Texas Lixiviant Caused by Adsorption onto the Iron-Oxide-Coated Sand for Duplicate Experiments, b) Change in Uranium Concentration in Texas Lixiviant and Iron-Oxide-Coated Sand After Adding 0.01 molar Na_2S at 23 h

two with enough Na_2S added to give a 0.01 molar Na_2S solution and two more with 0.001 molar Na_2S . In each experiment, 75 g of the Texas leached ore was added to 750 mL of lixiviant, and this mixture was allowed to stand for about 7 days before the Na_2S was added. The uranium concentrations in the lixiviant were measured during this initial period of time to determine the importance of the dissolution of any oxidized uranium minerals that may have been present in the ore. A large increase in uranium concentration was not expected because the uranium content in the ore was relatively low in comparison to the total amount of uranium in the lixiviant, and in fact, the dissolved uranium slowly decreased (Figure 35). This decrease to a somewhat steady value of 30 to 33 ppm was probably caused by the adsorption of uranium onto the clays and oxides present in the leached ore and was observed in all four of the experiments.

The Na_2S was added to the mixtures at 164 hours for the 0.01 molar Na_2S solutions and at 160 hours for the 0.001 molar Na_2S solutions. Soon after the addition of the sulfide, the uranium concentrations decreased to low levels in all four experiments. The uranium concentrations in the 0.01 molar Na_2S solution remained at less than 1 ppm for about 100 hours before slowly increasing (Figure 35). In the 0.001 molar Na_2S solutions, the dissolved uranium remained at lowered values for about 50 hours (Figure 35) before increasing at a relatively more rapid rate than seen in the 0.01 molar Na_2S solutions.

The addition of sulfide caused predictable changes in the pH and Eh in these experiments. The pH increased and the Eh decreased rapidly after adding Na_2S (Figure 36). After the increase, the pH returned to values slightly higher than those measured before the Na_2S addition. Similarly, the Eh quickly returned to high values. The rapid decrease in dissolved uranium corresponded to the decrease in Eh that occurred just after the sulfide addition. This suggests that the dissolved uranium was precipitated, probably as uranium oxide, $\text{UO}_2\text{-U}_3\text{O}_8$, in response to the more reducing conditions. The period of lowered Eh and probable uranium precipitation is indicated to have lasted only a short time before the Eh returned to higher values. Consequently, the uranium concentration began to slowly increase with the return to more oxidizing conditions. The slower response of the dissolved uranium in comparison to the Eh was probably caused by the relatively slower dissolution rates of the precipitated uranium oxides. The results of these experiments indicate that the leached ore was sufficiently oxidizing to rapidly oxidize most of the added sulfide. In fact, sulfide concentrations were below detection limits in lixiviant samples collected only 30 min after the sulfide addition. Dissolved oxygen was also expected to be a significant oxidizing agent. Its concentrations in the lixiviants were reduced from 8.2 ppm to less than 0.1 ppm at the end of each experiment.

It was also noted that adding Na_2S caused the leached ore to change from a light gray-brown color to dark gray-green in the 0.01 molar Na_2S experiments. A much less noticeable color change was observed in the 0.001 molar Na_2S solutions. It is difficult to explain the exact cause of the color change, but it may have been caused by the formation of iron sulfides. A white precipitant, identified as $(\text{Ca,Mg})\text{SO}_4 \cdot x\text{H}_2\text{O}$, also formed just after the addition of the sulfide. The presence of increased amounts of sulfate in the experiments was another indication that the added sulfide was rapidly oxidized.

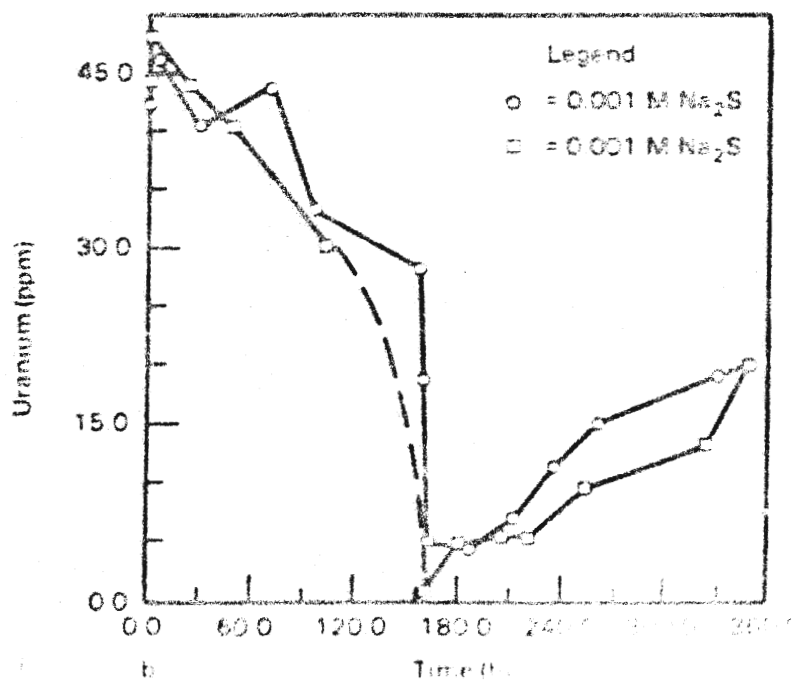
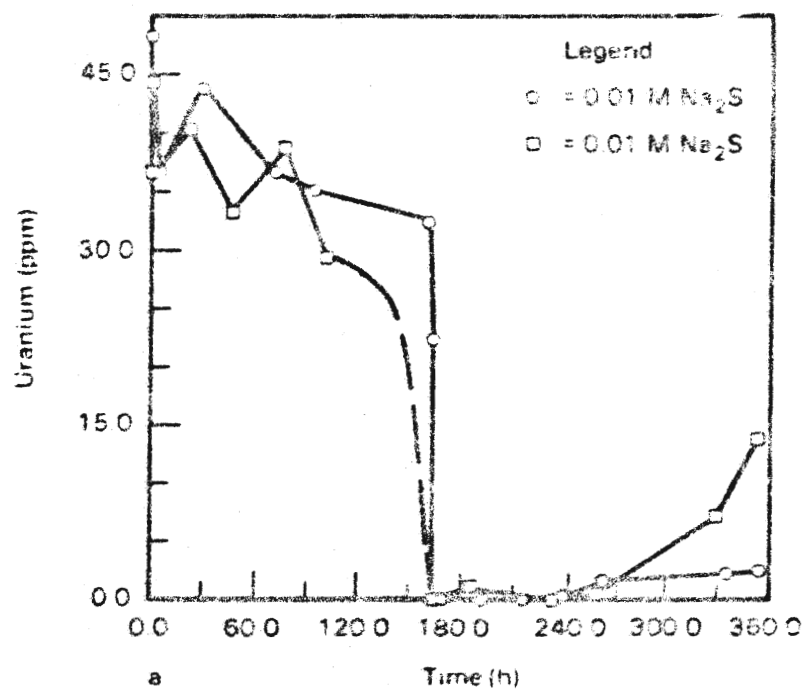


FIGURE 35. Changes in Uranium Concentration in Mixture of lixiviant and Texas Leached Ore Showing the Effects of Na_2S Addition.
a) 0.01 molar Na_2S Added at 164 h. b) 0.01 molar Na_2S Added at 160 h

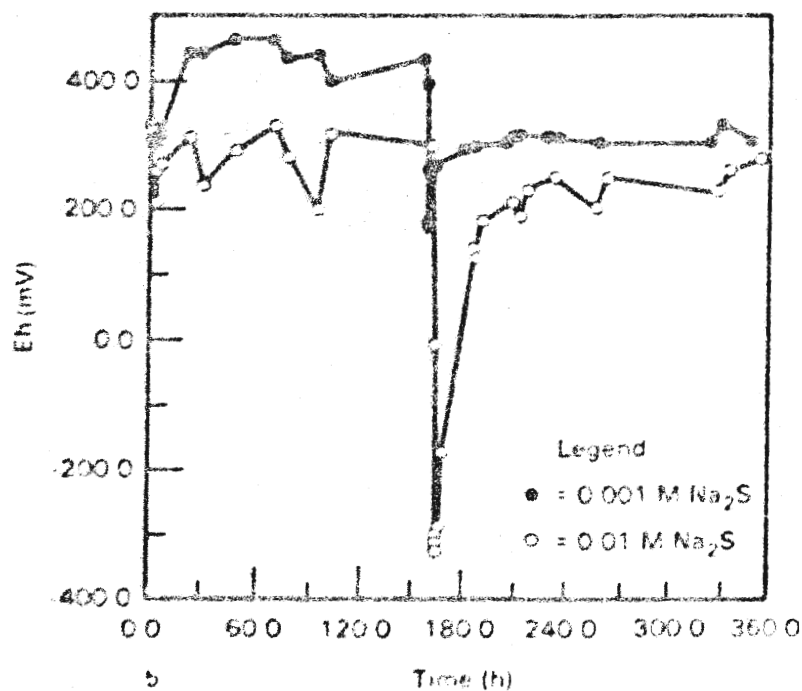
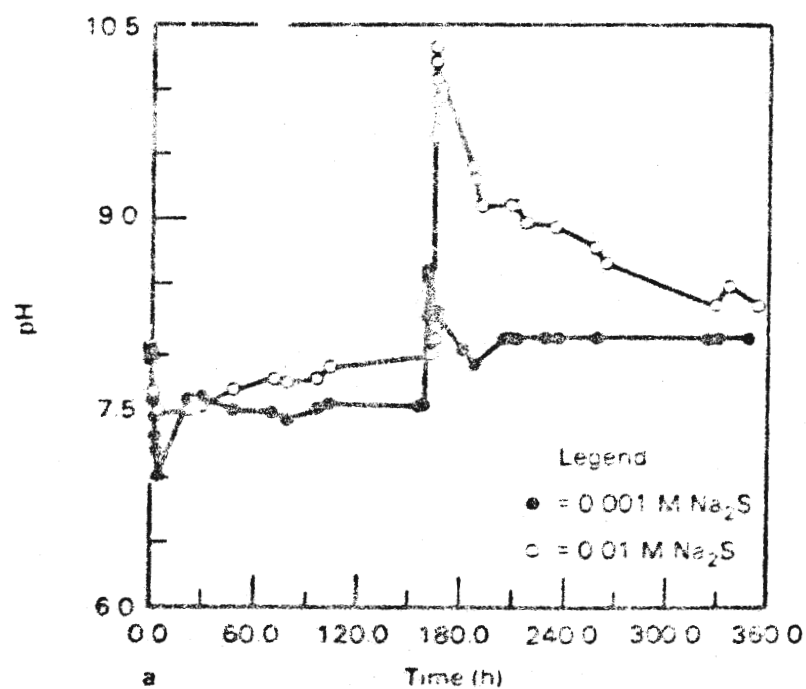


FIGURE 34. Results from Four Experiments With Texas Lixiviant and Texas Leached Ore Showing Changes in a) pH after Na_2S addition at 160 h, and b) Eh after Na_2S addition at 164 h.

Although these were very qualitative experiments and it was difficult to clearly identify the important processes, it can be concluded that the addition of Na_2S caused a reduction of the uranium concentrations in the Texas lixiviant. In all of the experiments, adding sulfide significantly reduced the measured oxidation potentials, and in response, the uranium concentrations were also significantly reduced. However, in the experiments with the iron-oxide-coated sand and the Texas leached ore, the Eh remained at lowered values for only a short time. The added sulfide was rapidly oxidized, and the Eh quickly returned to pre-sulfide-addition levels. Consequently, the dissolved uranium slowly increased as a result of the return to oxidizing conditions. The adsorption of uranium (possibly onto iron oxides and clays in the sediment) also caused a measurable decrease in the uranium concentration, but it seems unlikely that adsorption processes alone are capable of reducing dissolved uranium to the low values required for aquifer restoration, especially in oxidizing environments.

Results of Chemical Addition Column Experiments

A series of column experiments were conducted during August through October 1984 to simulate aquifer restoration aided by the addition of sodium sulfide to spent lixiviant pumped through leached ore. Samples of leached ore and lixiviant from the Benavides in situ mine in Texas were used in the experiments. In the first set of experiments, the lixiviant alone was pumped through duplicate columns of sediment to equilibrate the system and remove any effects on the sediment induced by its two-year storage period. Approximately 10 pore volumes of solution were pumped through each of these columns. After the equilibration period, sodium sulfide was added to the same lixiviant, and the mixture was pumped through the columns for an additional 10 to 13 pore volumes. The concentration of sulfide in the influent solution was 5×10^{-3} molar. The residence time of the solution in the column was approximately 1 day. The effluent solution composition and changes in sediment characteristics provide a means of evaluating the effect of sodium sulfide on aquifer restoration.

The compositions of the effluent solutions are given in Appendix D, Tables D.1 to D.2. The uranium concentration of the spent lixiviant that was used as the influent solution in all these experiments was 2.8 mg/L. Because, in effect, we were simulating ground-water sweeping during the equilibration experiments and leached ore was used as the sediment, we expected that increased concentrations of dissolved uranium would be found in the effluents because of the dissolution of uranium minerals remaining in the ore. This had occurred during the ground-water sweeping experiments described previously (Figure 29). However, as shown in Figure 37, the uranium concentration did not increase dramatically during this experiment. This probably occurred because an unusually small amount of uranium was left in these sediments after leaching, and in this respect, the sediment does not precisely represent typical leached ore. The sulfide added to the lixiviant pumped through the columns definitely affected the effluent solution concentration for uranium. Figure 37 shows a gradual, continual decrease of dissolved uranium, resulting in final

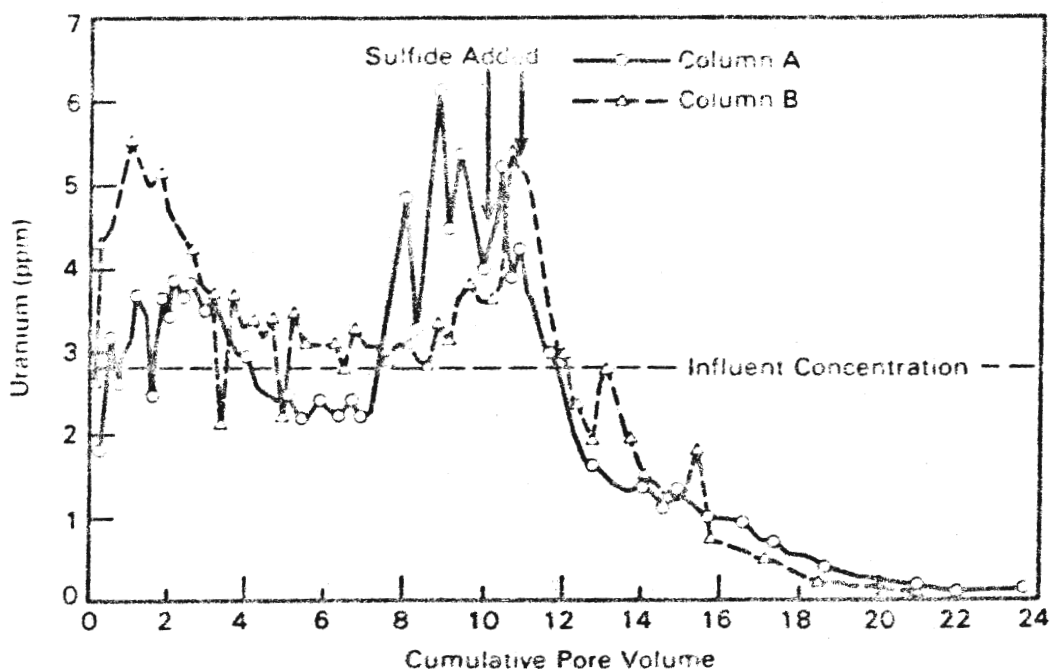


FIGURE 37. Uranium Concentration in Column Effluents from Sulfide Addition Experiments

values of 0.01 and 0.14 mg/L for the two columns at the end of the experiment. The reason for this drop is discussed with the interpretation of the other column data.

The initial high calcium and sulfate concentrations of the effluent solutions (Figures 38 and 39) once again suggest that calcium and sulfate are present in the sediment as the highly soluble mineral gypsum. Gypsum is not a native mineral in these sediments, and was probably produced as a by-product of pyrite oxidation and calcite dissolution during leaching of the sediment and storage of the core before the experiment. As the lixiviant flows through the columns, gypsum is dissolved and removed from the sediment. This is shown by the decrease in solution concentration of calcium and sulfate for both the equilibration and sulfide addition periods of the experiment.

The pH and Eh of the effluent solutions were measured using an in-line system connected to the effluent line of one of the columns. The pH is plotted versus pore volumes eluted in Figure 40. For the equilibration period, it shows that the pH of the effluent was generally lower than the influent value of 7.45, but was in most cases, within 1.5 pH units of the influent solution pH. When sulfide was added to the lixiviant, its pH increased to 10.5; however, contact with the sediment effectively lowered this value. Throughout the first 6 pore volumes of flow of lixiviant with sulfide, the pH of the effluent

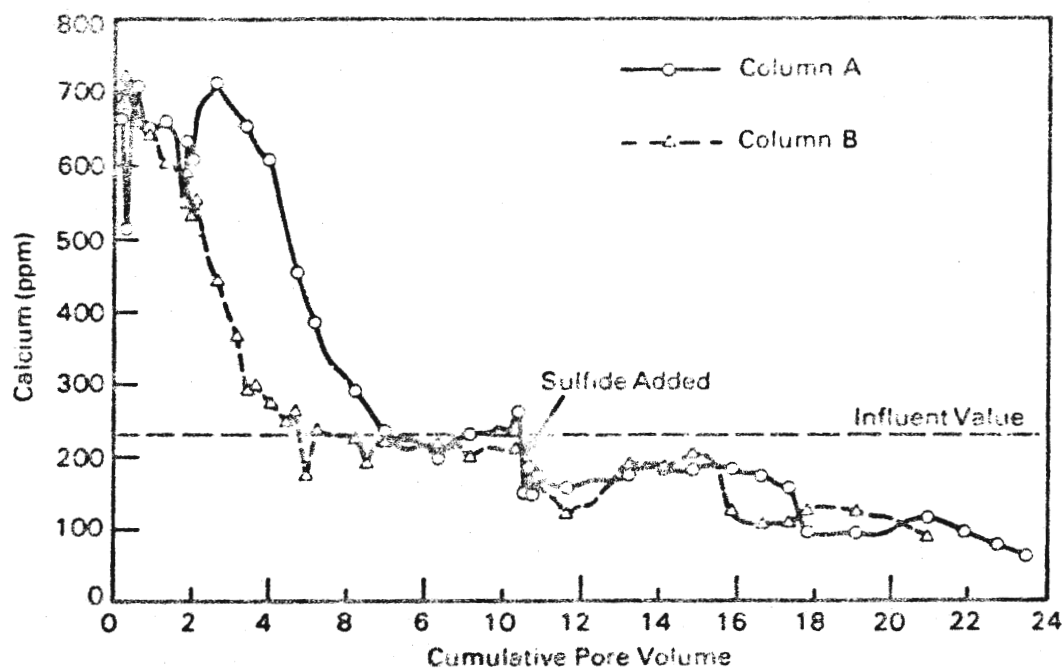


FIGURE 38. Calcium Concentration of Column Effluents from the Sulfide Addition Experiments

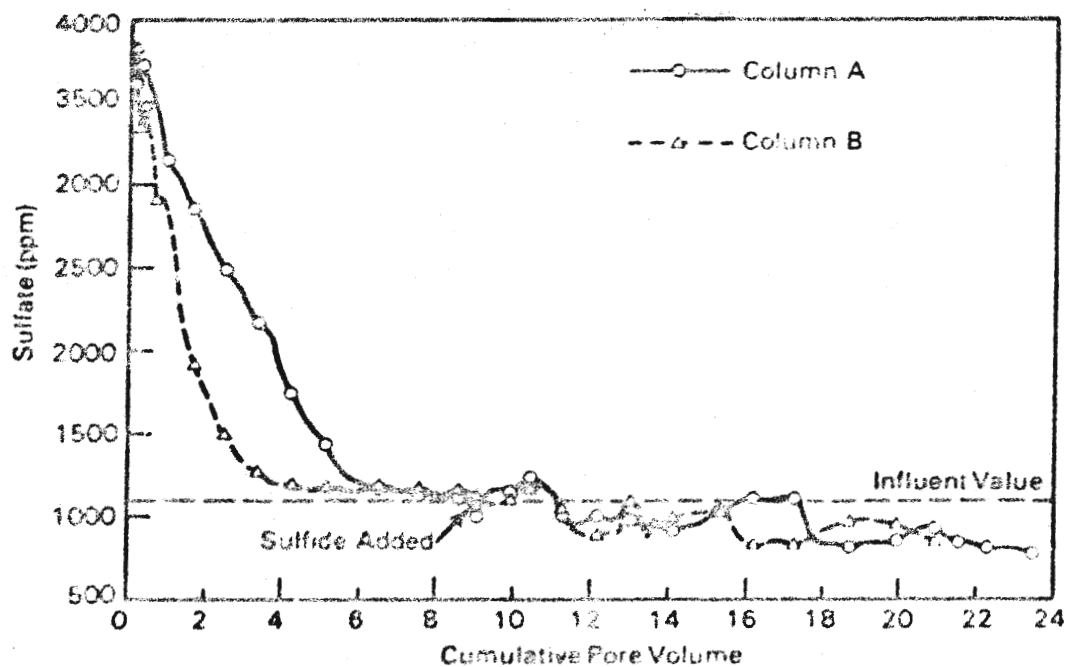


FIGURE 39. Sulfate Concentration of Column Effluents from the Sulfide Addition Experiments

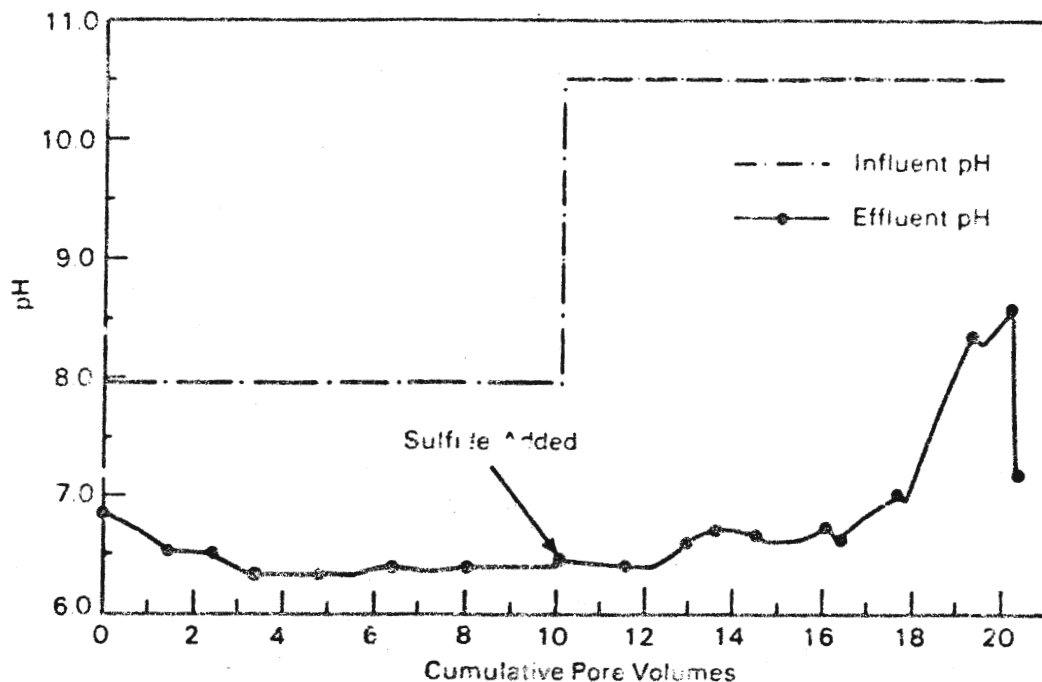


FIGURE 40. pH of Influent and Effluents from Sulfide Addition Column Experiment

solution remained fairly stable (Figure 40). After this point in the experiment, the pH increased to greater than 8, and subsequently declined to 7.22 after 11.8 pore volumes of flow.

The Eh of the effluent stayed close to the influent value (+400 mV) during the equilibration phase of the experiments (Figure 41). Under these Eh and pH conditions, uranium would be expected to be mobile as a U(VI) species and iron would be limited to low concentration by insoluble ferric hydroxide compounds. When sulfide was added to the lixiviant, the effluent Ehs began a precipitous decline to values less than -200 mV. Under these conditions, U(IV) minerals are stable and relatively insoluble. Consequently, the dissolved uranium concentration is expected to be low. This was shown to be the case in Figure 37 where uranium concentration decreased to the tenths of a part per million level after sulfide was added to the influent solution. The dissolved iron concentrations were very low (in most cases less than the detection limit of 0.05 mg/L) throughout the entire experiment. This occurred because of the low solubility of ferric hydroxide during the oxidizing, equilibration phase of the experiments, and the low solubility of ferrous sulfides during the sulfide addition phase.

As the solution composition changed during the experiment, there occurred a related change in the characteristics of the sediment in the columns. Throughout the equilibration experiments, in which more than 10 pore volumes of solution contacted the sediment, the color of the sediment remained a light

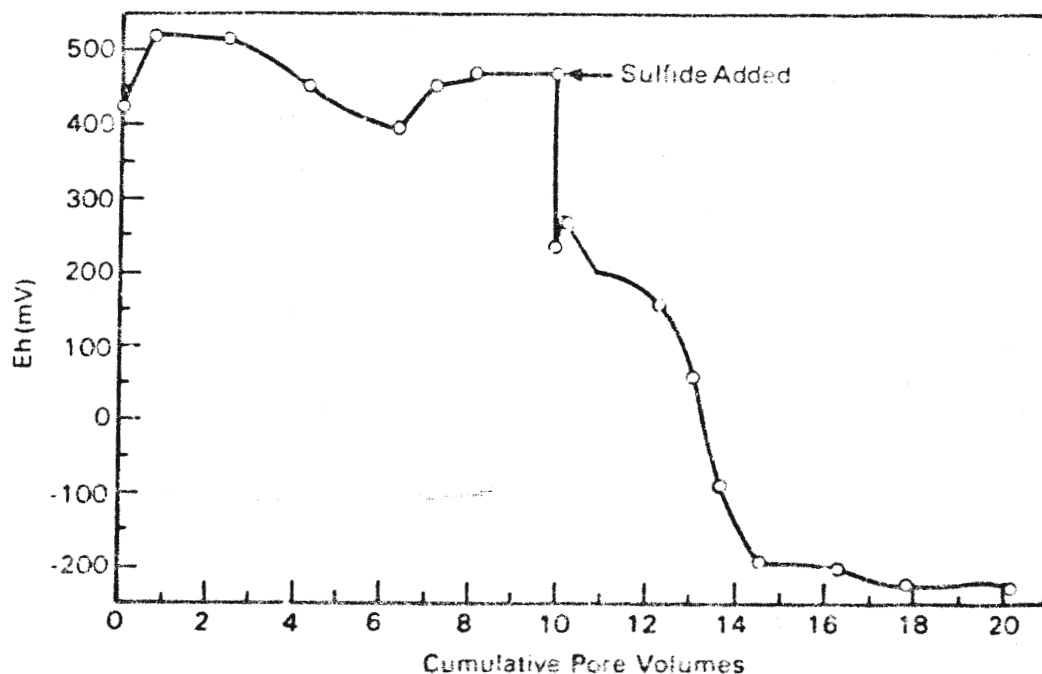


FIGURE 41. Eh of Column Effluents from Sulfide Addition Experiment

sandy color. However, after approximately 1 pore volume of the sulfide-added lixiviant contacted the sediment, the color near the influent end of the column changed to a dark black. The interface between the light and dark sediment moved through the columns in the direction of flow as additional solution contacted the sediment. After about 10 pore volumes of flow of the sulfide-added lixiviant, both of the columns were dark black. The color change was probably caused by the same reactions that we hypothesized for some of the natural restoration batch experiments in which ferrous sulfide minerals are formed in response to the reduction of iron and sulfate.

In the columns, sulfide was present in solution and iron was present in the oxidized state, Fe(III), in iron oxide minerals. The sulfide lowers the redox potential of the solution. Under these conditions, the iron oxides are not stable and iron dissolves. Iron sulfide minerals are not very soluble under these conditions and they form rapidly. Berner (1967a) has shown that noncrystalline FeS (amorph) is the original solid formed when dissolved sulfide reacts with ferrous iron. Given sufficient time (weeks) and conditions similar to the experiments, the amorphous compound may alter to crystalline FeS (mackinawite), but this was not expected to be the case in our short-term experiments. Mackinawite is a precursor to more stable ferrous sulfide minerals such as pyrite (Berner 1967b), which are present in the original ore zone sediments. Consequently, we expect that introducing a sulfide solution into a leached-ore zone during restoration will initiate the reactions necessary to reproduce the original reducing conditions present in the aquifer in

the ore zone. This will help immobilize redox-sensitive elements, as was shown for uranium, and produce a stable environment in which the redox-sensitive elements will remain immobile.

The use of sodium sulfide shows promise towards accelerating the process of aquifer restoration by reestablishing reducing conditions in the leached zone. However, in an aquifer restoration effort, enough sulfide may have to be injected into a leached ore body to consume all of the available oxidizing species. Once this is accomplished and reducing conditions are established, dissolved uranium concentrations should be greatly reduced. At this time, further research is needed to identify the important reactions controlling uranium precipitation and sulfide oxidation. In addition, associated reactions caused by sulfide addition that may have adverse effects on aquifer permeabilities need to be defined to more fully assess the use of sulfide as an aid to aquifer restoration.

SUMMARY OF EXPERIMENTAL RESULTS

During the past 3 years, batch and column experiments have been conducted to study the mobility of contaminants produced during in situ leach mining of uranium ore deposits and evaluate aquifer restoration methods following mining. Ground water, lixiviant, and sediment samples from mine operations in Texas and Wyoming were used to simulate field conditions in the laboratory. Both natural restoration and induced restoration techniques were evaluated.

Natural restoration is the process by which contaminants are removed from the leaching solution as a result of chemical interactions between the solution and the aquifer sediments. As the residual leaching solution in the aquifer moves out of the leach field in response to the natural hydrologic gradient it will contact fresh sediment that could help reestablish the aquifer conditions and ground-water chemistry that existed before mining. The experiments show that the reducing capacity of these sediments remains very high, even for the leached ore, and that the redox-sensitive element, uranium, can be removed from solution by water/sediment interactions. The dissolved concentrations of the nonredox-sensitive elements, chloride and sulfate, must be considered as contaminant levels during mining and they do not appear to be removed by natural restoration. The concentration of major cations in the ground water (calcium, magnesium, sodium, and potassium) and their ion-exchanging activities. Their concentration may be affected by ion-exchange processes between the aquifer and the leaching solution. As the solution moves through the aquifer, they will increase or decrease depending on the relative affinity of the ions between the ions in solution and the aquifer sediments. The experiments could theoretically increase the concentration of one ion without decreasing that of another if a lixiviant is added to the solution. The lixiviant acts with the aquifer sediments.

One of the commonly used methods for natural restoration of the leach field is to pump the wells after mining to draw fresh ground water to dilute and replace the lixiviant. This natural sweeping method of restoration was found to be very effective for the removal of contaminant species and for the major cations normally found in the ground water.

Column experiments designed to evaluate ground-water sweeping and operator experience at several mines showed that this restoration method is not effective for the redox-sensitive elements (especially uranium) because the oxidizing ground water brought into the leach field continues to mobilize uranium, producing concentrations above the restoration limit. Uranium may be adsorbed onto ferric hydroxides present under these oxidizing conditions, but it appears that this process will not adequately lower uranium concentrations to the level found under normal reducing conditions in the ore zone.

To enhance the induced restoration methods, it has been suggested that sulfide compounds be added to solution circulated through the leached ore to aid in reestablishing the original reducing conditions of the aquifer in the vicinity of the leach field. Batch and column experiments with sodium sulfide showed that this reductant can produce reducing conditions in the solution and the sediment. At the concentrations studied (10^{-2} to 10^{-4} molar sulfide), the lixiviant with sulfide added did not appear to significantly decrease the permeability of the sediment, and the buffering capacity of the system remained sufficient to keep the pH of the solution close to that of the original ground water. Furthermore, the color of the oxidized leached ore changes to that approaching fresh reduced sediment as the sulfide-rich solution moves through the columns. The uranium concentration is lowered from the parts-per-million range to approximately 0.1 ppm as reducing conditions are established in the system. This method of chemical reduction does not restore the other major cations and anions to ground-water concentration levels, consequently the techniques should be used in concert with one of the other induced techniques such as ground-water sweeping or surface treatment and recirculation.

REFERENCES

- Amell, A. R. and D. Langmuir. 1978. Factors Influencing Solution Rate of Uranium Dioxide Under Conditions Applicable to In Situ Leaching. Open-File Report OFR 84-79 (NTIS PB-299 947) U.S. Bureau of Mines, Washington, D.C.
- Ames, L.L., R. E. McGarrah, B. A. Walker and P. F. Salter. 1983. "Uranium and Radium Sorption on Amorphous Ferric Oxyhydroxide." Chem. Geol. 40:135-148.
- Berner, R. A. 1964. "Iron Sulfides Formed From Aqueous Solutions at Low Temperatures and Atmospheric Pressures." J. Geol. 72:293-306.
- Berner, R. A. 1967a. "Diagenesis of Iron Sulfides in Recent Marine Sediments." Am. Assoc. Adv. Sci. 83:268-272.
- Berner, R. A. 1967b. "Thermodynamic Stability of Sedimentary Iron Sulfides." Am. J. Sci. 265(9):773-785.
- Bishop, A. L. 1980. "Non-Production Zone Excursions." Chapter 8 in Fourth Annual Uranium Seminar, pp. 75-80, Soc. Mining Engineers. New York, New York.
- Buma, G., J. R. Riding, L. Downey and T. D. Chatwin. 1979. "Geochemical Arguments for Natural Stabilization Following In Situ Leaching of Uranium." Proc. New Orleans Symposium on In Situ Uranium Mining and Ground Water Restoration, ed. W. J. Schlitt and D. A. Shock, pp. 7-22, AIME, Soc. Min. Eng., New Orleans, Louisiana.
- Buma, G., P. H. Johnson, G. K. Bienck, C. G. Watson, H. Moyes and R. Capuano. 1981. Analysis of Ground Water Criteria and Recent Restoration Attempts After In Situ Uranium Leaching. Contract Report No. J0295019, Final Report to U.S. Department of Interior, Bureau of Mines, Washington, D.C.
- Champ, D. R., J. Gulens and R. E. Jackson. 1979. "Oxidation-reduction Sequences in Ground Water Flow Systems." Can J. Earth Sci. 16:12-23.
- Chatham, J. R., R. B. Wanty and D. Langmuir. 1981. Groundwater Prospecting for Sandstone-Type Uranium Deposits: The Merits of Mineral-Solution Equilibria Versus Single Element Tracer Methods. Report No. GJ8X-129 (81), U.S. Department of Energy, Grand Junction Office, Grand Junction, Colorado.
- Dahl, A. R. and J. L. Hagnafer. 1974. "Genesis and Characteristics of the Southern Powder River Basin Uranium Deposits, Wyoming, USA." In IAEA Proceedings, IAEA-SM-183/5, International Atomic Energy Agency, Vienna, Austria.

- Deutsch, W. J., R. J. Serne, N. E. Bell, and W. J. Martin. 1983. Aquifer Restoration at In-Situ Leach Uranium Mines: Evidence for Natural Restoration Processes. NUREG/CR-3136 (PNL-4505), U.S. Nuclear Regulatory Commission, Washington, D.C.
- Deutsch, W. J., N. E. Bell, B. W. Mercer, R. J. Serne, J. W. Shade and D. R. Tweeton. 1984. Aquifer Restoration Techniques for In-Situ Leach Uranium Mines. NUREG/CR-3104 (PNL-4583), U.S. Nuclear Regulatory Commission, Washington D.C.
- DeVoto, R. H. 1978. "Uranium in Phanerozoic Sandstones and Volcanic Rocks." In Short Course in Uranium Deposits: Their Mineralogy and Origin, ed., M. M. Kimberly, pp. 293-306, Min. Assoc. Canada, Toronto, Canada.
- Doi, K., S. Hirano and Y. Sakamaki. 1975. "Uranium Mineralization by Ground Water in Sedimentary Rocks, Japan." Econ. Geol. 70:628-646.
- Dunler, D. L. and A. L. Bishop. 1980. "In-Situ Uranium Leach Mining: Considerations for Monitor Well Systems". Paper No. SPE 9505, Soc. Petroleum Eng., Dallas, Texas.
- Felmy, A. R., D. C. Girvin and E. A. Jenne. 1984. MINTEQA--A Computer Program for Calculating Aqueous Geochemical Equilibria. EPA-600/3-84-032 (NTIS PB84-167148), U.S. Environmental Protection Agency, Athens, Georgia.
- Folk, R. L. 1968. Petrology of Sedimentary Rocks. University of Texas, Austin, Texas.
- Franson, M. H. (ed.). 1981. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, D.C.
- Galloway, W. E. and W. R. Kaiser. 1980. Catahoula Formation of the Texas Coastal Plain: Origin, Geochemical Evolution, and Characteristics of Uranium Deposits. Report of Investigation 100, Bureau of Economic Geology, University of Texas, Austin, Tex.
- Garling, R. A. 1981. "Evaluation of Electrodialysis for Process Water Treatment for In Situ Mining." In 5th Uranium Seminar, Albuquerque, New Mexico, AIME, Society of Mining Engineers, Littleton, Colorado.
- Gent, C. A. 1977. "Preparation of Pyrite-Coated Sand Grains for Research on Roll-Type Uranium Deposits." J. Res. U.S. Geol. Survey 5:595-596.
- Giblin, A. M. Batts, B. D. and Swaine, D. J. 1981. "Laboratory Simulation Studies of Uranium Mobility in Natural Waters." Geochim. Cosmo. Acta 45:699-709.
- Goldhaber, M. B. 1983. "Experimental Study of Metastable Sulfur Oxyanion Formation During Pyrite Oxidation at pH 6-9 and 30°C." Am. J. Sci. 283:193-217.

- Goldhaber, M. B. and R. L. Reynolds. 1977. Geochemical and Mineralogical Studies of a South Texas Roll Front Uranium Deposit. Open-File Report 77-821, U.S. Geological Survey, Reston, Virginia.
- Granger, H. C. and C. G. Warren. 1969. "Unstable Sulfur Compounds and the Origin of Roll-Type Uranium Deposits." Econ. Geol. 64:160-171.
- Granger, H. C. and C. G. Warren. 1974. "Zoning in the Altered Tongue Associated with Roll-Type Uranium Deposits". In IAEA Proceedings, IAEA-SM-183/6, International Atomic Energy Agency, Vienna, Austria.
- Harshman, E. N. 1972. "Geology and Uranium Deposits, Shirley Basin Area, Wyoming." Professional Paper 745, U. S. Geological Survey, Washington, D.C.
- Harshman, E. N. 1974. "Distribution of Elements in Some Roll Type Uranium Deposits." In IAEA Proceedings, IAEA-SM-183/4, International Atomic Energy Agency, Vienna, Austria.
- Humenick, M. J. and K. Garwacka. 1982. "Oxidative Destruction of Ammonia for Restoration of Uranium Solution Mining Sites." SME-AIME Annual Meeting Paper No. 82-105, Society of Mining Engineers, Littleton, Colorado.
- Humenick, M. J., L. J. Turk and M. P. Colchin. 1980. "Methodology for Monitoring Ground Water at Uranium Solution Mines." Ground Water 18(3):262-273.
- Humenick, M. J., R. S. Schechter and L. J. Turk et al. 1978. Literature Review and Preliminary Analysis of Inorganic Ammonia Pertinent to South Texas Uranium In Situ Leach. Technical Report CRMK-155, EHE 78-01, Center for Research in Water Resources, University of Texas, Austin, Texas.
- Humenick, M. J., R. S. Schechter, M. Breland, K. Garwacka, D. Johnson and M. Walsh. 1979. Investigation of the Fate of Ammonia from In Situ Uranium Solution Mining. Environmental Health Engineering Technical Report EHE-79-01, University of Texas at Austin, Austin, Texas.
- Jackson, M. L. 1956. Soil Chemistry Analysis--Advanced Course. Department of Soils, University of Wisconsin, Madison, Wisconsin.
- Kasper, D. R., H. W. Martin, L. D. Munsey, R. B. Bhappu and C. K. Chase. 1979. Environmental Assessment of In Situ Mining. Final Report for Contract No. J0265022, prepared for U.S. Department of Interior, Bureau of Mines by PRC Toups, Orange, California and Mountain States Research and Development, Tucson, Arizona.
- Kehrmann, R. F. 1979. Detection of Lixiviant Excursions with Geophysical Resistance Measurements During In Situ Uranium Leaching. Final Report for Contract No. J0148080, prepared for U.S. Department of Interior, Bureau of Mines by Westinghouse Electric Corporation, Boulder, Colorado.

- Langmuir, D. 1978. "Uranium Solution-Mineral Equilibria at Low Temperatures with Applications to Sedimentary Ore Deposits." Geochim. Cosmo. Acta 42:547-569.
- Larson, W. C. 1978. Uranium In Situ Leach Mining in the United States. U.S. Bureau of Mines Information Circular No. 8777, Washington, D.C.
- Larson, W. C. 1981. "In Situ Leach Mining--Current Operations and Production Statistics." U.S. Bureau of Mines Information Circular No. 8852, pp. 3-7, Washington, D.C.
- Lord, C. J. III. 1982. "A Selective and Precise Method for Pyrite Determination in Sedimentary Materials." J. Sed. Pet. 52:654-666.
- Mortimer, C. H. 1941. "The Exchange of Dissolved Substances between Mud and Water in Lakes. Parts I and II." J. Ecology, 29:280-329.
- Mortimer, C. H. 1942. "The Exchange of Dissolved Substances between Mud and Water in Lakes. Parts III and IV." J. Ecology, 30:147-201.
- Naumov, G. B., B. N. Ryzhenko, and I. L. Khodakovsky. 1974. Handbook of Thermodynamic Data. USGS-WRD-74-001, U.S. Geological Survey, Reston, Virginia.
- Orion Research Incorporated. 1970. Instruction Manual--Sulfide Ion Activity Electrode. Form IM94-16/074, Orion Research Inc., Cambridge, Massachusetts.
- Pyzik, A. J. and Sommer, S. E. 1961. "Sedimentary Iron Monosulfides: Kinetics and Mechanisms of Formation." Geochim. Cosmo. Acta 45:687-698.
- Rickard, D. T. 1974. "Kinetics and Mechanisms of the Sulfidation of Goethite." Am. J. Sci. 274:941-952.
- Riding, J. R. and F. J. Rossow. 1979. Restoration of Ground-Water Quality after In Situ Uranium Leaching. Contract No. J0275026, prepared by Ford, Bacon and Davis Utah, Inc. for U.S. Department of Interior, Bureau of Mines, Washington, D.C.
- Robie, R. A., Hemingway, B. S., and Fisher, J. R. 1978. "Thermodynamic Properties of Minerals and Related Substances at 298.15K and 1 bar (10⁵ Pascals) Pressure and at Higher Temperatures." U.S. Geol. Survey Bull. 1452, U.S. Geological Survey, Washington, D.C.
- Rothrock, R. A. 1981. A Statistical Methodology for Assays of Ground-Water Quality in Uranium Solution Mines. Preprint No. 81-365, Soc. Mining Engineers, Littleton, Colorado.

- Sherwood, D. R., C. J. Hostetler and W. J. Deutsch. 1984. "Identification of Chemical Processes Influencing Constituent Mobility During In-Situ Uranium Leaching." PNL-SA 12173, Presented at the Symposium on Practical Applications of Grand Water Models, Columbus, Ohio. August 15-17, 1984.
- Tatom, A., R. S. Schechter and L. W. Lake. 1981. "Factors Influencing the In Situ Leaching Rates of Uranium Areas." SME-AIME Paper No. 81-310, Society of Mining Engineers, Littleton, Colorado.
- Thompson, W. E., W. V. Swarzenski, D. L. Warner, G. E. Rouse, O. F. Carrington, and R. Z. Pyrih. 1978. Ground-Water Elements of In Situ Leach Mining of Uranium. NUREG/CR-0311 (NTIS PB 286856). U.S. Nuclear Regulatory Commission, Washington, DC.
- Trace Metal Data Institute. 1981. "Restoration of In Situ Uranium Leaching Sites, Incorporating Reverse Osmosis Technology." Bulletin 605, Trace Metal Data Institute, El Paso, Texas.
- Tweeton, D. R. 1981a. "Restoring Ground Water Quality Following In Situ Leaching." In In Situ Mining Research, U.S. Bureau of Mines Information Circular No. 8852, Washington, D.C.
- Tweeton, D. R. 1981b. "Application of Geophysical Resistance Measurements to in situ Leaching." In Proceedings: Bureau of Mines Technology Transfer Seminar, Bureau Mines Information Circular 8852, Bureau of Mines, Washington, D.C.
- Tweeton, D. R. and K. A. Peterson. 1981. "Selection of Lixiviants for In Situ Uranium Leaching." U.S. Bureau of Mines Information Circular No. 8851, Washington, D.C.
- Van Der Weijden, C. H., Arthur, R. C., and Langmuir, D. 1976. "Sorption of Uranyl by Hematite: Theoretical and Geochemical Implications." *Geol. Soc. Am. Abstracts with Programs*, 1152.
- Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and H. Schumm. 1968. "Selected Values of Chemical Thermodynamic Properties." NBS Technical Note 270-3, National Bureau of Standards, Washington, D.C.
- Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and J. H. Schumm. 1969. "Selected Values of Chemical Thermodynamic Properties." NBS Technical Note 270-4, National Bureau of Standards, Washington, D.C.
- Walsh, M. P. 1979. "A Model for Predicting the Restoration of an Ammonium Migration from In Situ Mine Sites." In Proceeding of South Texas Uranium Seminar, Ch. 4, pp. 29-38, Am. Inst. Mining, Metal. and Petrol. Eng., Inc., New York.

- Warren, C. G. 1972. "Sulfur Isotopes as a Clue to the Genetic Geochemistry of a Roll-Type Uranium Deposit." Econ. Geol. 67:759-767.
- Warren, C. G. and H. C. Granger. 1973. "The Concept of Growth and Maturity of Ore-Stage Pyrite in Roll-Type Uranium Deposits." J. Res. U.S. Geol. Survey 1(2):151-155.
- Yan, T. Y. and W. F. Espenscheid. 1982. "Removal of Ammonium Ions from Subterranean Formations by Flushing with Lime Saturated Brines." SME-AIME Annual Meeting Paper No. 82-02, Society of Mining Engineers, Littleton, Colorado.

APPENDIX A

ANALYTICAL DATA FROM BATCH EXPERIMENTS WITH TEXAS SEDIMENTS

P.1

APPENDIX A

ANALYTICAL DATA FROM BATCH EXPERIMENTS WITH TEXAS SEDIMENTS

The six tables in this appendix contain solution chemical data obtained from the batch experiments in which lixiviant was mixed with various types of Texas sediment that had been collected at an in situ uranium mine. Each table represents a time series of data obtained from an experiment with a single sediment type. The tables are ordered as follows:

- Table A.1 - Texas Reduced Sediment
- Table A.2 - Texas Oxidized Sediment
- Table A.3 - Texas Ore Zone Sediment
- Table A.4 - Texas Ore Amended with 5% Pyrite
- Table A.5 - Texas Ore Amended with FeS-Coated Sand
- Table A.6 - Texas Leached Ore

The results of these experiments are discussed on pages 40 to 46 of this report.

TABLE A.1. Solution of the Batch Experiment with Texas Reduced Sediment
(all concentration units are ppm)

Parameter	Sample Number							
	LIX 666	RS2A	RS2B	RS4A	RS4B	RS8A	RS8B	RS16A
1 Duration (days)	0	2	2	4	4	8	8	16
2 pH	8.05	7.84	7.86	7.79	7.82	7.66	8.15	7.81
3 Eh (mV)	340	335	347	378	380	409	422	440
4 pE	5.75	5.66	5.87	6.39	6.42	6.91	7.13	7.44
5 Alkalinity (mg/L Ca CO ₃)	144	127	132	N.D.	N.D.	N.D.	N.D.	N.D.
6 Ca	200	360	390	475	367	495	330	370
8 Mg	81.9	107	114	127	109	121	95	108
9 Na	1165	1250	1250	1240	1200	1110	1000	1210
12 K	32	54	41	43	40	33	32	45
11 Cl	1030	970	1030	860	890	780	780	860
12 SO ₄	1320	2010	1810	1910	1910	1580	1710	1640
14 Fe ICP	<0.03	0.1	0.11	0.15	0.06	0.15	0.07	0.37
15 Fe AA	0.022	0.717	0.042	0.09	0.038	0.136	0.088	0.151
17 Al ICP	<0.03	0.56	0.6	0.5	0.4	0.4	0.28	<0.03
18 Al AA	0.023	0.019	0.012	0.026	0.02	0.019	0.013	0.096
20 Li	0.019	0.22	0.2	0.21	0.19	0.19	0.19	0.26
22 Cd	<0.01	<0.01	<0.01	<0.01	0.01	0.015	<0.01	0.02
23 Sr	5.1	8.3	9	10	5.6	9.9	7.6	8.7
24 Ba	<0.02	0.024	0.018	0.018	0.015	0.015	<0.002	0.018
25 Mn	<0.02	0.25	0.32	0.58	0.3	0.75	0.3	0.38
26 Co	0.03	0.631	0.036	0.036	<0.01	0.036	0.03	0.02
27 Cu	0.1	0.07	0.06	0.03	0.032	0.044	0.02	0.09
28 Zn	<0.02	0.075	0.075	0.09	0.06	0.04	<0.02	0.09
29 Pb	<0.06	<0.06	<0.06	0.3	<0.06	0.3	<0.06	<0.06
30 Si	6.5	6.6	6.7	6.8	5.9	6.5	4.9	5.7
31 B	1.35	1.28	1.48	1.38	1.18	1.18	1.08	1.18
32 As	<0.07	<0.08	0.24	0.14	<0.08	<0.08	<0.08	<0.08
33 U	52.8	11.5	13	16.8	11.1	11.2	9.6	18
34 Se AA	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
35 Mo	<0.01	0.2	0.16	0.16	0.17	0.13	0.14	0.15

ND = Not determined

TABLE A.1. (Contd)

Parameter	Sample Number						
	RS16B	RS36A	RS36B	RS75A	RS75B	RS101A	RS101B
1 Duration (days)	16	36	36	75	75	101	101
2 pH	7.99	7.8	7.9	8.28	8.06	8.12	8.06
3 Eh (mV)	432	280	274	18	118	256	203
4 pE	7.3	4.73	4.62	0.304	1.99	4.33	3.43
5 Alkalinity (mg/L Ca CO ₃)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
6 Ca	320	388	357	294	520	276	294
8 Mg	96	109	102	90	138	85	89
9 Na	1140	1064	1127	1150	1320	1060	1090
10 K	36	37	35	36	58	38	40
11 Cl	860	800	880	920	1040	910	940
12 SO ₄	1840	2300	2400	1850	2400	1925	2000
14 Fe ICP	0.17	4.01	3.81	1.4	2.4	0.16	1.8
15 Fe AA	0.105	3.9	3.4	1.45	2.16	0.102	0.849
17 Al ICP	<0.03	0.13	0.33	<0.03	<0.03	<0	<0.03
18 Al AA	0.147	0.074	0.069	0.044	0.021	0.052	
20 Li	0.3	0.2	0.19	<0.05	<0.05	0.18	0.18
22 Cd	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
23 Sr	7.7	9.25	8.61	7.8	11.6	7.2	7.4
24 Ba	0.018	0.015	0.024	<0.002	<0.002	<0.002	<0.002
25 Mn	0.31	<0.02	0.626	<0.002	<0.002	<0.002	<0.002
26 Co	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
27 Cu	0.09	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
28 Zn	0.07	0.094	0.11	0.09	0.04	<0.02	0.27
29 Pb	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
30 Si	5.5	5.82	5.94	5.9	7	7.2	8
31 B	1.19	0.72	0.66	1.2	1.2	1.1	1.1
32 As	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
33 U	17.1	1.8	0.83	0.12	3.25	0.19	0.62
34 Se AA	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
35 Mo	0.17	0.074	0.122	<0.01	<0.01	0.07	0.07

ND = Not determined.

TABLE A.2. Solution Analysis of Batch Experiment with Texas Oxidized Sediment

1 Texas Oxidized								
Parameter	Supernatant	2 Syn. U.S. 963	3 TXOX 2A	4 TXOX 2B	5 TXOX 4A	6 TXOX 4B	7 TXOX 8A	8 TXOX 9H
1 Duration (days)	NA	NA	2	2	4	4	8	8
2 Sat. pH	7.9	NA	7.35	7.34	7.29	7.3	7.33	7.26
3 Fil. Sol. (mM)	8.12	7.68	8.52	8.12	8.4	8.26	8.5	8.4
4 Sat. Th (mM)	301	NA	433	420	299	303	216	234
5 Fil. Sol. Th (mM)	311	381	316	306	240	280	172	182
6 Alkalinity (meq/L CaCO ₃)	178	356	225	ND	262	243	260	321
7 U. Lower (ppm)	48.81	44.29	14	10	10.38	11.21	9.17	8.66
8 U. IOP (ppm)	40.4	39.2	13.1	10.1	11.4	10.8	9.8	8.5
9 Al AA (ppm)	0.163	0.038	0.224	0.161	1.36	0.166	0.09	0.147
10 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
11 B (ppm)	2.2	1.4	1.1	1.1	1.1	1.1	0.9	0.8
12 Ba (ppm)	0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Ca (ppm)	363	311	237	225	244	241	211	208
14 Fe AA (ppm)	<0.05	<0.05	<0.02	<0.02	0.098	<0.07	<0.05	0.072
15 K (ppm)	60	50	30	30	30	30	30	30
16 Mn (ppm)	186	114	89.9	86.3	88.2	89.4	73.1	72.6
17 Na (ppm)	21	1340	1040	982	973	991	803	798
18 Si (ppm)	18	13	11	11	11	11	9	8
19 Sr (ppm)	11.1	8.0	6.1	5.8	6	6.1	5	4.8
20 Mo AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
21 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
22 Cl (ppm)	1701	1690	1045	1034	1007	1023	820	767
23 SO ₄ (ppm)	2514	1632	1257	1257	1234	1246	1040	949

Al, As, Fe, Mn, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser

Fluorimetry (uranium only).

NA = Not applicable.

ND = Not determined.

TABLE A.2. (Contd)

Parameter	9 TXOX 16A	10 TXOX 16B	11 TXOX 36A	12 TXOX 36B	13 TXOX 36A	14 TXOX 36B	15 TXOX 101A	16 TXOX 101B
1 Duration (days)	16	16	36	36	75	75	101	101
2 Sat. pH	ND	ND	6.68	6.76	6.88	6.81	7.01	6.95
3 Fil. Sol. (pH)	8.27	8.12	8.53	8.44	8.68	8.91	8.27	8.45
4 Sat. Eh (mV)	ND	ND	65	82	213	160	285	201
5 Fil. Sol. Eh (mV)	-42	-15	216	210	246	223	204	193
6 Alkalinity (mo/L CaCO_3)	321	311	236	ND	107	204	171	316
7 U, Laser (ppm)	9.66	7.75	2.7	2.3	2.03	3.05	1.71	1.68
8 U, ICP (ppm)	7.8	6.6	1.9	2.6	2.3	3.7	4.6	2.4
9 Al AA (ppm)	0.191	0.123	0.02	0.02	0.105	0.064	0.03	<0.02
10 As AA (ppm)	0.033	<0.015	<0.015	<0.015	<0.015	<0.02	<0.05	
11 B (ppm)	1	1	0.9	1	0.6	0.7	0.8	0.8
12 Ba (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Ca (ppm)	219	217	170	207	79	123	100	118
14 Fe AA (ppm)	<0.05	<0.05	<0.05	<0.05	0.123	<0.05	0.112	0.023
15 K (ppm)	40	30	30	30	<2.0	30	40	40
16 Mg (ppm)	90.7	97.3	71.6	84.2	50.8	57.4	63.2	56.5
17 Na (ppm)	1100	1070	896	1010	693	797	970	835
18 Si (ppm)	8	8	6	7	6	6	8	7
19 Sr (ppm)	5.7	5.6	4.5	5.5	2.7	3.5	4	3.7
20 Mo AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
21 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
22 Cl (ppm)	1009	1011	852	998	671	748	82	840
23 SO_4 (ppm)	1195	1200	969	1131	684	860	775	775

Al, As, Fe, Mo, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

ND = Not determined

TABLE A.3. Solution Analysis of Batch Experiment with Texas Ore Zone Sediment

Parameter	1 Texas Ore Supernatant	2 SYN. LIX. 953	3 TXOR 2A	4 TXOR 2B	5 TXOR 4A	6 TXOR 4B	7 TXOR 8A	8 TXOR 8B
1 Duration (days)	NA	NA	2	2	4	4	8	8
2 Sat. pH	8.1	NA	7.11	7.09	7.17	7.15	7.11	7.06
3 Fil. Sol. (ppt)	8.4	7.68	8.62	8.4	8.1	8.02	8.5	8
4 Sat. Eh (mV)	261	NA	337	250	206	290	170	167
5 Fil. Sol. Eh (mV)	227	381	298	231	230	243	25	55
6 Alkalinity (meq/L CaCO_3)	323	336	393	393	346	543	547	94
7 U. Laser (ppm)	144	44.29	255	210	130	185.71	250	ND
8 U. ICP (ppm)	136	39.2	159	140	123	167	176	212
9 Al AA (ppm)	0.055	0.038	0.206	0.194	0.312	0.114	0.15	0.057
10 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
11 B (ppm)	1.1	1.4	1.2	1.1	0.8	1.1	1.1	1
12 Ba (ppm)		<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1
13 Ca (ppm)	436	311	532	511	445	604	626	780
14 Fe AA (ppm)	<0.05	<0.05	<0.05	<0.05	<0.07	<0.05	<0.07	0.05
15 K (ppm)	50	50	50	50	30	50	50	50
16 Mg (ppm)	123	114	129	122	101	132	140	165
17 Mn (ppm)	1290	1340	1310	1230	921	1270	1340	1280
18 Si (ppm)	10	13	11	10	7	10	11	10
19 Sr (ppm)	10.1	8.5	11.4	10.7	9	11.8	12.4	14
20 Th (ppm)	0.2	<0.01	0.4	0.4	0.4	0.7	0.7	10
21 Mo AA (ppm)	<0.075	<0.015	<0.15	<0.1	<0.075	<0.1	<0.1	<0.015
22 Sn AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23 Cl (ppm)	818	1090	913	853	637	880	883	887
24 SO ₄ (ppm)	2159	1632	2398	2295	1943	2432	2511	2591

Al, As, Fe, Mn, and Sr analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

NA = Not applicable.

TABLE A.3. (Contd)

Parameter	9 TXOR 16A	10 TXOR 16B	11 TXOR 36A	12 TXOR 36B	13 TXOR 75A	14 TXOR 75B	15 TXOR 101A	16 TXOR 101B
1 Duration (days)	16	16	36	36	75	75	101	101
2 Sat. pH	ND	ND	7.07	6.95	6.9	7.04	7.11	7.09
3 Fil. Sol. (mM)	8.28	8.17	8.36	7.69	8.45	8.44	8.52	8.48
4 Sat. Eh (mV)	ND	ND	-53	-49	64	49	50	54
5 Fil. Sol. Eh (mV)	-5	-20	-17	197	160	203	202	179
6 Alkalinity (meq/L CaCO ₃)	236	132	188	ND	193	233	225	161
7 B. Laser (ppm)	172.3	249	20	28	15.71	31.15	14.1	40
8 U. ICP (ppm)	157	183	24	34.8	15.9	29.5	10.36	29.8
9 Al AA (ppm)	0.021	0.443	<0.02	<0.02	0.121	0.081	0.037	0.027
10 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
11 B (ppm)	1	0.8	0.7	0.7	0.6	0.6	1.5	0.5
12 Ba (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Ca (ppm)	539	489	288	349	315	352	714	253
14 Fe AA (ppm)	<0.05	0.066	<0.05	<0.05	<0.05	<0.05	0.05	0.023
15 K (ppm)	50	70	40	30	30	80	90	30
16 Mg (ppm)	124	113	73.6	84.7	74.9	83.2	170.2	64
17 Na (ppm)	1220	1060	711	799	635	724	1760	616
18 Si (ppm)	22	8	18	18	5	8	25	6
19 Sr (ppm)	11.1	10.1	6.2	7.5	6.4	7.1	14.8	5.4
20 Mn (ppm)	0.6	0.5	0.03	0.04	0.4	0.5	0.1	0.1
21 Mo AA (ppm)	<0.015	<0.1	<0.015	<0.015	<0.05	<0.05	<0.05	<0.015
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23 Cl (ppm)	770	640	440	512	334	452	804	222
24 SO ₄ (ppm)	2630	2025	1560	1740	1697	1863	4380	1395

Al, As, Fe, Mn, and Se analytes by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (barium only)

ND = Not determined.

••

TABLE A.4. Solution Analyses of Batch Experiment with Texas Ore Amended with 5% Pyrite

Parameter	1 Texas Ore Supernatant	2 SYN. LIX. 953	3 TEX. 5% 2A	4 TEX. 5% 2B	5 TEX. 5% 4A	6 TEX. 5% 4B	7 TEX. 5% 8A
1 Duration (days)	NA	NA	2	2	4	4	8
2 Sat. pH	8.1	NA	6.6	6.62	6.78	6.84	6.47
3 Fil. Sol. (ppt)	8.4	7.88	7.37	7.2	7.5	7.52	7.88
4 Sat. Eh (mv)	261	NA	135	128	122	126	130
5 Fil. Sol. Eh (mV)	227	381	47	161	50	23	209
6 Alkalinity (mg/L CaCO ₃)	393	356	462	490	528	518	ND
7 U. Laser (ppm)	144	44.29	80	205.71	171.43	ND	248
8 U. ICP (ppm)	136	39.2	156	174	178	181	201
9 Al AA (ppm)	0.035	0.036	0.074	0.14	0.031	0.045	0.426
10 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
11 B (ppm)	1.1	1.4	1.4	1.4	1.3	1.3	1.4
12 Ba (ppm)		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Ca (ppm)	436	511	649	641	668	661	621
14 Fe AA (ppm)	<0.05	<0.05	<0.05	<0.05	0.52	0.14	0.051
15 K (ppm)	50	50	60	50	50	50	60
16 Mg (ppm)	125	114	167	163	164	162	163
17 Mn (ppm)	1290	1340	1350	1300	1230	1390	1440
18 Si (ppm)	10	13	11	11	11	11	12
19 Sr (ppm)	10.1	8.5	12.9	13.3	13.2	13	13.4
20 Th (ppm)	0.2	<0.01	1.1	0.9	1.2	1	0.9
21 Mo AA (ppm)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23 Cl (ppm)	919	1090	932	966	896	897	935
24 SO ₄ (ppm)	2159	1632	2591	255	2437	2480	2625

Al, As, Fe, Mn, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or Laser Fluorimetry (uranium only).

NA = Not applicable.

A.R

TABLE A.4. (Contd)

Parameter	8 Test, 98 00	9 Test, 98 10A	10 Test, 98 10B	11 Test, 98 35A	12 Test, 98 35B	13 Test, 98 75A	14 Test, 98 75B
1 Duration (days)	8	16	16	36	36	75	75
2 Sat. pH	6.48	7.83	7.78	6.5	6.73	6.65	6.87
3 Fil. Sol. (mg)	8.19	9.14	9.21	8.36	8.92	7.43	7.24
4 Sat. Eh (mV)	135	114	102	167	171	102	98
5 Fil. Sol. Eh (mV)	219	67	52	170	154	199	216
6 Alkalinity (meq/L CaCO ₃)	ND	443	481	452	462	439	354
7 H ₂ Laser (ppm)	236	240	216	ND	ND	320	203
8 U ₂ ICP (ppm)	212	174	152	170	174	189	140
9 Al AA (ppm)	0.262	0.036	0.109	<0.02	0.039	0.026	0.088
10 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
11 B (ppm)	1.5	1.2	1.1	1.1	1.3	1.4	0.9
12 Ba (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Ca (mg)	682	579	519	573	614	678	557
14 Fe AA (ppm)	<0.05	0.032	0.086	<0.05	<0.05	<0.05	0.064
15 K (ppm)	60	60	60	50	50	60	50
16 Mg (ppm)	177	145	128	142	158	181	139
17 Mn (ppm)	1480	1220	1090	1090	1230	1290	921
18 Si (ppm)	12	10	10	7	8	7	6
19 Sr (ppm)	14.7	12	10.6	11.9	13	14.6	11.1
20 Na (ppm)	1	0.9	0.8	0.8	0.9	1.3	1
21 Mo AA (ppm)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23 Cl (ppm)	973	798	692	699	847	946	50
24 SO ₄ (ppm)	2850	2340	2113	2405	2675	2814	2450

Al, As, Fe, Mo, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).
ND = Not determined.

TABLE A.4. (Contd)

Parameter	15 TEX, 5% IOIA	16 TEX, 5% IOIA
1 Duration (days)	103	103
2 Sat. pH	6.04	7.05
3 Fil. Sol. (mM)	8.39	8.15
4 Sat. Eh (mV)	133	98
5 Fil. Sol. Eh (mV)	66	220
6 Alkalinity (mg/L CaCO ₃)	434	375
7 U. Laser (ppm)	83	140
8 U. ICP (ppm)	141	115
9 Al AA (ppm)	0.075	<0.02
10 As AA (ppm)	<0.015	<0.015
11 B (ppm)	1	0.7
12 Br (ppm)	<0.1	<0.1
13 Ca (ppm)	823	520
14 Fe AA (ppm)	0.112	0.023
15 K (ppm)	50	40
16 Mg (ppm)	136	123
17 Na (ppm)	1100	830
18 Si (ppm)	7	6
19 Sr (ppm)	12.1	9.8
20 Zn (ppm)	1.1	0.8
21 Mn AA (ppm)	<0.01	<0.01
22 Se AA (ppm)	<0.02	<0.02
23 Cl (ppm)	531	349
24 SO ₄ (ppm)	2639	2169

Al, As, Fe, Mn, and Se analyzed by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

TABLE A.5. Solution Analyses of the Batch Experiment with Texas Ore Amended with FeS-Coated Sand

Parameter	1 Texas Red, Supernatant	2 SYN, LIX, 943	3 TEX, FES 2A	4 TEX, FES 2B	5 TEX, FES 4A	6 TEX, FES 4B	7 TEX, FES 8A
1 Duration (days)	NA	NA	2	2	4	4	8
2 Sol. pH	8.1	NA	7.27	7.29	7.18	7.16	6.83
3 Fil. Sol. (mM)	8.4	7.60	7.48	7.59	7.45	7.85	7.9
4 Sol. Eh (mv)	261	NA	146	172	182	180	176
5 Fil. Sol. Eh (mv)	227	381	238	193	156	178	250
6 Alkalinity (me/L CaCO ₃)	393	356	518	518	518	556	613
7 U. Laser (ppm)	144	44.29	386.66	359.04	334.28	176.78	500
8 U. ICP (ppm)	136	39.2	281	269	285	268	301
9 Al AA (ppm)	0.035	0.038	0.324	0.162	0.28	0.051	0.064
10 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
11 B (ppm)	1.1	1.4	1.2	1.1	1.1	1.1	1.2
12 Ba (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Ca (ppm)	458	311	465	452	473	457	479
14 Fe AA (ppm)	<0.05	<0.05	<0.05	<0.055	<0.05	<0.05	<0.05
15 K (ppm)	50	50	40	40	40	40	50
16 Mg (ppm)	125	114	110	107	109	105	113
17 Mo (ppm)	1290	1340	1240	1230	1210	1190	1350
18 Si (ppm)	10	13	11	10	10	10	11
19 Sr (ppm)	10.1	8.5	10	9.6	10	9.4	10.3
20 Zn (ppm)	0.2	<0.01	0.3	0.3	0.4	0.4	0.5
21 Mn AA (ppm)	<0.075	<0.013	<0.075	<0.075	<0.075	<0.075	<0.075
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23 Cl (ppm)	968	1090	961	938	945	882	949
24 SO ₄ (ppm)	2159	1632	2023	1989	2023	1920	2113

Al, As, Fe, Mo, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (barium only).

NA = not applicable.

A.11

TABLE A.5. (Contd)

Parameter	8 TEX. FES MB	9 TEX. FES MA	10 TEX. FES MB	11 TEX. FES MA	12 TEX. FES MB	13 TEX. FES MA
1 Duration (days)	8	16	16	36	36	75
2 Sat. pH	6.85	7.78	7.69	6.77	6.67	6.9
3 FFI, Sol. (ppt)	8.08	9.19	9.15	8.42	8.54	7.25
4 Sat. En (mv)	206	154	156	182	171	175
5 FFI, Sol. En (mv)	239	225	199	78	148	223
6 Alkalinity (mg/L CaCO ₃)	622	679	811	764	688	713
7 V. Loss (ppm)	500	346.7	433.3	49	ND	460
8 V. ICP (ppm)	298	351	299	385	378	300
9 Al AA (ppm)	0.062	0.023	0.037	0.025	<0.02	0.065
10 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
11 B (ppm)	1.11	1.3	1.1	1.2	1.2	0.9
12 Br (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Ca (ppm)	473	606	487	557	538	403
14 Co AA (ppm)	<0.03	0.414	0.19	<0.05	<0.05	0.694
15 K (ppm)	30	60	60	40	30	30
16 Mg (ppm)	110	136	111	123	121	83.4
17 Mn (ppm)	1280	1530	1300	1390	1440	902
18 Si (ppm)	10	12	10	-	7	6
19 Sr (ppm)	10.1	12.1	10.2	11.8	11.3	1.2
20 Na (ppm)	0.5	0.6	0.5	0.6	0.5	0.6
21 Mo AA (ppm)	<0.075	<0.015	<0.015	<0.075	<0.075	<0.01
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23 Cl (ppm)	923	1070	839	1002	949	563
24 SO ₄ (ppm)	2075	2340	1899	2209	2195	1670

Al, Fe, Mn, and Se analysed by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

ND = Not determined.

TABLE A.5. (Contd)

Parameter	14 TEX, FES 750	15 TEX, FES 101A	16 TEX, FES 101B
1 Duration (days)	75	105	105
2 Sat. pH	6.81	7.06	7.03
3 Fil. Sol. (ml)	7.33	8.09	8.01
4 Sat. Eh (mV)	153	144	240
5 Fil. Sol. Eh (mV)	219	132	198
6 Alkalinity (mg/L CaCO ₃)	932	793	793
7 U, Laser (ppm)	550	1000	1360
8 U, ICP (ppm)	394	383	409
9 Al AA (ppm)	<0.02	0.035	0.025
10 As AA (ppm)	<0.015	<0.015	<0.015
11 B (ppm)	1.2	0.8	1
12 Cu (ppm)	<0.1	<0.1	<0.1
13 Ca (ppm)	363	491	628
14 Fe AA (ppm)	<0.05	<0.02	<0.02
15 K (ppm)	50	50	50
16 Mg (ppm)	123	95	131
17 Mo (ppm)	130	96	1340
18 Si (ppm)	7	7	7
19 Sr (ppm)	11.9	9.5	12.5
20 Zn (ppm)	0.7	0.6	0.8
21 Mn AA (ppm)	<0.06	<0.05	<0.05
22 Se AA (ppm)	<0.02	<0.02	<0.02
23 Cl (ppm)	909	426	757
24 SO ₄ (ppm)	2234	1939	2352

Al, As, Fe, Mo, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

TABLE A.6. Solution Analysis of the Batch Experiment with Texas Leached Ore (all concentration units are ppm)

Parameter	Sample Number							
	LIX 666	L02A	L02B	L04A	L04B	L06A	L06B	L016A
1 Duration (days)	0	2	2	4	4	8	8	16
2 pH	8.05	7.48	7.52	7.49	7.5	7.31	7.46	7.43
3 Eh (mV)	340	368	360	374	375	330	302	278
4 pE	5.75	6.22	6.09	6.32	6.34	5.58	5.11	4.7
5 Alkalinity (mg/L CaCO ₃)	144	115	106	101	107	N.D.	N.D.	N.D.
6 Ca	200	560	745	550	550	520	530	480
8 Mg	81.9	138	160	135	136	126	127	126
9 Na	1165	1250	1300	1200	1250	1160	1160	1240
10 K	32	32	34	29	30	30	30	36
11 Cl	1030	1000	970	830	890	830	890	860
12 SO ₄	1320	2500	2300	2240	2400	2240	2570	2340
14 Fe ICP	<0.03	0.22	0.23	0.43	0.27	9.77	11.57	22
15 Fe AA	0.022	0.053	0.063	0.234	0.564	19.7	14.9	25.4
17 Al ICP	<0.03	0.8	0.9	0.8	0.9	0.5	0.5	0.33
18 Al AA	0.023	0.018	0.02	0.012	0.011	0.025	0.012	0.045
20 Li	0.019	0.23	0.25	0.19	0.2	0.22	0.19	<0.05
22 Cd	<0.01	0.015	0.024	0.018	0.024	0.018	0.024	<0.01
23 Sr	5.3	3.4	11	9.2	9.3	8.9	9	8.9
24 Ba	<0.002	0.004	0.004	<0.002	0.001	<0.001	0.001	0.02
25 Mn	<0.002	1	1.9	1.2	1.1	1.5	1.5	1.6
26 Co	0.03	0.06	0.07	0.06	0.07	0.04	0.06	<0.01
27 Cu	0.1	0.08	0.09	0.09	0.08	0.04	0.05	0.1
28 Zn	<0.02	0.075	0.12	0.081	<0.02	<0.02	<0.02	0.1
29 Pb	<0.05	0.23	0.42	<0.05	0.32	0.22	0.32	0.33
30 Si	6.5	5.1	6.1	4.8	4.8	5	4.9	5.2
31 B	1.35	1.28	1.38	1.18	1.18	1.18	1.18	1.18
32 As	<0.07	0.24	0.34	0.24	0.34	0.24	0.24	0.19
33 U	32.8	15.5	21.5	22.5	23.5	22	23.8	2
34 Se AA	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
35 Mo	<0.01	0.04	0.05	0.05	0.05	0.04	0.05	0.03

ND = Not determined

TABLE A.6. (Contd)

Parameter	Sample Number						
	L016B	L036A	L036B	L075A	L075B	L0101A	L0101B
1 Duration (days)	16	36	36	75	75	101	101
2 pH	7.4	7.6	7.6	8.21	7.85	6.26	7.88
3 Eh (mV)	300	140	201	14	98	123	215
4 pE	5.07	2.37	3.4	0.24	1.66	2.08	3.63
5 Alkalinity (mg/L Ca CO ₃)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
6 Ca	520	516	843	440	660	290	470
8 Mg	126	118	164	110	142	79	107
9 Na	1240	1094	1247	1162	1250	1000	1060
10 K	31	26	36	44	36	30	33
11 Cl	880	880	970	950	980	910	940
12 SO ₄	2400	3100	2400	2030	2380	1750	1825
14 Fe ICP	26	35	27.2	1.8	6.4	0.32	2.2
15 Fe AA	27.8	28.7	24.8	2.87	6.23	0.35	2.8
17 Al ICP	0.3	0.12	0.32	0.03	<0.03	<0.03	<0.03
18 Al AA	0.027	0.018	0.019	0.057	0.047	0.019	0.025
20 Li	<0.05	0.18	0.2	<0.05	<0.05	0.16	0.16
22 Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
23 Sr	9	8.8	12.1	7.8	10.4	5.8	7.8
24 Ba	0.02	0.022	0.019	0.03	<0.001	<0.001	<0.001
25 Mn	1.6	<0.002	1.73	<0.002	<0.002	<0.002	<0.002
26 Co	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
27 Cu	0.05	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
28 Zn	0.08	0.078	0.114	0.012	<0.02	<0.02	<0.02
29 Pb	0.32	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
30 Si	5.2	5.21	6.3	8.4	7.4	8.2	9
31 B	1.18	0.46	0.66	1.4	1.2	1.2	1.2
32 As	0.1	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
33 U	3	0.25	13.8	0.13	0.4	0.19	0.76
34 Se AA	<0.15	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
35 Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

APPENDIX B

ANALYTICAL DATA FROM BATCH EXPERIMENTS WITH WYOMING SEDIMENTS

P.i

APPENDIX B

ANALYTICAL DATA FROM BATCH EXPERIMENTS WITH WYOMING SEDIMENTS

The five tables in this appendix contain solution chemical data obtained from the batch experiments in which lixiviant was mixed with various types of Wyoming sediment that had been collected at an in situ uranium mine. Each table represents a time series of data obtained from an experiment with a single sediment type. The tables are ordered as follows:

Table B.1 - Wyoming Reduced Sediment

Table B.2 - Wyoming Reduced Sediment Amended with 1% Pyrite

Table B.3 - Wyoming Reduced Sediment Amended with 5% Pyrite

Table B.4 - Wyoming Reduced Sediment Amended with FeS-Coated Sand

Table B.5 - Wyoming Oxidized Sediment

The results of these experiments are discussed on pages 46 to 52 of this report.

TABLE B.1. Solution Analyses of the Batch Experiment with Wyoming Reduced Sediment

Parameter	Supernatant	2 SYN. LIX.	3 WYRED 2A	4 WYRED 2B	5 WYRED 4A	6 WYRED 4B	7 WYRED 8A	8 WYRED 8B
1 Duration (days)	NA	NA	2	2	4	4	8	8
2 Sat. pH	7.72	NA	7.07	7.03	7.06	7.12	7.02	7.15
3 Fil. Sol. (pH)		7.79	8.57	8.72	7.5	7.42	8.04	8.21
4 Sat. Eh (mV)	310	NA	264	40	56	6	65	78
5 Fil. Sol. Eh (mV)	332	397	320	292	145	124	-122	-119
6 Alkalinity (meq/L CaCO_3)	179	443	253	300	290	281	349	339
7 U, Laser (ppm)	10.3	29.6	12.72	14.54	14.7	12.7	10.91	10
8 U, ICP (ppm)	10.5	26.8	13.5	15.4	13.8	ND	5.1	7.3
9 Al AA (ppm)	0.055	0.038	0.3	0.078	0.285	0.061	0.024	0.038
10 As AA (ppm)	0.055	0.04	0.016	0.018	0.045	0.048	0.059	0.06
11 B (ppm)	0.2	<0.1	0.1	0.1	0.1	ND	0.1	0.01
12 Ba (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	ND	<0.1	<0.1
13 Ca (ppm)	247	98	190	196	213	ND	197	197
14 Fe AA (ppm)	0.05	0.05	0.05	0.05	1.47	1.430	7.3	7.08
15 K (ppm)	30	<2.0	20	20	30	ND	30	30
16 Mg (ppm)	61.3	46.2	46.8	49.6	52	ND	51.6	49.7
17 Mo (ppm)	284	446	254	292	277	ND	332	357
18 Si (ppm)	5	5	4	5	5	ND	7	7
19 Sr (ppm)	2.5	0.3	1.8	1.9	2	ND	1.8	1.7
20 Mn (ppm)						ND	0.2	0.2
21 Mo AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	ND	<0.015	<0.015
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	ND	<0.02	<0.02
23 Cl (ppm)	118	139	95	110	105	104	112	114
24 SO_4 (ppm)	850	439	648	693	723	710	685	666

Al, As, Fe, Mo, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser (fluorimetry (uranium only)).

ND = Not determined.

NA = Not applicable.

TABLE B.1. (Contd)

Parameter	9 HYRED 16A	10 HYRED 16B	11 HYRED 36A	12 HYRED 36B	13 HYRED 75A	14 HYRED 75B	15 HYRED 101A
1 Duration (days)	16	16	36	36	75	75	101
2 Sat. pH	ND	ND	7.23	7.23	6.9	6.8	6.41
3 Fil. Sol. (pH)	ND	8.37	8.4	8.36	8.21	8.4	8.01
4 Sat. Eh (mV)	ND	ND	-163	-149	79	118	140
5 Fil. Sol. Eh (mV)	-147	-54	185	133	172	204	209
6 Alkalinity (mg/L CaCO ₃)	415	198	415	292	321	279	77
7 U, Laser (ppm)	0.18	3.74	3.07	2.98	3.81	3.08	0.33
8 U, ICP (ppm)	0.05	0.7	3.9	3.6	0.2	3.7	0.5
9 Al AA (ppm)	0.023	0.041	<0.02	<0.02	0.023	0.026	<0.02
10 As AA (ppm)	<0.015	0.034	0.021	0.015	<0.015	<0.015	<0.015
11 B (ppm)	0.1	0.1	0.1	<0.1	<0.1	<0.1	0.1
12 Ba (ppm)	ND	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Ca (ppm)	151	166	145	142	165	169	174
14 Fe AA (ppm)	0.05	0.05	0.05	0.05	0.05	0.05	
15 K (ppm)	20	20	30	20	20	30	20
16 Mg (ppm)	48.3	51.4	47.9	44.6	46.1	48.7	48.5
17 Mo (ppm)	275	311	319	292	275	260	262
18 Si (ppm)	7	8	7	7	6	6	6
20 Mn (ppm)							
21 Pb AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23 Cl (ppm)	1303	129	118	108	117	109	95.6
24 SO ₄ (ppm)	583	590	485	424	632	679	897

Al, As, Fe, Mn, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

ND = Not determined.

TABLE B.1. (Contd)

Parameter	16 WYRED 1918
1 Duration (days)	101
2 Sat. pH	6.41
3 Fil. Sol. (pH)	7.78
4 Sat. Eh (mV)	97
5 Fil. Sol. Eh (mV)	180
6 Alkalinity (mg/L CaCO ₃)	134
7 U, Laser (ppm)	0.47
8 U, ICP (ppm)	0.6
9 Al AA (ppm)	0.044
10 As AA (ppm)	<0.015
11 B (ppm)	0.1
12 Ba (ppm)	<0.1
13 Ca (ppm)	108
14 Fe AA (ppm)	
15 K (ppm)	<0.1
16 Hg (ppm)	51.4
17 Mo (ppm)	276
18 Si (ppm)	6
19 Sr (ppm)	2.1
20 Mn (ppm)	
21 Mo AA (ppm)	<0.015
22 Se AA (ppm)	<0.02
23 Cl (ppm)	110
24 SO ₄ (ppm)	932

Al, As, Fe, Mo, and Se analyzed by atomic absorption spectroscopy, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

TABLE B.2. Solution Analyses of the Batch Experiment with Wyoming Reduced Sediment Amended with 1% Pyrite

Parameter	1 WVO, RED, SUPER	2 SVH, LIX	3 WVO, 1% 2A	4 WVO, 1% 2B	5 WVO, 1% 4A	6 WVO, 1% 4B	7 WVO, 1% 8A
1 Duration (days)	NA	NA	2,000	2,000	4,000	4,000	8,00
2 Sol. pH	7.70	NA	6.00	7.10	7.12	6.97	6.62
3 Fil. Sol. (ml)		7.70	8.30	8.30	8.10	8.02	8.03
4 Sol. Eh (mV)	310,000	NA	169,000	118,000	166,000	179,000	191,00
5 Fil. Sol. Eh (mV)	317,000	397,000	178,000	192,000	193,000	110,000	235,00
6 Alkalinity (meq/L CaCO ₃)	179	443	189	217	2	160	226
7 B. Laser (ppm)	10,300	29,400	3,420	2,360	2,420	2,260	2.73
8 U. LP (ppm)	10,300	29,400	3,700	2,900	2,900	3,000	2.70
9 Al AA (ppm)	0.038	0.038	0.428	0.270	0.358	0.605	0.04
10 As AA (ppm)	0.023	0.040	<0.015	<0.015	<0.015	<0.015	<0.015
11 B (ppm)	0.300	<0.1	0.700	0.700	1.300	0.300	0.20
12 Ba (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Co (ppm)	247,000	96,000	269,000	304,000	319,000	287,000	341,00
14 Fe AA (ppm)	0.030	0.030	0.084	0.036	0.155	0.079	0.03
15 K (ppm)	30,000	<2.0	30,000	30,000	40,000	30,000	30,00
16 Mg (ppm)	61,300	46,200	63,000	68,200	79,300	64,600	77,00
17 Mo (ppm)	284,000	466,000	211,000	200,000	246,000	203,000	244,00
18 Si (ppm)	5,000	5,000	7,000	6,000	8,000	7,000	6,00
19 Sr (ppm)	2,300	0.300	2,900	3,100	3,400	2,900	3.40
20 Zn (ppm)				0.100		0.100	0.10
21 Mn AA (ppm)	<0.013	<0.013	<0.013	<0.013	<0.013	<0.013	<0.013
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23 Cl (ppm)	110,000	139,000	113,000	107,000	123,000	107,000	120,00
24 SO ₄ (ppm)	630,000	439,000	882,000	882,000	1020,000	912,000	988,00

Al, As, Fe, Mo, and Se analyzed by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorescence (concentrations only).

NA = Not applicable.

TABLE B.2. (Contd)

Parameter	9 WYO, 15 60	9 WYO, 15 16A	10 WYO, 15 16B	11 WYO, 15 36A	12 WYO, 15 36B	13 WYO, 15 73A
1 Duration (days)	5	15	15,000	35,000	36,000	75,000
2 Sat. pH	6.3	6.9	6.930	6.250	6.010	5.700
3 Fil. Sol. (mg)	0.180	0.59	0.540	7.540	7.600	6.630
4 Sat. Eh (mv)	140	140	128,000	120,000	166,000	151,000
5 Fil. Sol. Eh (mv)	224	35	35,000	42,000	-2,000	297,000
6 Alkalinity (mg/L CaCO ₃)	207	113	104	57	38	16
7 U ₂ Later (ppm)	2.74	0.21	0.190	ND	ND	0.170
8 U ₂ ICP (ppm)	1.6	0.5	0.500	2,300	<0.5	<0.5
9 Al AA (ppm)	0.458	0.054	0.052	<0.02	<0.02	0.285
10 Al AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
11 U (ppm)	0.2	0.3	0.400	0.100	0.400	0.600
12 U ₂ (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Cu (ppm)	324	379,000	0.000	314,000	350,000	470,000
14 Fe AA (ppm)	0.05	3.438	0.205	0.019	2,348	3,295
15 K (ppm)	30	60,000	40,000	30,000	60,000	40,000
16 Mg (ppm)	73.8	87,300	88,200	74,300	91,800	166,000
17 Na (ppm)	120	230,000	241,000	244,000	304,000	262,000
18 Si (ppm)	7	9,000	10,000	9,000	11,000	20,000
19 Sr (ppm)	3.2	3,700	3,700	3,100	3,700	4,700
20 Ba (ppm)	0.2	0.000	0.400	0.400	0.400	0.700
21 Mn AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23 Cl (ppm)	111	146,000	124,000	92,300	132,000	105,000
24 SO ₄ (ppm)	940	1342,000	1354,000	1209,000	1460,000	1780,000

Al, As, Fe, Mn, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

ND = Not determined.

TABLE B.2. (Contd)

Parameter	14 WVO, 18 750	15 WVO, 18 101A	16 WVO, 18 101B
1 Duration (days)	75	101	101
2 Set. pH	5.71	5.18	5.15
3 Fil. Sol. (pH)	7.77	5.07	5.08
4 Set. En (mV)	162	211	212
5 Fil. Sol. En (mV)	271	352	380
6 Alkalinity (meq/L CaCO ₃)	48	11	11
7 U. Layer (ppm)	0.36	0.23	0.19
8 U. IP ₂ (ppm)	<0.2	<0.2	<0.5
9 Al AA (ppm)	<0.02	1.44	1.981
10 Ag AA (ppm)	<0.015	<0.015	<0.015
11 B (ppm)	0.4	0.6	0.6
12 Ba (ppm)	<0.1	<0.1	<0.1
13 Ca (ppm)	369	524	538
14 Fe AA (ppm)	0.171	5.53	5.39
15 K (ppm)	30	30	40
16 Mg (ppm)	90.1	115	119
17 Na (ppm)	226	242	262
18 Si (ppm)	12	36	37
19 Sr (ppm)	5.9	5	5.1
20 Zn (ppm)	0.5	0.9	0.9
21 As AA (ppm)	<0.015	<0.015	<0.015
22 Se AA (ppm)	<0.02	<0.02	<0.02
23 Cl (ppm)	83	129	140
24 SO ₄ (ppm)	1485	1836	1885

Al, As, Fe, Mo, and Se analyzed by atomic absorption spectroscopy, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

TABLE B.3. Solution Analyses of the Batch Experiment with Wyoming Reduced Sediment Amended with 5% Pyrite

Parameter	1 Wyoming Reduced Sediment									
	Substrate									
	2 5W, LIX.	3 WVO, 2d 2A	4 WVO, 3d 2B	5 WVO, 5d 4A	6 WVO, 5d 4B	7 WVO, 7d 8A				
1 Duration (days)	NA	2	2	2	4	4				
2 Sat. pH	7.12	5.74	5.98	5.98	6.01	5.87				
3 Fil. Sol. (pH)	7.19	7.42	7.2	7.2	7.36	5.5				
4 Sat. Eh (mV)	310	171	204	204	170	171				
5 Fil. Sol. Eh (mV)	312	2	4	4	161	124				
6 Alkalinity (mg/L CaCO ₃)	179	443	57	57	66	94				
7 H ₂ Loss (ppm)	10.5	29.6	0.03	0.13	0.1	0.11				
8 U ₁ ICP (ppm)	10.5	29.6	0.3	0.3	0.3	0.3				
9 Al AA (ppm)	0.028	0.038	5.53	0.23	<0.02	1.08				
10 Al AA (ppm)	0.029	0.04	<0.015	<0.015	<0.015	<0.015				
11 B (ppm)	0.2	<0.1	0.4	0.3	0.6	1				
12 Cu (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1				
13 U ₂ AA (ppm)	247	98	476	529	636	611				
14 Fe AA (ppm)	0.05	0.03	19.22	13.53	55.66	52.12				
15 K (ppm)	30	<2.0	40	50	60	60				
16 Mg (ppm)	61.3	46.2	112	122	153	146				
17 Mn (ppm)	784	446	227	277	318	316				
18 Si (ppm)	5	5	9	10	13	14				
19 Sr (ppm)	2.3	0.3	4.6	5	5.6	5.8				
20 Na (ppm)			0.8	0.8	1.5	1.3				
21 Na AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015				
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02				
23 Cl (ppm)	118	139	52	112	121	122				
24 SO ₄ (ppm)	850	439	1610	1776	2132	2101				

Al, As, Fe, Mn, and Se analyses by static observation spectroscopy, remainder of dissolved cations by ICP or laser fluorescence (uranium only).
NA = Not applicable.

TABLE B.3. (Contd)

Parameter	WVO, 95 BA	9 WVO, 95 BA	10 WVO, 95 BA	11 WVO, 95 BA	12 WVO, 95 BA	13 WVO, 95 BA	14 WVO, 95 BA
1 Duration (days)	8	16	16	36	36	36	73
2 Sat. pH	7.24	6.17	6.32	5.81	5.66	5.51	5.51
3 Fil. Sol. (gH)	5.13	7.37	6.63	7.32	7.17	6.2	6.2
4 Sat. Eh (mV)	159	63	123	100	111	193	193
5 Fil. Sol. Eh (mV)	215	120	179	82	80	164	164
6 Alkalinity (meq/L CaCO ₃)	127	73	73	92	ND	21	21
7 U, Lower (ppm)	0.13	0.1	0.46	ND	ND	0.15	0.15
8 U, IOP (ppm)	0.5	0.5	0.3	0.5	0.5	0.5	0.5
9 Al AA (ppm)	0.179	0.016	0.109	0.027	<0.02	0.328	0.328
10 As AA (ppm)	0.024	<0.013	<0.015	<0.015	<0.015	<0.015	<0.015
11 Zn (ppm)	0.6	0.5	0.5	0.5	0.5	1	1
12 Cu (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Co (ppm)	633	594	623	522	513	694	694
14 Fe AA (ppm)	83.9	70.54	72.23	40	46.43	20.5	20.5
15 K (ppm)	50	60	50	50	40	50	50
16 Mg (ppm)	134	140	148	127	124	179	179
17 Mn (ppm)	268	257	268	236	222	514	514
18 Si (ppm)	17	15	16	16	16	31	31
19 Sr (ppm)	6	3.6	3.7	5	4.9	7.7	7.7
20 Ba (ppm)	1.7	1.6	1.7	1.5	1.4	1.8	1.8
21 Pb AA (ppm)	<0.013	<0.013	<0.013	<0.013	<0.013	<0.013	<0.013
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23 Cl (ppm)	120	123	92	63.5	100	344	344
24 SO ₄ (ppm)	2215	2120	1734	1957	1975	2417	2417

Al, As, Fe, Mn, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorescence (uranium only).
ND = not determined.

TABLE B.3. (Contd)

Parameter	14 MW, 28 TPa	15 MW, 28 TPa	16 MW, 28 TPa	17 MW, 28 TPa
1 Duration (days)	73	101	101	101
2 Sat. pH	3.27	4.32	4.32	4.37
3 Fil. Sol. (µM)	3.96	4.39	4.39	4.35
4 Sat. Eh (mV)	177	220	220	205
5 Fil. Sol. Eh (mV)	301	338	338	375
6 Alkalinity (mg/L CaCO ₃)	16	10.7	10.7	10.7
7 U, Laser (ppm)	0.26	0.29	0.29	0.79
8 U, ICP (ppm)	0.5	0.5	0.5	0.5
9 Al AA (ppm)	1.09	6.32	6.32	3.8
10 As AA (ppm)	<0.015	<0.015	<0.015	<0.015
11 B (ppm)	0.9	0.9	0.9	0.8
12 Ba (ppm)	<0.1	<0.1	<0.1	<0.1
13 Ca (ppm)	644	671	671	613
14 Fe AA (ppm)	15.12	16.01	16.01	13.8
15 K (ppm)	70	50	50	40
16 Mg (ppm)	167	170	170	155
17 Mn (ppm)	514	530	530	488
18 Si (ppm)	34	34	34	31
19 Sr (ppm)	7	7.2	7.2	6.6
20 Na (ppm)	1.9	2.3	2.3	2.3
21 Na AA (ppm)	<0.015	<0.015	<0.015	<0.015
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02
23 Cl (ppm)	419	415	415	375
24 SO ₄ (ppm)	2379	2367	2367	2204

Al, As, Fe, K, Mg, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

TABLE B.4. Solution Analyses of Batch Experiment with Wyoming Reduced Sediment Amended with FeS-Coated Sand

Parameter	1 WVO, 0.0% SUCRA	2 5%W, 1.1% SUCRA	3 10%W, 2.2% SUCRA	4 10%W, 2.2% SUCRA	5 10%W, 2.2% SUCRA	6 10%W, 2.2% SUCRA	7 10%W, 2.2% SUCRA
1 Poration (days)	NA	NA	NA	2	2	4	4
2 Sol. pH	7.72	7.79	7.79	7.79	7.33	7.3	7.1
3 Fil. Sol. (mM)	NA	7.79	7.79	0.3	0.29	0.03	7.97
4 Sol. Fe (mM)	310	NA	154	154	156	67	93
5 Fil. Sol. Fe (mM)	312	397	214	214	208	97	92
6 Alkalinity (meq/L CaCO ₃)	179	443	264	264	243	226	226
7 H ₂ Loss (mmol)	10.3	29.6	6.25	6.25	7.91	4.66	6
8 H ₂ Loss (mmol)	10.3	29.6	6.25	6.25	7.91	4.66	6
9 H ₂ Loss (mmol)	0.055	0.038	0.194	0.194	0.36	0.333	0.399
10 H ₂ Loss (mmol)	0.055	0.04	<0.015	<0.015	<0.015	<0.015	<0.015
11 H ₂ Loss (mmol)	0.2	<0.1	0.1	0.1	0.1	0.1	0.2
12 H ₂ Loss (mmol)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 H ₂ Loss (mmol)	217	98	215	215	189	199	227
14 H ₂ Loss (mmol)	0.09	0.09	<0.02	<0.02	<0.02	<0.02	<0.02
15 H ₂ Loss (mmol)	30	42.0	30	30	30	20	30
16 H ₂ Loss (mmol)	61.3	46.2	52.3	52.3	50.3	45.3	50.3
17 H ₂ Loss (mmol)	284	465	247	247	217	172	216
18 H ₂ Loss (mmol)	3	3	3	3	4	4	3
19 H ₂ Loss (mmol)	2.5	0.3	2.2	2.2	2.1	2	2.3
20 H ₂ Loss (mmol)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
21 H ₂ Loss (mmol)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
22 H ₂ Loss (mmol)	116	139	114	114	110	79	108
23 H ₂ Loss (mmol)	850	459	649	649	617	523	559
24 H ₂ Loss (mmol)							

Al, As, Fe, Mn, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry
 (continued on p. 11)
 NA = Not applicable.

TABLE B.4. (Contd)

Parameter	8 WVO, FeS 80	9 WVO, FeS 15A	10 WVO, FeS 16B	11 WVO, FeS 16A	12 WVO, FeS 16B	13 WVO, FeS 15A
1 Duration (days)	0	16	16	36	36	75
2 Sol. pH	6.8	7.46	7.5	6.66	6.87	6.42
3 Fil. Sol. (ml)	0.02	9.49	9.47	8.37	8.34	8.58
4 Sol. Th (ml)	108	65	65	76	90	93
5 Fil. Sol. Th (ml)	221	-87	-86	190	143	186
6 Alkalinity log ₁₀ CaCO ₃	273	150	160	226	226	139
7 Fe, Lesser (ppm)	1.87	0.5	0.42	140	ND	0.43
8 Fe, ICP (ppm)	2.3	0.2	0.7	1.2	6	0.7
9 Al AA (ppm)	0.005	0.000	0.001	<0.02	0.04	<0.02
10 Fe AA (ppm)	<0.015	<0.023	<0.023	<0.015	<0.015	<0.015
11 Fe (ppm)	0.2	0.1	0.1	0.1	0.2	0.2
12 Fe (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Fe (ppm)	216	240	236	201	213	144
14 Fe AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
15 Fe (ppm)	20	50	36	20	30	20
16 Fe (ppm)	49	53.4	52.4	52.3	58.2	33.2
17 Fe (ppm)	160	175	181	187	215	111
18 Si (ppm)	3	6	5	5	6	4
19 Si (ppm)	2.2	2.4	2.2	2.3	2.5	1.5
20 Si (ppm)	0.1	0.1				
21 Mn AA (ppm)	<0.013	<0.013	<0.013	<0.013	<0.015	<0.015
22 Mn AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23 Si (ppm)	93	173	127	100	115	91
24 Si ₂ (ppm)	376	631	595	649	676	432

Al, Fe, Mn, and Si analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorescence (uranium only).
ND = Not determined.

TABLE 3.1. (Contd)

Parameter	14 MW, FeS 120	15 MW, FeS 101	16 MW, FeS 101B
1 Duration (days)	75	101	101
2 Sat. RM	6.34	6.88	6.97
3 Fil. Sol. (m)	8.78	8.19	8.15
4 Sat. Eh (mV)	103	106	129
5 Fil. Sol. Eh (mV)	106	228	195
6 Alkalinity (meq/L CaCO ₃)	246	177	155
7 U. Lower (ppm)	0.37	0.94	0.96
8 U. 10% (ppm)	2.3	1.2	1.8
9 Al AA (ppm)	0.077	0.05	0.13
10 As AA (ppm)	<0.015	<0.015	<0.015
11 B (ppm)	0.2	0.1	0.1
12 Cu (ppm)	<0.1	<0.1	<0.1
13 Ca (ppm)	218	218	193
14 Fe AA (ppm)	<0.02	<0.02	<0.02
15 K (ppm)	20	20	20
16 Mg (ppm)	31	53.2	48.6
17 Mn (ppm)	189	186	174
18 Si (ppm)	4	4	4
19 Sr (ppm)	2.4	2.4	2.2
20 Zn (ppm)			
21 Pb AA (ppm)	<0.015	<0.015	<0.015
22 Se AA (ppm)	<0.02	<0.02	<0.02
23 Cl (ppm)	78	83	62
24 SO ₄ (ppm)	654	782	714

Al, As, Fe, Pb, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

TABLE B.5. Solution Analyses of the Batch Experiment with Wyoming Oxidized Sediment

Parameter	1 Wyoming Oxidized Supernatant	2 SYN. LIX.	3 WYOM 2A	4 WYOM 2B	5 WYOM 4A	6 WYOM 4B	7 WYOM 8A	8 WYOM 8B
1 Duration (days)	NA	NA	2	2	4	4	8	8
2 Sat. pH	8.09	NA	7.62	7.66	7.62	7.65	7.16	7.2
3 Fil. Sol. (ppt)	0.30	7.79	6.52	8.54	8.44	8.43	8.38	8.28
4 Sat. Eh (mV)	286	NA	338	396	295	297	136	96
5 Fil. Sol. Eh (mV)	253	397	333	259	275	282	-143	-116
6 Alkalinity (mg/L CaCO ₃)	253	463	309	262	290	328	346	339
7 H ₂ Laser (ppm)	20.1	20.6	15.27	11.5	10.91	9.54	0.32	0.3
8 U ₂ ICP (ppm)	20.1	26.0	15.2	11.8	12.5	11	0.05	1.2
9 Al AA (ppm)	0.027	0.030	0.308	0.416	0.114	0.088	<0.02	<0.02
10 As AA (ppm)	0.027	0.04	0.024	0.022	0.069	0.069	0.27	0.26
11 B (ppm)	<0.1	<0.1	0.1	0.2	0.1	0.1	0.1	0.1
12 Br (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Ca (ppm)	112	98	138	141	149	136	160	158
14 Fe AA (ppm)	0.03	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
15 K (ppm)	20	<2.0	30	30	30	30	20	20
16 Mg (ppm)	39.3	46.2	40.1	37.9	40.2	35.5	40.7	40
17 Mn (ppm)	279	446	282	236	268	243	216	218
18 Si (ppm)	5	5	9	6	6	5	7	7
19 Sr (ppm)	1.5	0.3	2.3	1.5	1.6	1.4	1.6	1.6
20 Na (ppm)	0.3	0.3						
21 Mo AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23 Cl (ppm)	130	139	118	111	110	101	110	110
24 SO ₄ (ppm)	425	439	509	459	463	397	468	439

Al, As, Fe, Mn, and Se analyses by atomic absorption spectroscopy, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

NA = Not applicable.

TABLE B.5. (Contd)

Parameter	9 WY0X 36A	10 WY0X 36B	11 WY0X 36A	12 WY0X 36B	13 WY0X 75A	14 WY0X 75B	15 WY0X 101A	16 WY0X 101B
1 Duration (days)	15	15	36	36	75	75	101	101
2 Sat. pH	ND	ND	6.91	7.11	7.04	7.09	7.19	7.16
3 Fil. Sol. (pH)	8.29	8.24	8.3	8.44	8.4	8.55	8.7	8.6
4 Sat. Eh (mV)	ND	ND	-77	-80	63	50	43	23
5 Fil. Sol. Eh (mV)	-134	-101	223	173	206	192	66	61
6 Alkalinity (mg/L CaCO ₃)	302	226	330	283	278	321	332	380
7 H ₂ Laser (ppm)	0.56	1.65	1.04	1.2	1.32	1.92	5.56	3.7
8 H ₂ ICP (ppm)	0.6	1.1	1.3	1.6	1.7	1.5	5.8	3.3
9 Al AA (ppm)	0.056	0.027	<0.02	0.021	0.049	0.036	0.02	3.3
10 As AA (ppm)	0.184	0.194	0.082	0.142	0.027	0.025	<0.02	0.103
11 B (ppm)	0.1	0.1	0.1	0.1	<0.1	<0.1	0.1	0.1
12 Br (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
13 Ca (ppm)	141	134	121	114	101	101	85	77
14 Fe AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.103
15 K (ppm)	20	20	20	20	<0.1	20	20	<0.1
16 Mg (ppm)	39.6	36.6	39.3	37	32.9	34.6	48.5	51.4
17 Mn (ppm)	185	168	290	291	195	200	222	248
18 Si (ppm)	6	6	7	8	7	7	6	7
19 Sr (ppm)	1.6	1.5	1.4	1.4	1.8	1.3	1.2	1.1
20 Na (ppm)	0.3	0.3	0.1	0.1				
21 Mo AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
22 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23 Cl (ppm)	116	106	509	124	114	119	113	108
24 SO ₄ (ppm)	433	401	401	382	453	291	342	311

Al, As, Fe, Mo, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

ND = Not determined.

APPENDIX C

ANALYTICAL DATA FROM COLUMN EXPERIMENTS ON NATURAL RESTORATION

APPENDIX D

ANALYTICAL DATA FROM COLUMN EXPERIMENTS ON NATURAL RESTORATION

The two tables in this appendix contain solution chemical data on samples obtained from column experiments designed to evaluate natural restoration at a Wyoming in situ mine site. Each table contains data from one of the duplicate columns used in the experiments. The composition of the influent solution is given in column 1 of each table followed by the composition of effluent samples divided on the basis of cumulative pore volumes of solution collected. The columns had a pore volume of 150 mL. The results of these experiments are discussed on pages 54 to 62 of this report.

TABLE C.1. Solution Analyses of Effluents from Column 1 of the National Restoration Experiment with Wyoming Reduced Sediment and Synthetic Lixiviant

Parameter	1 Synthetic Lixiviant	2 1-1	3 1-2	4 1-3	5 1-4	6 1-5	7 1-6	8 1-7	9 1-8	10 1-9
1 Cumulative Pore Volume	0	0.28	0.79	0.93	1.06	1.2	1.35	1.42	1.57	1.72
2 pH	7.12	8.4	8	8.2	8.25	8.32	8.36	8.4	7.87	8.25
3 Eh (mv)	371	195	185	188	175	178	175	175	227	200
4 Alkalinity (mg/L CaCO ₃)	309	200	168	152	216	208	208	208	252	184
5 U, Linear (ppm)	15	0.099	0.165	0.307	0.616	0.78	1.210	2.07	2.2	2.8
6 U, ICP (ppm)	180	0.05	0.9	1.3	1.9	1.4	2.3	3.4	3.1	3.3
7 Cu (ppm)	79	388	308	286	262	237	223	223	216	168
8 Ni (ppm)	43.8	86.1	76.9	75	69.5	67.9	60.5	59.8	57.9	56.1
9 Mn (ppm)	414	72	77	78	92	105	125	142	165	182
10 K (ppm)	<2	110	70	70	70	80	80	80	80	80
11 Cl (ppm)	196	132	273	247	251	242	236	231	248	265
12 SO ₄ (ppm)	496	1204	621	610	570	557	526	516	511	557
13 Fe AA (ppm)	<0.2	<0.02	0.032	0.029	0.043	0.078	0.021	0.034	0.138	0.024
14 Al AA (ppm)	<0.2	0.045	0.034	0.033	0.037	0.037	0.029	0.036	0.037	0.022
15 Sr (ppm)	0.3	4.1	3.4	3	2.9	2.5	2.4	2.5	2.4	1.8
16 Zn (ppm)	80	2.5	2.4	2.3	2.8	2.7	2.7	2.3	2.1	1.9
17 Si (ppm)	5	3	3	4	3	3	10	3	4	4
18 B (ppm)	<0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.3	0.2	0.2
19 As AA (ppm)	<0.02	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
20 Mo AA (ppm)	<0.015	0.057	0.068	0.314	0.265	0.186	0.179	0.104	0.1	0.09
21 Se AA (ppm)	<0.015	0.467	0.113	0.08	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

Parameter	11 1-10	12 1-11	13 1-12	14 1-13	15 1-14	16 1-15	17 1-16	18 1-17	19 1-18	20 1-19
1 Cumulative Pore Volume	1.87	2.02	2.17	2.32	2.47	2.62	2.77	2.91	3.06	3.21
2 pH	8.05	8.06	8.08	8.13	8.06	8.02	8.09	8.22	8.24	8.3
3 Eh (mv)	195	198	189	187	190	190	188	161	178	179
4 Alkalinity (mg/L CaCO ₃)	192	192	192	236	216	232	264	208	208	248
5 U, Linear (ppm)	3.19	3.94	4.02	3.7	4.7	5.77	9.84	6.32	7.11	7.94
6 U, ICP (ppm)	4	4.5	5.2	5.7	5.9	7.5	7.5	8.2	9.5	9.7
7 Cu (ppm)	164	151	194	179	135	120	118	114	122	114
8 Ni (ppm)	53.1	49.1	49.8	42.2	42.4	38.4	36.6	36.1	37	35.3
9 Mn (ppm)	208	210	254	236	236	243	253	264	280	307
10 K (ppm)	70	70	70	70	80	60	60	60	60	60
11 Cl (ppm)	234	245	246	244	245	243	234	239	236	227
12 SO ₄ (ppm)	522	522	511	511	514	506	486	504	495	471
13 Fe AA (ppm)	0.1	0.06	0.066	0.049	<0.02	0.033	0.029	0.113	0.079	0.032
14 Al AA (ppm)	0.03	0.028	0.018	0.028	<0.02	0.022	<0.02	0.047	0.023	0.013
15 Sr (ppm)	1.1	1.5	1.6	1.4	1.3	1.4	1.3	1.3	1.4	1.4
16 Zn (ppm)	1.2	2.1	1.7	2.5	<0.05	1.8	1.9	2	2.3	2.1
17 Si (ppm)	4	4	4	3	4	4	4	3	4	4
18 B (ppm)	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2
19 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
20 Mo AA (ppm)	0.029	0.036	0.036	0.04	0.041	0.042	0.041	0.033	0.03	0.022
21 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

Al, As, Fe, Mn, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or Searl fluorimetry (amplitude only).
 Mo: trace determination.

TABLE C.1. (Contd)

Parameter	21 1-20	22 1-21	23 1-22	24 1-23	25 1-24	26 1-25	27 1-26	28 1-27	29 1-28	30 1-29
1 Cumulative Pore Volume	3.36	3.51	3.66	3.81	3.96	4.24	4.38	4.86	5.17	5.48
2 pH	8.39	8.31	8.5	8.51	8.4	8.42	8.4	8.36	8.43	8.6
3 EM (mV)	164	170	162	165	163	159	164	167	168	161
4 Alkalinity (mg/L CaCO ₃)	280	283	305	281	337	337	249	274	241	237
5 U, Lower (ppm)	7.57	8.78	8.23	8.29	8.42	9.5	10.48	10.73	11.14	11.25
6 U, TOP (ppm)	9.6	10.7	10.9	11.5	11.6	12.6	13.2	13.8	13.9	14.7
7 Ca (ppm)	108	105	101	103	107	99	54	65	71	65
8 Mg (ppm)	32.5	32	31.5	30.6	29.8	28.5	27.8	26.8	26	25.3
9 Na (ppm)	282	284	316	304	301	337	343	355	344	348
10 K (ppm)	60	50	60	40	50	60	60	50	40	40
11 Cl (ppm)	230	238	278	232	229	227	239	227	229	226
12 SO ₄ (ppm)	489	500	486	489	493	486	486	486	493	486
13 Fe AA (ppm)	0.048	0.055	0.028	0.052	0.108	0.041	0.082	0.036	0.136	0.032
14 Al AA (ppm)	0.038	0.051	0.057	0.042	0.022	0.41	0.022	0.02	0.076	0.021
15 Sr (ppm)	1.2	1.2	1.2	1.3	1.2	1.3	1.2	1.1	0.9	1
16 Zn (ppm)	2.4	2.2	2.1	1.8	1.8	2.2	3	1.8	2.1	1.7
17 Si (ppm)	4	3	3	3	3	4	4	3	3	4
18 B (ppm)	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.01	0.1
19 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
20 Mo AA (ppm)	0.027	0.02	0.025	0.022	0.021	0.02	0.017	0.017	0.023	0.02
21 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

Parameter	31 1-30	32 1-31	33 1-32	34 1-33	35 1-34	36 1-35	37 1-36	38 1-37	39 1-38	40 1-39
1 Cumulative Pore Volume	5.78	6.09	6.39	6.7	7	7.51	7.61	7.92	8.22	8.53
2 pH	8.3	8.4	8.5	8.54	8.56	8.54	8.56	8.51	8.46	8.42
3 EM (mV)	164	180	170	163	176	169	170	173	171	168
4 Alkalinity (mg/L CaCO ₃)	275	281	249	265	224	224	240	240	252	240
5 U, Lower (ppm)	11.46	11.75	11.5	11.39	11.63	12.69	11.51	13.05	12.6	13
6 U, TOP (ppm)	15	15.5	15.2	15.5	15.8	15.9	15.2	15.6	17	16.9
7 Ca (ppm)	79	66	64	88	48	40	58	67	54	58
8 Mg (ppm)	24.2	23.6	23	23	23.6	22.7	22.6	22.3	23.7	22.3
9 Na (ppm)	323	309	319	339	383	409	411	439	430	395
10 K (ppm)	40	40	40	40	40	50	50	50	40	40
11 Cl (ppm)	272	219	259	314	277	225	222	271	274	234
12 SO ₄ (ppm)	479	471	504	638	469	482	441	475	443	504
13 Fe AA (ppm)	0.104	0.058	0.021	0.053	0.074	0.021	0.054	0.131	0.025	0.025
14 Al AA (ppm)	<0.02	0.025	0.026	0.025	<0.02	0.027	0.021	0.015	<0.02	0.023
15 Sr (ppm)	1	1.1	0.8	1	0.6	0.9	0.6	0.9	0.8	0.7
16 Zn (ppm)	2.2	2.4	2	2.2	2.4	2.6	3.2	0.9	1.8	2.2
17 Si (ppm)	5	4	4	4	4	4	5	4	4	4
18 B (ppm)	0.1	0.1	0.1	0.1	0.1	0.01	0.01	0.01	0.01	0.01
19 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
20 Mo AA (ppm)	0.014	0.015	0.014	0.017	<0.015	0.018	0.015	0.015	<0.015	<0.015
21 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

Al, As, Fe, Mg, and Se analyzed by atomic absorption spectrometry, remainder of dissolved cations by ICP or Inductively Coupled Plasma (ICP-MS).

TABLE C.1. (Contd)

Parameter	41 1-56	42 1-58	43 1-60	44 1-62	45 1-64	46 1-66	47 1-68	48 1-70	49 1-72	50 1-74
1 Cumulative Pore Volume	8.83	9.14	9.45	9.75	10.06	10.36	10.67	10.97	11.28	11.58
2 pH	8.39	8.37	8.59	8.58	8.54	8.56	8.74	8.7	8.57	8.57
3 EC (mv)	170	171	169	172	168	163	161	158	154	184
4 Alkalinity (mg/L CaCO ₃)	249	249	261	275	265	265	257	249	208	
5 U, Laser (ppm)	13.15		13.5	13.68	14.06	13.68	14.36	13.68	13.29	12.05
6 U, ICP (ppm)	17	16.9	17.5	17.7	17.6	18.5	18.1	17.5	18.6	16.5
7 Ca (ppm)	60	66	74	79	78	100	84	87	85	65
8 Mg (ppm)	22.3	21.5	21.7	21.6	2	22	21.3	20.9	21.1	19.9
9 Na (ppm)	391	400	391	386	362	395	389	419	405	384
10 K (ppm)	40	40	40	40	40	40	40	40	50	50
11 Cl (ppm)	220	215	218	215	212	215	327	355	225	225
12 SO ₄ (ppm)	489	475	479	472	461	468	481	447	469	475
13 Fe AA (ppm)	0.041	0.044	0.116	0.045	0.164	0.035	0.033	0.049	0.065	
14 Al AA (ppm)	<0.02	0.021	0.04	0.031	0.19	<0.02	0.02	0.02	0.077	
15 Sr (ppm)	0.6	0.7	0.8	0.8	0.9	1	0.9	1	1	0.8
16 Zn (ppm)	2.2	1.9	1.8	2.4	2.3	2.3	2.2	1.8	3.1	1.9
17 Si (ppm)	4	4	4	4	4	4	4	4	4	4
18 R (ppm)	0.01	0.1	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
19 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
20 Mo AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
21 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	

Al, As, Fe, Mo, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

TABLE C.2. Solution Analyses of the Effluent from Column 2 for the Natural Restoration Experiment with Wyoming Reduced Sediment and Synthetic Lixiviant

Parameter	1 Synthetic Lixiviant	2 2-1	3 2-2	4 2-3	5 2-4	6 2-5	7 2-6	8 2-7	9 2-8	10 2-9	11 2-10
1 Cumulative Pore Volume	0	0.15	0.31	0.46	0.61	0.77	0.93	1.09	1.25	1.41	1.58
2 pH	7.12	8.37	8.15	8.79	8.2	8.37	7.69	8.15	8.1	8.17	8.15
3 Eh (mV)	371	175	176	176	176	173	197	187	177	174	174
4 Alkalinity (mg/L CaCO ₃)	309	128	170	136	144	152	120	112	128	152	
5 U ₂ Laser (ppm)	15	0.075	0.096	0.096	0.052	0.063	0.243	0.48	0.62	0.8	1.4
6 U ₂ IOP (ppm)	ND						0.6		0.9	1.1	1.8
7 Ca (ppm)	79	915	472	422	349	331	278	266	236	254	191
8 Mg (ppm)	43.8	113	102	92	78	75	66	73	64	67	57
9 Na (ppm)	414	89	82	73	70	70	83	89	86	133	142
10 K (ppm)	42	60	50	50	40		40	40	50	40	40
11 Cl (ppm)	196	30	17	125		179	190	192	199	217	201
12 SO ₄ (ppm)	496	1665	1279	942		636	582	524	532	559	484
13 Fe AA (ppm)	40.2	0.047	0.022	0.068	0.048	0.103	0.049	0.035	0.039	0.036	0.049
14 Al AA (ppm)	40.2	0.04	0.025	0.046	0.031	0.079	0.051	0.02	0.011	0.026	0.049
15 Sr (ppm)	0.5	5.2	4.8	4.4	3.7	3.5	3	3.1	2.9	2.2	2.2
16 Zn (ppm)	ND	3.1	1.6	5.3	2.1	1.7	2.2	2.8	2.9	1.9	2.3
17 Si (ppm)	5	5	3	3	3	3	3	3	3	3	3
18 B (ppm)	40.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.2	0.2	0.2
19 As AA (ppm)	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015
20 Mo AA (ppm)	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015
21 Se AA (ppm)	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015

Parameter	12 2-11	13 2-12	14 2-13	15 2-14	16 2-15	17 2-16	18 2-17	19 2-18	20 2-19	21 2-20	22 2-21
1 Cumulative Pore Volume	1.73	1.89	2.05	2.21	2.37	2.53	2.69	2.85	3.01	3.17	3.33
2 pH	8.19	8.2	8.26	8.08	7.96	8.1	7.98	8.2	8.22	8.18	8.33
3 Eh (mV)	175	168	190	169	173	166	168	164	163	163	157
4 Alkalinity (mg/L CaCO ₃)		131		72	131	130	111	138	164	157	131
5 U ₂ Laser (ppm)	1.92	2	2.88	3.2	3.7	4.84	5.14	6.6	6.3	7	8.3
6 U ₂ IOP (ppm)	2.3	2.8	3.4	4	4.9	5.8	6.4	7.2	7.7	8.7	8.7
7 Ca (ppm)	192	183	195	163	154	157	133	136	130	126	110
8 Mg (ppm)	39	53	49	53	49	48	43	44	41	41	40
9 Na (ppm)	178	168	176	228	217	257	203	264	248	258	289
10 K (ppm)	30	40	30	40	30	40	30	50	30	36	30
11 Cl (ppm)	202	196	214	208	205	201	198	216	201	195	208
12 SO ₄ (ppm)	480	463	490	494	473	461	448	472	460	448	468
13 Fe AA (ppm)	0.075	0.045	0.075	0.045	0.027	0.07	0.19	0.071	0.04	0.064	0.04
14 Al AA (ppm)	0.029	0.028	0.02	0.028	0.026	0.074	0.031	0.033	0.02	0.031	0.022
15 Sr (ppm)	2.2	1.8	1.7	1.6	1.9	1.9	2	1.9	1.8	1.8	1.5
16 Zn (ppm)	4.5	2	1.1	2.5	2.7	2.6	2.9	1.9	2.4	2.1	1.9
17 Si (ppm)	3	3	3	3	3	3	3	3	3	3	3
18 B (ppm)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
19 As AA (ppm)	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015
20 Mo AA (ppm)	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015
21 Se AA (ppm)	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015	40.015

At, As, Fe, Mo, and Se analyzed by solid absorption spectrometry, remainder of dissolved cations by ICP or lower flame (ppt).

TABLE C.2. (Contd)

Parameter	25 2-77	26 2-75	25 2-74	26 2-73	27 2-76	28 2-75	29 2-71	30 2-73	31 2-75	32 2-77	33 2-79
1 Cumulative Pore Volume	5.49	5.65	5.81	5.97	6.12	6.21	6.31	6.26	5.98	5.9	6.22
2 pH	8.44	8.47	8.49	8.51	8.44	8.49	8.49	8.4	8.4	8.56	8.6
3 EC (mc)	176	155	161	163	171	149	180	184	177	176	170
4 Alkalinity (mg/L CaCO ₃)	137.6	185	185	186.6	183	170	150	210	216	203	216
5 U, Lower (ppm)	7.5	8.4	8.62	8.69	8.52	9.1	9.7	10.38	10.42	10.98	11.01
6 U, OF (ppm)	8.6	9.7	9.4	10.7	10.4	11.5	10.5	12.2	12.8	12.7	13.1
7 Ca (ppm)	110	128	114	124	84	81	62	84	100	92	89
8 Mg (ppm)	39	37	32	34	34	32	28	30	29	27	27
9 Na (ppm)	272	301	271	312	338	333	313	373	397	356	368
10 K (ppm)	20	30	20	30	30	20	20	30	20	20	30
11 Cl (ppm)	205	172	236	213	219	221	221	226	215	215	219
12 SO ₄ (ppm)	304	412	300	496	512	308	304	312	300	304	304
13 Fe AA (ppm)	0.156	0.051	0.077	0.044	0.253	0.042	0.104	0.007	0.007	0.038	<0.02
14 Al AA (ppm)	0.05	0.034	0.025	0.036	0.08	<0.02	<0.02	0.051	0.02	0.021	<0.02
15 Sr (ppm)	1.2	1.5	1.4	1.6	0.8	0.9	0.7	1.1	1.1	1.1	1
16 Zn (ppm)	2.3	1.8	3.2	2.1	1.6	2.4	2.1	3.2	2.3	2.3	2.3
17 Si (ppm)	3	3	3	3	3	3	3	4	3	3	3
18 B (ppm)	0.100	0.1	0.1	0.2	0.1	0.1	0.1	0.3	0.1	0.1	0.1
19 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
20 Mo AA (ppm)	0.002	0.035	0.031	0.025	0.028	0.03	0.027	0.022	0.022	0.022	0.024
21 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

Parameter	34 2-81	35 2-83	36 2-85	37 2-87	38 2-89	39 2-91	40 2-93	41 2-95	42 2-97	43 2-99	44 2-81	45 2-83
1 Cumulative Pore Volume	6.34	6.66	7.17	7.5	7.82	8.14	8.46	8.78	9.1	9.42	9.34	10.07
2 pH	8.43	8.50	8.55	8.53	8.58	8.54	8.57	8.57	8.5	8.79	8.4	8.58
3 EC (mc)	174	167	179	173	167	178	177	126	179	175	179	174
4 Alkalinity (mg/L CaCO ₃)	197	177	283	158	177	158	197	210	210	210	223	273
5 U, Lower (ppm)	11.29	11.27	11.08	11.67	12.08		12.9	13.5	12.42	13.44	13.78	12.87
6 U, OF (ppm)	13.7	13.5	14.1	14.8	15	11.8	15.6	15.9	15.7	16.4	14.8	14.7
7 Ca (ppm)	88	30	48	68	38	37	35	64	71	69	71	82
8 Mg (ppm)	26	27	25	25	26	20	25	24	24	23	21	22
9 Na (ppm)	340	349	388	392	422	323	415	408	407	402	362	342
10 K (ppm)	20	18	20	20	20	20	20	20	20	20	20	20
11 Cl (ppm)	220	221	220	234	241	234	236	224	227	225	214	215
12 SO ₄ (ppm)	300	308	308	300	351	351	330	312	309	308	308	308
13 Fe AA (ppm)	0.153	0.055	0.039	0.158	0.252	0.08	0.032	0.04	0.028	0.161	0.047	0.032
14 Al AA (ppm)	<0.02	0.027	0.057	<0.02	0.057	0.031	0.03	<0.02	<0.02	0.02	0.024	<0.02
15 Sr (ppm)	1.2	0.5	1	1	0.6	0.5	0.8	0.7	0.7	1	0.8	1
16 Zn (ppm)	3.1	3.1	2.6	2.6	2.8	1.5	2.8	2.4	1.9	1.5	1.9	1.8
17 Si (ppm)	3	4	3	3	4	3	3	3	3	3	3	3
18 B (ppm)	0.1	0.1	0.1	0.1	0.1	<0.01	0.1	0.1	0.1	<0.01	<0.01	<0.01
19 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
20 Mo AA (ppm)	0.021	0.02	0.021	0.021	0.026	0.019	0.021	0.014	0.017	0.015	<0.015	<0.015
21 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

Si, As, Mo, and Se analyzed by atomic fluorescence spectrometry, remainder of dissolved cations by ICP or laser fluorescence spectrometry.

TABLE C.2. (Contd)

Parameter	46 2-65	47 2-67	48 2-69	49 2-71	50 2-73	51 2-75
1 Calculated Pore Volume	10.38	10.71	11.03	11.35	11.67	11.99
2 pH	8.49	8.45	8.74	8.7	8.52	8.38
3 EM (mv)	176	176	175	181	202	198
4 Alkalinity (mg/L CaCO ₃)	210	216	223			
5 U, Laccar (ppm)	13.48	12.86	13.36	13.33	13.78	14.7
6 U, HCP (ppm)	17.5	17	17.2	16.5	17	17.8
7 Ca (ppm)	91	89	92	73	78	85
8 Mg (ppm)	22	23	27	21	22	21
9 Na (ppm)	394	424	426	395	416	392
10 K (ppm)		20		20	20	
11 Cl (ppm)	219	277	216	273	212	227
12 SO ₄ (ppm)	564	528	594	665	684	546
13 Fe AA (ppm)	0.031	0.043	0.035			
14 Ar AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
15 Sn (ppm)	1.1	1	1.1	0.9	1	1
16 Zn (ppm)	1.3	1.5	1.5	1.5	1.5	1.5
17 Si (ppm)	3	3	3	3	4	3
18 E (ppm)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
19 As AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
20 Mo AA (ppm)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
21 Se AA (ppm)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

Al, As, Fe, Mo, and Se analyzed by atomic absorption spectrometry, remainder of dissolved cations by ICP or Laccar fluorimetry (laccar only).

APPENDIX D

ANALYTICAL DATA FROM SULFIDE ADDITION EXPERIMENTS

D.1

APPENDIX D

ANALYTICAL DATA FROM SULFIDE ADDITION EXPERIMENTS

The two tables in this appendix contain solution chemical data on samples obtained from column experiments designed to study the effect on restoration of adding sodium sulfide to spent lixiviant recirculated through a leached ore zone. Sediments and solutions were obtained from a Texas in situ mine. Each table contains data from one of the duplicate columns used in the experiments. The composition of the influent solution is given in column 1 of each table followed by the composition of effluent samples divided on the basis of cumulative pore volumes of solution collected. The columns had a pore volume of 150 mL. After approximately 10 pore volumes had been collected from each column, sodium sulfide was added to the influent solution to give an initial concentration of 0.005 molar. An additional ten pore volumes of solution were collected and analyzed from each column. The results of these experiments are discussed on pages 76 to 81 of this report.

TABLE D.1. Solution Analyses of Columns A and F Effluents from the Sulfide Addition Experiment

Parameter	12 A11	13 A12	14 A13	15 A14	16 A15	17 A16	18 A17	19 A18	20 A19	21 A20	22 A22	23 A24
1 Cumulative Flow Volume	1.43	1.36	1.69	1.82	1.95	2.08	2.21	2.34	2.47	2.6	2.93	3.2
2 Total Flow pH	6.53							6.42				6.35
3 Flow Time (h)	916							517				491
4 Dissolved Solids (mg/L)	90	61	72	71	72	55	55	67	51	57		
5 SO_4^{2-} (mg/L)												
6 SO_4^{2-} (mg/L)	3.4	2.5	3.1	3.6	3.5	3.8	3.8	3.7	3.8	3.8	3.5	3.6
7 SO_4^{2-} (mg/L)	6.5	6.7	6.9	6.3	6.5	6.5	6.8	6.9	6.9	7.14	6.84	6.68
8 SO_4^{2-} (mg/L)	40	40	40	40	40	40	40	40	40	40	40	40
9 SO_4^{2-} (mg/L)	199	193	193	193	193	193	193	193	193	193	193	193
10 SO_4^{2-} (mg/L)	1290	1290	1290	1290	1290	1290	1290	1290	1290	1290	1290	1290
11 SO_4^{2-} (mg/L)	4	4	4	4	4	4	4	4	4	4	4	4
12 SO_4^{2-} (mg/L)	11.6	11.4	9.6	11.2	10.3	11.4	11.7	11.8	11.8	12	11.4	10.7
13 SO_4^{2-} (mg/L)	1	0.9	0.8	0.9	0.8	1	1.1	1.1	1.1	1.2	1.1	1.1
14 SO_4^{2-} (mg/L)	1027	1027	1031	1031	1031	1031	1031	1031	1031	1031	1031	1031
15 SO_4^{2-} (mg/L)	2038	2020	2063	2001	2105	2619	2482	2545	2461	2449	2351	2192

Al, Fe, Mn, Mg, and Zn analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorescence emission analysis.

TABLE D.I. (Contd)

Parameter	24 A26	25 A28	26 A30	27 A32	28 A34	29 A36	30 A38	31 A40	32 A42	33 A44	34 A46	35 A48
1 Combustion Pure Potassium	3.47	3.75	4	4.27	4.55	4.8	5.07	5.35	5.6	5.87	6.13	6.4
2 Reaction pH				6.19		6.54			6.92			6.41
3 Reaction (h. temp)				455		479			497			504
4 Absorbance	70			130			72			82		
5 H ₂ Linear Temp												
6 H ₂ MCP Temp	3.2	3	3	2.6	2.5	2.4	2.5	2.2	2.2	2.4	2.5	2.2
7 H ₂ Temp	6.4	6.15	6.05	6.54	6.7	6.91	7.04	7.08	7.08	7.08	7.08	7.08
8 H ₂ Temp	40	30	30	30	30	30	30	30	30	30	30	30
9 H ₂ Temp	145	137	120	103	90.4	80.6	72	64	56.8	48.4	40.4	32.5
10 H ₂ Temp	600	606	604	600	606	604	603	603	600	604	604	600
11 H ₂ Temp	4	4	4	3	3	3	3	3	3	3	3	3
12 H ₂ Temp	10.6	9.9	9.6	8.1	7.3	6.3	5.8	5	4.8	4.4	4.1	3.7
13 H ₂ Temp	0.9	0.8	0.6	0.8	0.7	0.4	0.3	0.2	0.3	0.4	0.4	0.4
14 H ₂ Temp	1000	1017	1013	1032	1015	1033	1044	1065	1077	1090	1094	1095
15 H ₂ Temp	2190	2073	1931	1747	1609	1529	1480	1398	1242	1211	1200	1168

Parameter	36 A50	37 A52	38 A54	39 A56	40 A58	41 A60	42 A62	43 A64	44 A66	45 A68	46 A70	47 A72
1 Combustion Pure Potassium	6.67	6.91	7.2	7.47	7.73	8	8.27	8.55	8.8	9.07	9.33	9.6
2 Reaction pH			6.19		6.57	6.4			6.4			
3 Reaction (h. temp)			455		481	465			470			
4 Absorbance	127			116			112			102		
5 H ₂ Linear Temp												
6 H ₂ MCP Temp	2.4	2.2	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
7 H ₂ Temp	252	256	253	277	277	275	294	294	293	293	293	293
8 H ₂ Temp	30	30	30	30	30	30	30	30	30	30	30	30
9 H ₂ Temp	60.5	37.6	32.9	38.4	32.9	37.3	33.6	36	37.2	37.6	38.1	37.5
10 H ₂ Temp	1160	1010	1030	1090	1110	1090	1090	1070	1170	1090	1130	1160
11 H ₂ Temp	3	3	3	3	3	3	3	3	3	3	3	3
12 H ₂ Temp	3.6	3.2	3.2	3.2	3.2	3.2	2.8	3.1	3.2	3.2	3.3	3.2
13 H ₂ Temp	0.9	0.8	0.8	0.8	0.8	0.8	0.5	0.5	0.4	0.4	0.4	0.4
14 H ₂ Temp	1033	1029	1035	1070	1070	1070	1010	1094	994	841	990	1018
15 H ₂ Temp	1170	1149	1170	1135	1169	1172	1144	1122	1144	977	1130	1172

A₂, A₃, A₄, A₅, and A₆ analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorescence.

TABLE D.1. (Contd)

Parameter	45 Åm	49 Åm	50 Åm, disc	51 Åm	52 Åm	53 Åm, 4 Å	54 Åm	55 Åm	56 Åm	57 Åm
1 Compton Peak Volume	0.0			10.26	10.32	10.5	10.52	10.74	10.8	10.95
2 Peak vol			10.5	6.45	6.47	6.41			6.59	5.59
3 Peak vol (C. diff)			-86	240	232	190			161	155
4 Absorption					204	421	127	592	235	343
5 W, linear (atom)										
6 W, MCP (atom)	0	5.1	7	4.5	6.6	5.2	4.3	3.9	3.9	4.3
7 C (atom)	242	275	115	252	260	259	151	186	191	179
8 K (atom)	90	30	31	60	50	40	40	40	30	80
9 Mg (atom)	49.1	57.7	90.8	41.2	40.9	41.2	40.6	40.2	39.4	34.4
10 Mg (atom)	1250	1190	1850	115	1180	1140	1150	1140	1160	1010
11 Si (atom)	5	5	14	5	5	5	5	5	5	5
12 Si (atom)	5.4	3.2	5.8	5.5	5.7	5.9	5.1	2.6	2.8	2.8
13 Mn (atom)	0.4	0.4		0.4	0.4	0.5	40.01	0.2	40.01	40.01
14 Cl (atom)	993	1035	1100	1065	1053	948	1048	1041	1034	945
15 Cl (atom)	1115	1194	1373	1215	1215	1243	1254	1274	1196	1168

Parameter	58 Åm	59 Åm	60 Åm	61 Åm	62 Åm	63 Åm	64 Åm	65 Åm	66 Åm	67 Åm	68 Åm	69 Åm
1 Compton Peak Volume	11.11	11.26	11.41	11.56	11.76	11.97	12.16	12.37	12.56	12.57	12.86	13.37
2 Peak vol		6.47	6.46				6.75			6.68	6.64	-197
3 Peak vol (C. diff)		60	59					-85			-196	-197
4 Absorption	205	157	137	106	157	127	118	88	78	69	69	
5 W, linear (atom)												
6 W, MCP (atom)	5.7	3.5	3.5	3.1	3	2.7	2.5	2	1.8	1.7	1.6	1.4
7 C (atom)	169	155	164	165	158	146	168	169	170	172	172	181
8 K (atom)	30	30	30	30	30	30	30	30	30	30	30	30
9 Mg (atom)	31.2	28.5	23.7	27.4	27.2	26.1	27.4	27.7	27.9	28.2	28	29.9
10 Mg (atom)	1040	952	996	976	914	985	979	988	959	925	884	952
11 Si (atom)	5	5	4	6	4	4	5	5	5	5	5	5
12 Si (atom)	2.6	2.4	2.5	2.3	2.5	2.5	2.5	2.4	2.5	2.4	2.4	2.4
13 Mn (atom)	0.1	40.01	0.2	0.3	0.2	0.2	0.5	0.5	0.5	0.5	0.5	0.5
14 Cl (atom)	105	77	719	328	341	365	345	340	374	365	385	386
15 Cl (atom)	1111	1028	948	942	942	969	1004	1015	951	960	1051	966

At. No., Fe, Mo, and Cu analyzed by atomic absorption spectrometry, remainder of dissolved cations by ICP or linear fluorimetry (correction made).

TABLE D.1. (Contd)

Parameter	70 F24	71 F26	72 F28	73 F30	74 F32	75 F34	76 F36	77 F38	78 F40	79 F42	80 F44	81 F46
1 Cumulative Pure Volume	15.77	14.77	14.57	14.46	15.53	15.71	15.88	16.78	16.7	17.1	17.43	17.83
2 Ionizing pH	6.44	6.81	6.72		6.84		6.09				8.3	
3 Ionizing Eh (mV)	-198	-187	-201		-216		-274				-275	
4 Absorbance	71				54			110			145	
5 mg/L CaCO_3												
6 H_2O_2 (ppm)	1.3	1.0	1.2	1.3	1.11	0.98	1.02	1	0.94	0.73	0.7	0.55
7 Cu (ppm)	185	125	181	185	192	188	194	178	175	162	167	97
8 Zn (ppm)	30	30	30	30	30	30	30	30	30	30	30	30
9 Mn (ppm)	29.5	29.2	29.2	29.5	29.5	29.1	28.9	28.2	27.1	25.5	25.4	15
10 Ni (ppm)	919	911	913	906	894	892	88.3	929	890	883	938	787
11 Fe (ppm)	5	5	5	5	5	5	5	5	4	3	4	5
12 Sr (ppm)	2.5	2.4	2.4	2.4	2.5	2.4	2.4	2.2	2.2	2.1	2	1.2
13 Na (ppm)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
14 Cl (ppm)	745	746	744	736	734	734	737	761	762	776	775	762
15 SO_4 (ppm)	904	908	944	962	1041	1041	1112	1103	1094	1121	1103	832

Parameter	82 F48	83 F50	84 F52	85 F54	86 F56	87 F58	88 F60	89 F62	90 F64	91 F66	92 F68	93 F70	94 F72
1 Cumulative Pure Volume	18.3	18.36	19.2	19.6	20	20.4	20.6	21.2	21.4	22	22.4	22.8	23.1
2 Ionizing pH	6.42			6.5						7.72			
3 Ionizing Eh (mV)	-274			-273						-272			
4 Absorbance	125				74			18			10		
5 mg/L CaCO_3													
6 H_2O_2 (ppm)	0.53	0.4	0.33	0.28	0.26	0.23	0.18	0.14	0.12	0.13	0.12	0.12	0.12
7 Cu (ppm)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	1.2
8 Zn (ppm)	30	30	30	30	30	30	30	30	30	30	30	30	30
9 Mn (ppm)	14.5	15.9	15.9	15.1	15.9	15.7	16.4	15.7	14.5	13	11.6	10.5	9.2
10 Ni (ppm)	758	758	724	737	715	791	815	807	825	810	819	836	850
11 Fe (ppm)	4	5	5	5	5	5	5	5	5	5	5	5	5
12 Sr (ppm)	1.1	1.1	1.1	1.1	1.1	1.2	1.3	1.3	1.2	1.1	1	0.8	0.8
13 Na (ppm)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	<0.01	<0.01	<0.01	<0.01
14 Cl (ppm)	550	549	540	549	542	627	679	691	671	676	662	676	679
15 SO_4 (ppm)	815	817	832	832	832	895	946	903	852	852	809	852	809

Al, As, Fe, Mn, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorescence (anion only).

TABLE D.1. (Contd)

Parameter	95 F/4
1 Cumulative Pore Volume	23.97
2 In-Line oil	
3 In-Line En (wt)	
4 Alkalinity	37
(eq/L CaCO ₃)	
5 U ₂ Layer (ppm)	0.14
6 U ₂ LIP (ppm)	1.1
7 Ca (ppm)	65
8 K (ppm)	<20
9 Mg (ppm)	6.5
10 Na (ppm)	876
11 Si (ppm)	3
12 Sr (ppm)	0.7
13 Mo (ppm)	40.01
14 Cl (ppm)	669
15 SO ₄ (ppm)	793

Al, As, Fe, Mo, and Se analyzed by atomic absorption spectrometry, remainder of dissolved cations by ICP or later fluorimetry (uranium only).

TABLE D.2. Solution Analyses from Column B of the Sulfide Addition Experiment

Parameter	1	2	3	4	5	6	7	8	9	10	11
	11.810	10.79	9.86	8.87	7.86	6.85	5.84	4.83	3.82	2.81	1.80
1 Cumulative Pure Volume	16	0.13	0.26	0.39	0.52	0.65	0.78	0.91	1.04	1.17	1.3
2 Absorbance		29	71	29	69	76	65	74	72	100	
3 U, Laser (ppm)	3.5	2.6	4.4	4.4	4.5	4.8	5	5.4	5.5	5.3	5.3
4 U, ICP (ppm)	1.4	0.5	0.5	0.5	0.5	0.6	0.7	0.9	1	1.1	1.2
5 Fe (ppm)	119	891	774	687	675	653	642	643	633	616	600
6 Cu (ppm)	30	30	30	30	30	30	30	30	30	30	30
7 K (ppm)	94.2	166	116	170	168	161	157	157	153	150	143
8 Mg (ppm)	1660	1290	1360	1590	1410	1350	1290	1290	1210	1220	1100
9 Si (ppm)	1.5	3	3	3	3	3	3	3	3	4	4
10 Sr (ppm)	9.5	12.5	13.2	12.6	12.2	11.8	11.5	11.2	10.5	10.4	
12 Mn (ppm)	40.01	0.8	1	0.9	0.9	0.8	0.8	0.7	0.7	0.5	0.5
13 Cl (ppm)	1076	806	796	905	1899	927	1002	1036	1034	1045	1046
14 SO ₄ (ppm)	1225	3859	3353	3481	3278	2911	2914	2865	2750	2678	2261

Parameter	17.811	13.812	14.813	15.814	16.815	17.816	18.817	19.818	20.819	21.820	22.822	23.824
1 Cumulative Pure Volume	1.63	1.36	1.69	1.82	1.95	2.08	2.21	2.34	2.47	2.6	2.86	3.12
2 Absorbance	157	133	118	88	88							
3 U, Laser (ppm)	3	3.1	3.1	3.2	4.7	4.7	4.5	4.4	4.3	4.1	3.8	3.7
4 U, ICP (ppm)	1.2	1.3	1.3	1.4	1.5	1.4	1.4	1.4	1.3	1.4	1.4	1.4
5 Fe (ppm)	603	504	592	560	531	553	524	486	453	444	405	371
6 Cu (ppm)	30	30	30	30	30	30	30	30	30	30	30	30
7 K (ppm)	142	138	131	130	129	123	116	107	101	96.6	87.9	72.7
8 Mg (ppm)	1060	1010	918	963	898	959	947	923	933	935	968	951
9 Si (ppm)	4	4	4	4	4	4	4	4	4	4	4	3
10 Sr (ppm)	10.3	10.1	9.9	9.2	9	9.1	8.6	8	7.4	7.2	6.5	5.8
12 Mn (ppm)	0.4	0.5	0.6	0.7	0.5	0.6	0.6	0.5	0.5	0.5	0.3	0.3
13 Cl (ppm)	1038	1009	1026	1046	1045	1018	1021	986	1010	1024	1033	1018
14 SO ₄ (ppm)	2125	1977	1898	1864	1773	1687	1651	1518	1497	1497	1341	1246

Al, As, Fe, Mn, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (carbonate only).

TABLE D.2. (Contd)

Parameter	24 R76	25 R74	26 R70	27 R52	28 R58	29 R56	30 R38	31 R40	32 R42	33 B44	34 B46	35 B48
1 Cumulative pore volume	5.58	5.64	5.9	4.16	4.42	4.68	4.94	5.2	5.46	5.72	5.98	6.24
2 Absorbance	34			80					155			
3 H ₂ (g/g)	2.1	5.7	5.5	5.4	5.2	5.4	2.20	5.5	5.10	5	5.1	3.1
4 H ₂ (g/g)	3.4	1.5	1.5	1.5	1.5	1.5	1.00	1.4	1.40	1.7	1	1.4
5 H ₂ (g/g)	292	302	280	270	246	239	10.00	24.0	278.00	22	275	275
6 H ₂ (g/g)	30	30	20	20	20	20	<20	20.0	20.00	20.0	<20	<20
7 H ₂ (g/g)	65.6	96.4	96.4	96.2	92.1	90	55.00	47.1	45.40	44.20	44.4	42.5
8 H ₂ (g/g)	1020	1050	1030	1080	1060	1060	814.00	1100.0	1100.00	1090.00	1120	1049
9 H ₂ (g/g)	5	3	4	3	3	3	2.00	3.0	3.00	3.00	4	4
10 H ₂ (g/g)	4.1	4.9	4.6	4.3	4	4	2.70	3.2	3.60	3.60	3.6	3.5
11 H ₂ (g/g)	<0.01	0.2	0.2	0.2	0.1	0.3	0.10	0.2	0.20	0.30	0.2	0.3
12 H ₂ (g/g)	1005	1002	1017	1008	1027	998	1035.00	1090.0	1019.00	989.00	985	1000
13 H ₂ (g/g)	1270	1202	1202	1191	1202	1157	1191.00	1169.0	1180.00	1146.00	697	1169

Parameter	36 R70	37 R52	38 R54	39 R50	40 R58	41 R50	42 R52	43 R54	44 R56	45 R58	46 R70	47 R72
1 Cumulative pore volume	6.5	6.76	7.02	7.28	7.54	7.8	8.06	8.32	8.59	8.84	9.1	9.36
2 Absorbance	121		165				247		161			
3 H ₂ (g/g)	2.8	5.5	5.1	5.1	2.9	5.1	3.1	2.9	2.8	3.5	3.1	3.7
4 H ₂ (g/g)	1.2	1.8	1.4	1.4	1.4	1.5	1.4	1.4	1.4	1.4	1.4	1.4
5 H ₂ (g/g)	195	222	225	214	208	218	214	209	210	218	199	208
6 H ₂ (g/g)	<20	<20	<20	20	30	20	30	30	30	30	30	30
7 H ₂ (g/g)	96.5	85.1	42.2	41.9	41.7	42.1	41.6	40.7	40.7	42.0	39.2	40.5
8 H ₂ (g/g)	606	1070	1030	1120	1190	1100	1150	1150	1120	1130	1090	1080
9 H ₂ (g/g)	5	4	4	4	4	5	5	5	5	5	6	6
10 H ₂ (g/g)	5	3.6	3.5	3.4	3.5	3.4	3.4	3.5	3.5	3.4	3.1	3.5
11 H ₂ (g/g)	0.2	0.2	0.3	0.3	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3
12 H ₂ (g/g)	1075	1057	992	1010	1056	1096	976	1010	1008	975	1108	1077
13 H ₂ (g/g)	1191	1191	1157	1172	1172	1159	1125	1159	1159	1114	1089	1050

H₂, Ar, Co, Mo, and Na analysed by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorescence for boron and Fe.

TABLE D.2. (Contd)

Parameter	48 814	49 816	50 818	51 820	52 (1st. 8198 with 0.0094 Sulfide)	53 81	54 82	55 83	56 84	57 85
1 Cumulative Pore Volume	9.52	9.88	10.14	10.4		10.6	10.8	11	11.2	11.4
2 Absorbance	98		208			176	196	215	167	220
3 H ₂ (ppm)	3.8	3.6	3.6	3.8	2	3.4	3.2	3.1	4.8	4.1
4 H ₂ (ppm)	1.2	1.4	1.4	1.3	1.6	1.4	1.4	1.5	1.5	1
5 H ₂ (ppm)	212	207	205	211	115	210	163	157	142	158
6 H ₂ (ppm)	<20	50	50	50	31	50	50	50	50	50
7 H ₂ (ppm)	40.4	41.9	41	41.7	98.6	49.6	46.7	44.2	36.1	50.5
8 H ₂ (ppm)	1080	1163	1110	1110	1870	1190	1270	1180	1040	969
9 H ₂ (ppm)	6	6	6	6	14	6	7	7	6	6
10 H ₂ (ppm)	5.2	5.3	5.2	5.4	5.8	5.6	5.4	5.1	2.6	2.3
11 H ₂ (ppm)	0.2	0.3	0.3	0.3	40.01					
12 H ₂ (ppm)	912	981	965	1015	1109	982	984	959	770	684
13 H ₂ (ppm)	1945	1127	1114	1100	1315	1172	1175	1182	1078	974

Parameter	58 86	59 87	60 88	61 89	62 810	63 811	64 812	65 813	66 814	67 815	68 816	69 817
1 Cumulative Pore Volume	11.5	11.62	11.75	11.9	12.07	12.25	12.4	12.57	12.75	12.9	13.06	13.23
2 Absorbance	191	176	171	191	171	125	122	93	108	196	167	230
3 H ₂ (ppm)	3.7	3.4	3.2	2.9	2.9	2.5	2.5	2.1	1.9	2.6	2.8	2.6
4 H ₂ (ppm)	0.8	0.7	0.4	0.6	0.5	0.5	0.5	0.5	0.5	0.6	0.6	0.5
5 H ₂ (ppm)	118	119	177	135	134	135	148	157	161	185	184	189
6 H ₂ (ppm)	20	50	<20	50	50	50	50	50	50	50	50	20
7 H ₂ (ppm)	27.5	26.5	26.6	24.9	26	26.9	28.7	30.3	31.7	35.5	35.2	35.6
8 H ₂ (ppm)	897	893	893	889	868	894	905	927	971	957	950	905
9 H ₂ (ppm)	5	5	4	4	4	4	4	4	4	5	4	4
10 H ₂ (ppm)	2.1	2	2	2	2.1	2.1	2.5	2.4	2.4	2.8	2.8	2.9
11 H ₂ (ppm)	645	654	659	640	644	654	686	786	728	796	752	744
12 H ₂ (ppm)	910	948	915	896	915	870	4	939	922	1104	1052	1678

As, Ba, Fe, Mn, and Se analysed by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (carbon multi).

TABLE D.2. (Contd)

Parameter	70 618	71 619	72 620	73 622	74 624	75 626	76 628	77 630	78 632	79 634	80 636	81 638
1 Cumulative Pore Volume	11.4	15.52	15.75	14.07	15.4	14.73	15.07	15.43	15.77	16.03	16.3	16.6
2 Absorbance (mV/cm ²)	186	152	147	84	145	119						
3 H ₂ Laser (ppm)	1.25	1.0	0.74	0.7	0.66	0.67						
4 H ₂ ICP (ppm)	2.3	2	1.9	1.4	1.4	1.2	1.1	0.7	0.7	0.5	0.5	0.6
5 S (ppm)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.6	0.6	0.4	0.6
6 Cu (ppm)	109	185	189	168	190	207	204	194	177	112	110	108
7 Fe (ppm)	30	30	30	30	30	3	3	30	20	20	20	<20
8 Ni (ppm)	36	33.3	35.8	35.1	36.4	37.5	38	35.8	23.6	21.1	20.7	20
9 Mn (ppm)	947	923	913	917	881	830	894	896	732	733	749	707
10 Al (ppm)	4	4	4	4	4	4	4	4	4	4	4	4
11 Se (ppm)	2.6	2.8	2.8	2.8	2.8	2.9	2.8	2.7	1.7	1.5	1.5	1.4
12 Zn (ppm)												
13 Cr (ppm)	641	768	713	758	768	759	772	789	593	564	559	553
14 SO ₄ (ppm)	896	991	946	1009	1000	1030	1015	1074	870	818	800	870

Parameter	82 640	83 642	84 644	85 646	86 648	87 650	88 652	89 654	90 656	91 658	92 660	93 662	94 664
1 Cumulative Pore Volume	16.83	17.1	17.37	17.63	17.9	18.07	18.43	18.7	19	19.4	19.7	20	20.25
2 Absorbance (mV/cm ²)	125					102			59			63	
3 H ₂ Laser (ppm)	0.92	0.48	0.48	0.4	0.35	0.29	0.25	0.22	0.22	0.16	0.16	0.15	0.15
4 H ₂ ICP (ppm)	0.5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
5 S (ppm)	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.5	0.5	0.5	0.6	0.6	0.6
6 Cu (ppm)	110	108	109	126	131	131	128	128	124	120	119	114	108
7 Fe (ppm)	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
8 Ni (ppm)	20.3	19.9	20.3	23.3	24.3	23.5	25.9	23.2	23.3	22.2	21.6	20.4	19.6
9 Mn (ppm)	734	726	730	803	820	767	812	805	822	831	823	805	861
10 Al (ppm)	4	4	4	4	4	3	4	4	4	4	4	4	4
11 Se (ppm)	1.5	1.4	1.4	1.7	1.7	1.7	1.7	1.6	1.6	1.5	1.5	1.4	1.4
12 Zn (ppm)													
13 Cr (ppm)	792	640	594	637	678	638	567	685	669	671	664	613	682
14 SO ₄ (ppm)	880	836	836	801	900	948	953	973	991	981	933	933	923

Al, Si, Fe, Mn, and Se analysed by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorescence (arbitrary units).

TABLE D.2. (Contd)

Parameter	95 (94)	96 (95)
1 Cumulative Pore Volume	20.6	20.9
2 Alkalinity (eq/L CaCO ₃)		67
3 U, Laser (ppm)	0.1	0.1
4 U, ICP (ppm)	<0.05	<0.05
5 B (ppm)	0.6	0.5
6 Ca (ppm)	102	92
7 K (ppm)	<20	<20
8 Mg (ppm)	18.1	16.5
9 Na (ppm)	829	852
10 Si (ppm)	4	4
11 Sr (ppm)	1.4	1.3
12 Mn (ppm)		
13 Cl (ppm)	648	662
14 SO ₄ (mm)	897	859

Al, As, Fe, Mo, and Se analyses by atomic absorption spectrometry, remainder of dissolved cations by ICP or laser fluorimetry (uranium only).

NRC FORM 335 12-84 NRC-1102 3207-3202		U.S. NUCLEAR REGULATORY COMMISSION		1. REPORT NUMBER (Assigned by TRC and Vol. No., if any) NUREG/CR-3709 PNL-5319	
2. TITLE AND SUBTITLE Methods of Minimizing Ground-Water Contamination from In Situ Leach Uranium Mining Final Report				3. LEAVE BLANK	
5. AUTHOR(S) W. J. Deutsch L. E. Eary W. J. Martin R. J. Serne				4. DATE REPORT COMPLETED MONTH: December YEAR: 1984	
7. PERFORMING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code) Pacific Northwest Laboratory Richland, WA 99352				6. DATE REPORT ISSUED MONTH: March YEAR: 1985	
10. SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code) Division of Radiation Programs and Earth Sciences Office of Nuclear Regulatory Research U.S. Nuclear Regulatory Commission Washington, DC				8. PROJECT/TASK/WORK UNIT NUMBER TD 1491	
12. SUPPLEMENTARY NOTES				9. FUNDING NUMBER B2379	
11. TYPE OF REPORT Technical Report				10. PERIOD COVERED (Include Dates)	
13. ABSTRACT (200 words or less) <p>This is the final report of a research project dealing with methods of minimizing ground-water contamination from in situ leach uranium mining. Field work and laboratory experiments were conducted to identify excursion indicators for monitoring purposes during mining, and to evaluate effective aquifer restoration techniques following mining. Many of the solution constituents were found to be too reactive with the aquifer sediments to reliably indicate excursion of leaching solution from the ore zone; however, in many cases, the concentrations of chloride and sulfate and the total dissolved solids level of the solution were found to be good excursion indicators.</p> <p>Aquifer restoration by ground-water pumping consumed ground water and was not effective for the redox-sensitive contaminants often present in the ore zone. Surface treatment methods were effective in lowering the amount of water used, but also had the potential for creating conditions in the aquifer under which the redox-sensitive contaminants would be mobile. In situ restoration by chemical reduction, in which a reducing agent is added to the solution recirculated through the ore zone during restoration, has the capability of restoring the ore zone sediment as well as the ground water. This method could lead to a stable chemical condition in the aquifer similar to conditions before mining.</p>					
14. DOCUMENT ANALYSIS - KEYWORDS OR DEcriptors ground-water contamination uranium mining in situ leaching aquifer restoration				15. SECURITY CLASSIFICATION Unlimited 16. SECURITY CLASSIFICATION Unclassified 17. SECURITY CLASSIFICATION Unclassified 18. NUMBER OF PAGES 19. PRICE	

