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Aquifer Restoration Techniques for In-Situ Leach Uranium Mines

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Pacific Northwest Laboratory
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ABSTRACT

In-situ leach uranium mines and pilot-scale test facilities are currently operating in the states of Wyoming, Texas, New Mexico and Colorado. This report summarizes the technical considerations involved in restoring a leached ore zone and its aquifer to the required level. Background information is provided on the geology and geochemistry of mineralized roll-front deposits and on the leaching techniques used to extract the uranium.

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1.0 EXECUTIVE SUMMARY

The in-situ leach uranium mining industry has made great progress since the initial testing of this mining technique in Wyoming during the early 1960s. Currently, 14 pilot-scale operations and 26 commercial plants are in various stages of development and production in the states of Wyoming, Texas, New Mexico, and Colorado. These mines currently produce about 10% of the domestic uranium. This report is a summary of the technical considerations involved in restoring a leached ore zone and its aquifer to the required level. Background information is provided on the geology and geochemistry of mineralized roll-front deposits and on the leaching techniques used to extract uranium.

Roll-front uranium deposits generally occur in fluvial sandstones under confined aquifer conditions. Uranium is leached from granitic or tuffaceous source material by oxidizing, alkaline ground water. Uranium is removed by the in-situ leaching process through the temporary re-establishment of oxidizing conditions in the ore zone region. A leaching solution (lixiviant) that contains an oxidant [primarily O_2(gas) or H_2O_2] and a complexing agent (carbonate) is injected to enhance the mobility of the dissolving uranium. Ammonium was widely used by the industry as the cation to inject with carbonate; however, ammonium is very difficult to remove from the aquifer during restoration because of its adsorption onto the sediments. Sodium, calcium, magnesium, and potassium are major constituents of the ground water associated with the ore; lixiviants based on these cations have been tested, and (in the case of sodium) are being used commercially.

The in-situ uranium mining industry is regulated at the federal level by the Nuclear Regulatory Commission (NRC) and the Environmental Protection Agency (EPA). Licensing and permitting authority may be delegated to states that have established regulatory programs meeting the approval of the NRC or EPA. All regulatory agencies require that an active restoration technique be used at in-situ leach sites. The natural system itself will have some capability for re-establishing pre-mining chemical conditions in the ore zone and for retarding the movement of contaminants in the aquifer. Natural restoration takes place by the dilution of leaching solution by native ground water, the dispersion of solutes as they move with the flow, and chemical interactions between the water and sediments.

Geochemical and hydrologic computer models can simulate the water flow and chemical interactions that occur during the restoration of an aquifer. With a proper data base and accurate field measurements, the models can be used to increase restoration efficiency and estimate the effectiveness of various natural restoration processes. Also, they can help formulate reasonable restoration criteria based on initial conditions of the aquifer and can be used to interpret laboratory experiments in leaching and restoration. To date, geochemical models have been used to aid in the exploration for ore deposits, study the factors influencing the rate of uranium mineral dissolution, and simulate ammonium migration during aquifer restoration.

The primary active (induced) restoration techniques are long-term sweeping, water injection with chemical additives (in-situ treatment), and surface treatment with reinjection. Restoration attempts at several pilot scale and commercial-scale leach facilities have been made. The techniques used included sweeping, surface treatment with reverse osmosis followed by reinjection, and the addition of calcium and magnesium to the recirculating water. None of the plants that used an ammonium-based lixiviant were able to reduce the ammonium concentration in the ground water to the required level. Evidently, if clays are present in the aquifer, the restoration criteria for ammonium set by the regulatory agencies cannot be met by using any of these current techniques. In the case of sodium-based lixiviants, one pilot-scale restoration effort in the Bison Basin of Wyoming was successful. The key to successful restoration may be choosing a lixiviant that is compatible with the native ground water and using a restoration technique geared toward removing specific contaminants at a particular site.

2.0 INTRODUCTION

This report contains information on restoration processes that apply to the in-situ uranium mining industry. The Pacific Northwest Laboratory (PNL) and the U.S. Bureau of Mines Twin Cities Research Center contributed to this document for the purpose of providing up-to-date information on restoration methods. This information is to guide experimental work at PNL on the effectiveness of restoration techniques. Portions of this document will be incorporated in technical reports covering various phases of the research.

To provide background information on restoration, the report starts with a discussion of the in-situ uranium leaching industry and the types of lixiviants used to extract uranium from its ore. Also included in this section is a discussion of the geology and geochemistry of uranium roll-front deposits. The various proposed or currently used restoration techniques are discussed, as well as the role that the natural water/rock system will play in removing leach-generated contaminants from the ground water.

3.0 BACKGROUND ON URANIUM IN-SITU LEACHING

Modern in-situ uranium leaching began in the 1960s. The Utah Construction and Mining Co. conducted leaching tests from 1961-63, and used this method for uranium production from 1963-69 at its Shirley Basin Site in Wyoming. Between 1969 and the early 1970s additional research and development was completed. In the mid-1970s, small-scale pilot tests were conducted in Wyoming, New Mexico, and Texas (Tweeton 1981).

At present, the greatest number of commercial in-situ uranium mining operations are in Texas. A short history of the development of leaching in Texas is given in Charbeneau et al. (1981). Wyoming has only one actively producing commercial site. New Mexico will soon have one; Colorado's planned commercial operation has been delayed. Table 3.1 lists significant in-situ leach operations in Texas, Wyoming, New Mexico, and Colorado.

The present level of activity represents some decline from the forecasts of several years ago. This decline is due primarily to the lower price of uranium. In December 1978 the price was $43.25; it is now about $23.00 per pound of U_3O_8. When adjusted for inflation, this is a truly drastic decline. Exxon has withdrawn from the Highland project because of the low price, and Teton and Rocky Mountain Energy are both waiting for uranium prices to go up before proceeding with commercial operations. The commercial Irigaray operation of Wyoming Mineral Corporation was temporarily shut down by the NRC because of excursions, and is now shut down for economic reasons. Generally, however, the in-situ uranium mining industry appears to be less drastically affected than conventional mining by the drastic decline in the real price of uranium, and the industry is progressively adapting to changing environmental requirements.

Perhaps the most significant technical change in the uranium mining industry is the trend away from ammonium carbonate-bicarbonate lixiviants. This trend is a result of regulatory agency requirements concerning the restoration of ground-water quality. Sodium carbonate-bicarbonate is substituted for the ammonium-based lixiviant where clay swelling is not excessive. Dissolved carbon dioxide can be used under certain conditions. Potassium carbonate-bicarbonate may be practicable where alternatives cannot be used. The use of sulfuric acid is limited to sites having an unusually low concentration of calcite.

3.1 THE LEACHING PROCESS

In general, in-situ uranium leach mining consists of injecting a leaching solution (lixiviant) into an ore zone, dissolving the uranium, pumping the uranium-bearing solution out of the aquifer, and processing the solution to recover uranium.

TABLE 3.1. Status of In-Situ Uranium Leaching Operations

Company and Site	Status
TEXAS	
Caithness - McBryde	Commercial, leaching
Chevron - Palangana	Commercial, on hold
Caithness - Silver Lake	R and D, permitted
Conoco - Trevino	Commercial, leaching
Everest Minerals - Hobson	Commercial, restoring
Intercontinental Energy - Pawnee	Commercial, restoring
Intercontinental Energy - Zamzow	Commercial, leaching
Mobil - Holiday - El Mesquite	Commercial, leaching
Mobil - Nell	Commercial, restoring
Mobil - O'Hern	Commercial, leaching
Tenneco - West Code	Commercial, leaching
Texaco - Hobson	Commercial, on hold
Uranium Resources - Benavides	Commercial, leaching
Uranium Resources - Longoria	Commercial, leaching
U.S. Steel - Burns	Commercial, leaching
U.S. Steel, N.M.U. - Boots	Commercial, leaching
U.S. Steel, N.M.U. - Clay West	Commercial, leaching
U.S. Steel, N.M.U. - Moser	Commercial, leaching
Wyoming Mineral Corp. - Bruni	Commercial, leaching
Wyoming Mineral Corp. - Sulfur Creek	Commercial, restoring
Urex - Santonino	R and D, leaching
WYOMING	
Arizona Public Service - Peterson	R and D, permitted
Cleveland Cliffs - Collins Draw	R and D, restoring
Exxon Minerals - Highland	Commercial, shut down
Kerr-McGee - Bill Smith Project	R and D, restoring
Kerr-McGee - Bill Smith Mine 6001	R and D, permitted
Kerr-McGee - Q Sand	R and D, permitted
Minerals Exploration - Battle Springs	R and D, restoring
Nubeth - Sundance	R and D, inactive
Ogle Petroleum - Bison Basin	Commercial, leaching
Rocky Mountain Energy - Reno Ranch	Commercial, permitted, on hold
Rocky Mountain Energy - Nine Mile Lake	R and D, restored
Teton Exploration - Leuenberger	Commercial, permitted, on hold
Uranerz - Johnson County	R and D, permitted
Uranium Resources - North Platte	R and D, permitted
Wyoming Mineral Corp. - Irigaray	Commercial, restoring, shut down
NEW MEXICO	
Mobil - Crown Point	Applied for commercial permit
Conoco - Borrego Pass	Applied for R and D permit
COLORADO	
Union Oil, Power Resources - Keota	Applied for commercial permit
Wyoming Mineral - Grover	R and D, restored

Several patterns of injection/production wells have been used in commercial in-situ leaching. Well pattern design is based on experience in petroleum production and brine injection. The most common patterns are the five-spot, the seven-spot, and the staggered (to match the ore body) (Figure 3.1). 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 lixiviant is recovered, thus reducing lixiviant costs and decreasing ground-water pollution.

Monitoring wells are located up- and down-gradient of the production area to determine if an excursion occurs (i.e., movement of lixiviant out of the production area). For R and D projects NRC requires a minimum of one monitor well in the aquifers immediately adjacent to the ore body aquifer. Excursions are identified by monitoring changes in water level, total dissolved solids, or a suite of dissolved constituents.

The efficiency of the leaching solution depends on the lixiviant used. The lixiviant serves two functions: 1) it oxidizes and dissolves uranium-bearing minerals, and 2) it provides a ligand which forms stable complexes with uranium under the conditions of the ore zone during mining. The most widely used lixiviants are alkaline solutions of ammonium or sodium carbonate/bicarbonate with oxygen or hydrogen peroxide. The oxygen or hydrogen peroxide in these solutions oxidizes the U^{4+} prevalent in roll-front uranium minerals (for example, uraninite UO_2 and coffinite $USiO_4$) to U^{6+}. The U^{6+} forms soluble complexes with the carbonate/bicarbonate. Typical alkaline leach reactions are shown below (Tweeton and Peterson 1981):

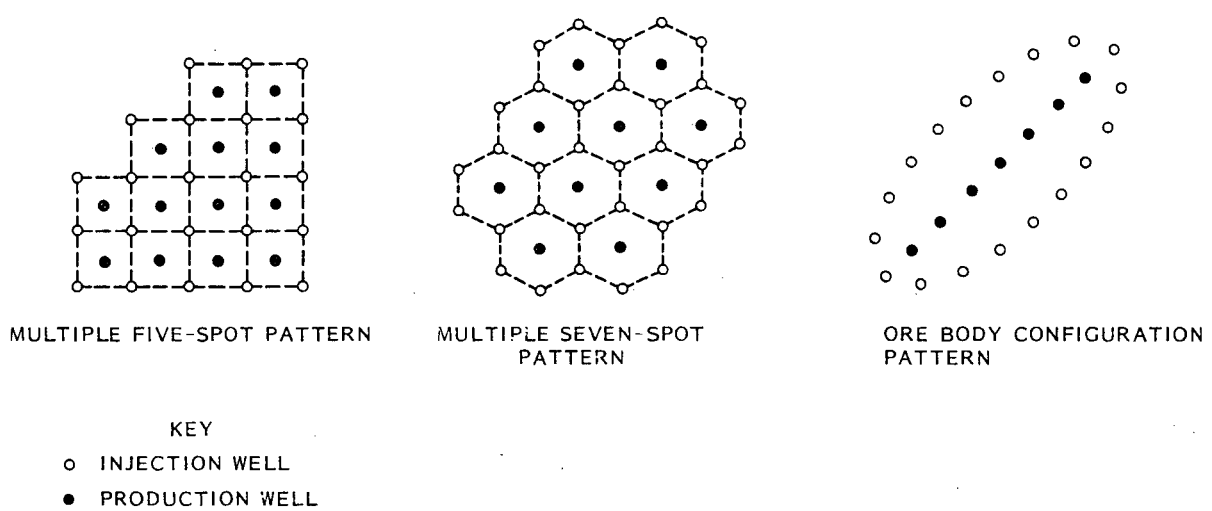

FIGURE 3.1. Typical Well Configurations (after Larson 1981)

Oxidation

$$UO_2 + \frac{1}{2} O_2 + 2H^+ = UO_2^{2+} + H_2O$$

$$UO_2 + H_2O_2 + 2H^+ = UO_2^{2+} + 2H_2O$$

Complexation

Ammonium Carbonate

$$UO_2^{2+} + 2(NH_4)_2 CO_3 = UO_2(CO_3)_2^{=} + 4NH_4^+$$

$$UO_2^{2+} + 2NH_4HCO_3 = UO_2(CO_3)_2^{=} + 2NH_4^+ + 2H^+$$

Sodium Carbonate

$$UO_2^{2+} + Na_2CO_3 + NaHCO_3 = UO_2(CO_3)_2^{=} + 3Na^+ + 1H^+$$

Most mining operations have used ammonium lixiviants because sodium can cause clays to swell and block the formation. 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. A substantial amount of ammonium is taken up from the lixiviant by ion exchange in clays and zeolites in the ore body 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 (1981) reports that of 11 field tests designed to restore ammonium to baseline concentrations, none reach targeted ammonium levels after 0.5 to 38 pore volumes. Complete restoration of ground-water quality may require 50 to 100 pore volumes.

Because of these restoration problems with ammonium lixiviants, new mines will use another type of alkaline lixiviant. Sodium carbonate/bicarbonate has been used in ore bodies where the clay content is low or where the sodium content of natural ground water is high. In at least two mines, carbon dioxide is 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. The use of acid lixiviants is not practical in ore bodies containing relatively large concentrations of alkaline minerals, such as calcite, which neutralize the acid. Even at low calcium concentrations calcium sulfate may precipitate and block the aquifer.

In an acid lixiviant, uranium may be oxidized by either Fe^{3+} present in the ore body or by oxygen added with the lixiviant (Amell and Langmuir 1979; Tatom, Schrechter and Lake 1981). Typical sulfuric acid leach reactions are shown below (Tweeton and Peterson 1981):

Oxidation $UO_2(s) + \frac{1}{2} O_2 + 2H^+ = UO_2^{2+} + H_2O$

$UO_2 + 2Fe^{+++} = UO_2^{++} + 2Fe^{++}$

Acid Leaching $UO_2^{2+} + H_2SO_4 = UO_2SO_4 + 2H^+$

$UO_2SO_4 + H_2SO_4 = UO_2(SO_4)_2^{=} + 2H^+$

$UO_2\ (SO_4)_2^{=} + H_2SO_4 = UO_2(SO_4)_3^{4-} + 2H^+$

3.2 URANIUM RECOVERY PROCESS

Once the uranium has dissolved, the lixiviant is pumped to the surface for treatment. The recovery process is shown in Figure 3.2. The anionic uranium complex [either $UO_2(CO_3)_2^{2-}$ or $UO_2(SO_4)_3^{4-}$] is removed from solution by strong base anionic (quaternary ammonium) exchange resins as shown below (Thompson et al. 1978):

Alkaline $2RCl + (UO_2)(CO_3)_2^{=} = R_2UO_2(CO_3)_2 + 2Cl^-$ (R is resin.)

Acid $4RCl + (UO_2)(SO_4)_3^{4-} = R_4UO_2(SO_4)_3 + 4Cl^-$

Several columns are used so that uranium is being exchanged in some, while the resin is being regenerated in others. During leaching, the lixiviant also dissolves calcium, magnesium, and other impurities. After uranium has been recovered, calcium is frequently removed from the lixiviant by ion exchange or precipitation. Additional reagent is then added to the lixiviant to bring it back to full strength and the lixiviant is pumped back to the well field.

Uranium is eluted from the loaded resin by exchange with a solution high in chloride.

Alkaline $R_2(UO_2)(CO_3)_2 + 2Cl^- = 2RCl + UO_2(CO_3)_2^{2-}$

Acid $R_4(UO_2)(SO_4)_3 + 4Cl^- = 4RCl + UO_2(SO_4)_3^{4-}$

During ion exchange the uranium concentration changes from 0.15 g/l in the lixiviant to 10 g/l in the eluant (Thompson et al. 1978). Eluant containing uranium dicarbonate is acidified to remove carbon dioxide. (This step is not required for acid lixiviants.) The acidic uranium solution is neutralized with ammonia to precipitate ammonium diuranate.

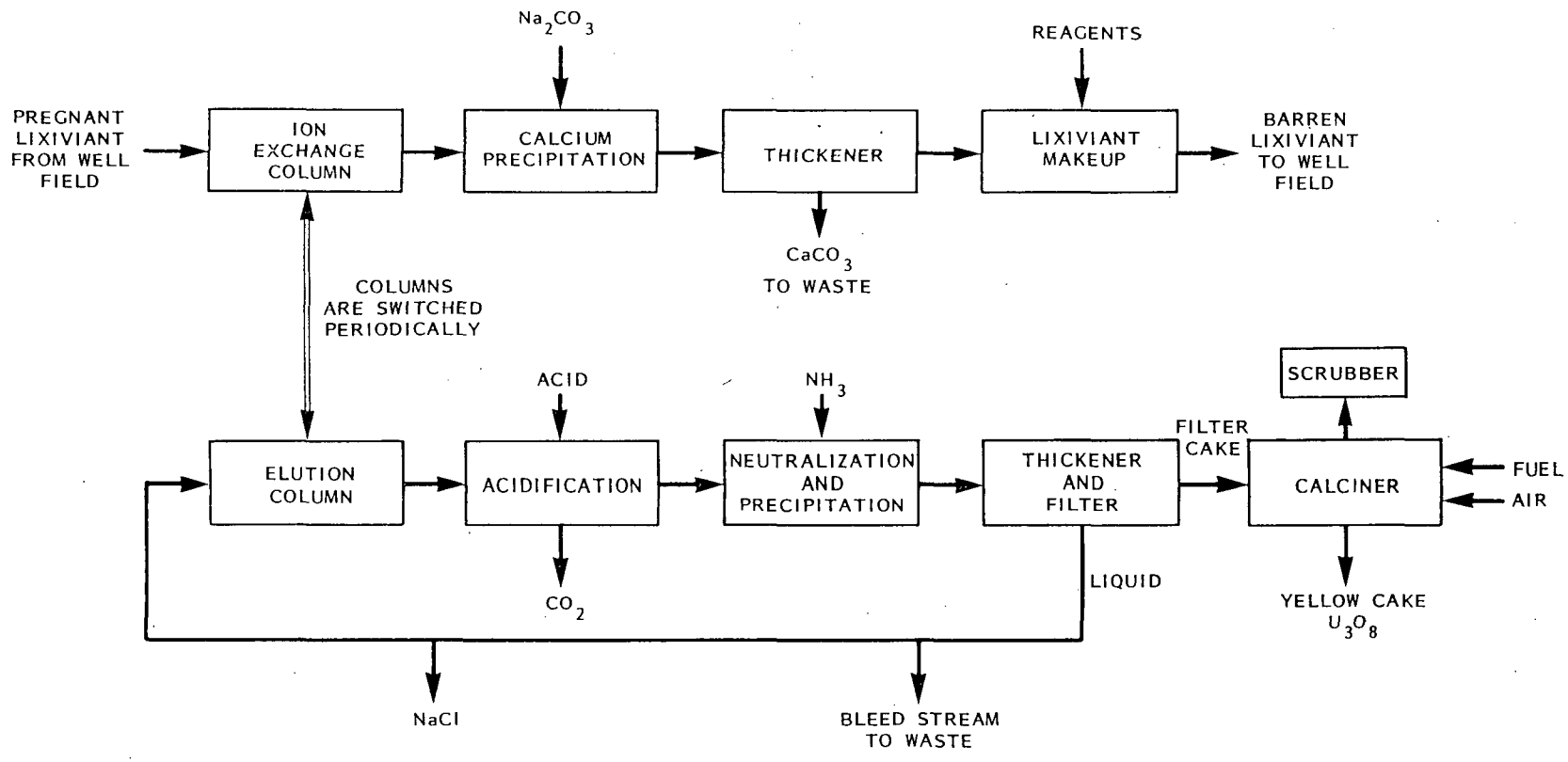

FIGURE 3.2. Typical Alkaline Uranium Recovery Process

Alkaline $(NH_4)_2(UO_2)(CO_3)_2 + 4HCl = (UO_2)(Cl_2)^0 + 2CO_2\uparrow + 2H_2O + 2NH_4Cl$

$2(UO_2)(Cl_2) + 6\ NH_3 + 3H_2O = (NH_4)_2\ U_2O_7 + 4NH_4Cl$

Acid $2H_4(UO_2)(SO_4)_3 + 14\ NH_3 + 3\ H_2O = (NH_4)_2(U_2O_7)\downarrow + 6(NH_4)_2(SO_4)$

The slurry is sent to a thickener and filter or centrifuge where the uranium solids are separated from the eluant. The eluant is then recycled to the elution column and a small bleed stream is taken from the eluant for contaminant control.The uranium solids are calcined to drive off ammonia, leaving a solid product--U_3O_8 (yellow cake).

In some plants, the acidic uranium solution is treated with hydrogen peroxide instead of NH_3 to precipitate uranyl peroxide. The slurry is neutralized with NaOH and sent to a thickener, which produces a thick slurry product (Texas Department of Health, 1979a,b).

3.3 URANIUM ABUNDANCE AND DISTRIBUTION

Uranium is widely distributed in the earth's crust; this is generally true for elements of variable oxidation state. The average crustal abundance is about 2.6 ppm, which places uranium abundance above 22 other naturally-occurring elements. In comparison with this crustal average, primary U tends to be enriched in felsic igneous or metamorphic rocks rather than in mafic or ultramafic rock types. For example, U abundance in granites ranges from 2.2 to 15 ppm; in volcanic glasses, which are usually high in granite components, U ranges from 0.8 to 18.4 ppm; in basalts the range is 0.1 to 0.9 ppm, and ultramafic rocks contain less than 0.8 ppm U (Dyck 1978). In general, U in igneous rocks increases with increasing silica content. Consequently, most U ore bodies are associated, either directly or indirectly, with alkali silicate igneous or metamorphic source rocks.

Approximately 160 known minerals have uranium as an essential constituent. These represent about six percent of all known mineral species, which further demonstrates the ubiquitous nature of uranium. Most of these minerals are rare and are of academic interest only; those of major economic importance are listed in Table 3.2.

Some accessory minerals in igneous and metamorphic rocks contain U and thorium (Th) and are important because of their durability and potential accumulation in sandstones or phosphate deposits. The more common radioactive accessory minerals include zircon, monazite, apatite, sphene, and allanite (an epidote group mineral).

The uranous ion (U^{4+}) has a radius of 1.05 Å, and exhibits extensive isomorphism with Th^{4+} and limited substitution with other elements such as Zr, W, Mo, and Nb. In general, minerals containing the uranous ion, $U(OH)_x^{4-x}$, are less soluble than minerals containing uranyl, $(U^{+6}O_2)^{2+}$, which in part explains

TABLE 3.2. Summary of Economically Important Uranium Minerals

Uraninite[a] (and var. Pitchblende)	UO_{2+X} with Th and Rare Earth Elements
Autunite	$Ca(UO_2)_2(PO_4)_2 \cdot 10\text{-}12H_2O$
Carnotite	$K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$
Tyuyamunite	$Ca(UO_2)_2(VO_4)_2 \cdot 5\text{-}8H_2O$
Uranophane	$Ca(UO_2)_2Si_2O_7 \cdot 6H_2O$
Coffinite	$U(SiO_4)_{1-x}(OH)_{4x}$
Thucholite	U hydrocarbon

(a) Also occurs as a secondary mineral in roll-front deposits.

uranium concentration in redox interface zones. The uranyl dioxide ion (UO_2^{2+}) usually forms part of a layer structure in minerals that can be expressed as $M[(UO_2)(RO_4)]_2 \cdot xH_2O$ where R is P^{5+}, As^{5+}, or V^{5+}.

Most roll-front uranium ore deposits occur in non-marine, fluvial sandstones in confined aquifer systems. The sandstone hosts also contain abundant tuffaceous material. Because magmatic differentiation concentrates uranium in felsic or alkalic rock, the tuffaceous material, which also contains readily leachable glass shards, is probably the source of uranium. Marine sandstones or other sands in nonvolcanic regions are usually barren.

3.4 GEOCHEMISTRY OF URANIUM ROLL-TYPE DEPOSITS

To describe the mobility of dissolved uranium species and explain the occurrence of uranium-bearing minerals we must understand uranium geochemistry. Mineralogy and solution chemistry are determined in studies designed to investigate the genesis of roll-type deposits and are considered in any investigation of leaching or restoration of the mineralized zone and surrounding aquifer. Hostetler and Garrels (1962) published one of the better-known early works on transportation and precipitation of uranium (and vanadium) in groundwater conditions. Their work was updated and expanded by Langmuir (1978), who also included a collection and critical evaluation of the thermodynamic data for many uraniuim solids and dissolved species. Langmuir's compilation of thermodynamic data forms the basis for many of the uranium data sets used in geochemical modeling codes (EQ3/6, Wolery 1980; WATEQ3, Ball, Jenne and Cantrell 1981; WATEQFC, Runnels and Lindberg 1981). Section 5.3 discusses the application of geochemical models to uranium roll-front studies.

Based on the thermodynamic data, uranium is mobile in the natural environment at the tenths of a part per million level in both acid, oxidizing conditions and oxidizing or mildly reducing alkaline conditions (Figure 3.3). For oxidizing conditions, neutral and anionic U(VI) carbonate species dominate at pH 5; and UO_2^{2+} is the most abundant species below this pH (Figure 3.4). For reducing or near-reducing conditions, U(IV) oxide hydroxide species become dominant. Uranium in the +5 valence state has a somewhat restricted stability field between U(IV) and U(VI). Figure 3.3 shows the region in which the common uranium minerals limit the concentration of uranium in solution. We should remember that within the region depicted as stable with respect to a given mineral, uranium species are still dissolved at a certain level. The dissolved level will be below that concentration for which the solid-solution border is drawn. The stippled zone in Figures 3.3 and 3.4 approximates typical groundwater conditions and shows that the predominant dissolved uranium species under these conditions would be a U(VI) carbonate complex or a U(IV or V) oxide or hydroxide.

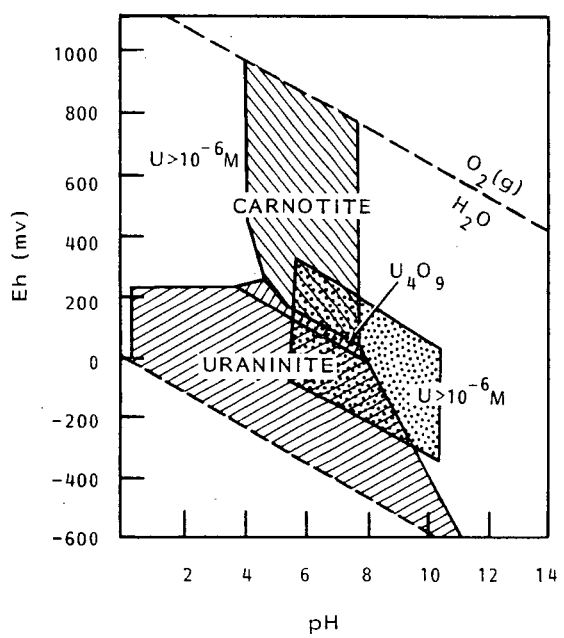

FIGURE 3.3. Eh-pH Diagram in the System K, U, V, O_2, H_2O, CO_2 at 25C. Stippled area represents typical ground-water conditions. Given:
$K = 10^{-3}M$ (39 ppm),
$\sum U = 10^{-6}M$ (0.24 ppm) at mineral-solution boundaries,
$\sum V = 10^{-6}M$ (0.1 ppm as VO_4), and
$P_{CO_2} = 10^{-2}$ atm. (after Langmuir 1978)

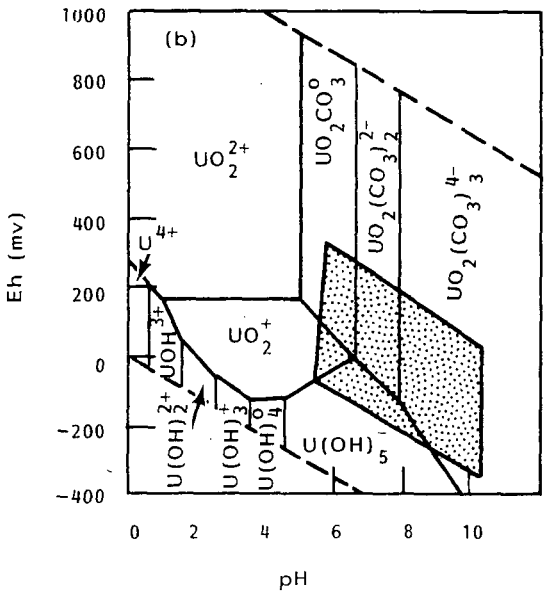

FIGURE 3.4. Eh-pH Diagrams Showing the Relative Importance of +4, +5 (as UO_2^+), and +6 Valent Uranium Species at 25C (after Langmuir 1978). $\sum U = 10^{-6}$M at a typical ground water CO_2 pressure of 10^{-2} atm.

Uranium in roll-front deposits can occur as the minerals uraninite (UO_2) and coffinite ($USiO_4$) (Harshman 1972; Doi, Hirono and Sakamaki 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. Other epigenetic minerals that occur in the ore are: pyrite (FeS_2), marcasite (FeS_2), native selenium, ferroselite ($FeSe_2$), hematite and calcite. 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 (Figure 3.5). In altered sandstone, pyrite occurs only near the ore zone, whereas it is generally absent further into the oxidized portion of the aquifer. Pyrite is commonly most abundant within the ore zone itself, where multiple generations of the mineral may exist. Harshman (1972) describes sand grains with inner and outer rims of pyrite that have a middle rim of uraninite. Presumably, the inner pyrite rim formed after deposition of the sands when reducing conditions were first established, and the outer pyrite rim formed during the uranium mineralization or subsequent to it. Marcasite is much less abundant than pyrite and its relatively high concentration in the ore zone suggests a possible link with the ore formation process. 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 region suggests that it is more readily reduced and subsequently immobilized than uranium (Figure 3.6). Calcite occurs as a cementing material associated

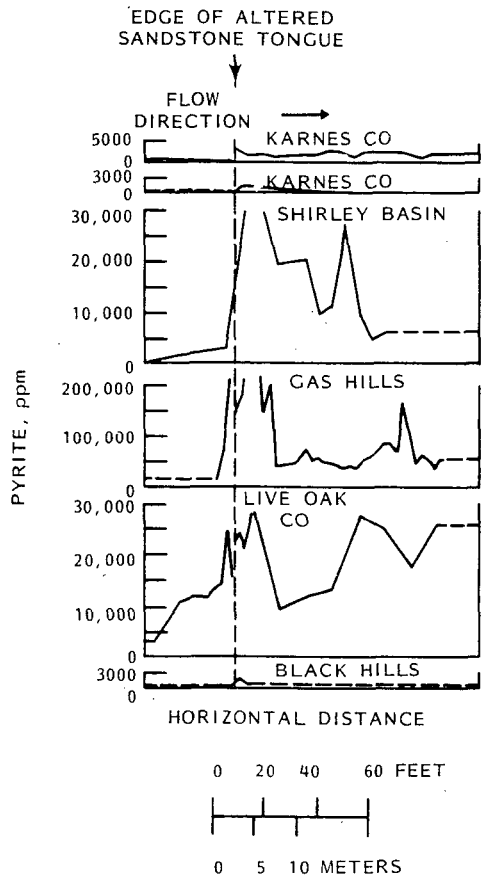

FIGURE 3.5. Distribution of Pyrite (after Harshman 1974)

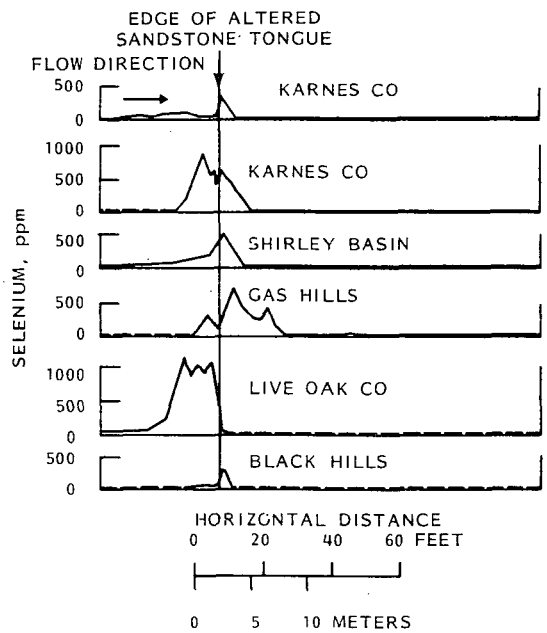

FIGURE 3.6. Distribution of Selenium (after Harshman 1974)

with some ore zones and the surrounding unaltered sands. An explanation for its rather localized occurrence may involve the increased solubility of carbonate minerals generated by the lowering of pH in response to pyrite dissolution. This situation is followed by calcium carbonate precipitation as pH increases in response to the alteration of the primary host minerals.

Hematite and limonite material, often associated with calcite, forms the red and yellow staining that is characteristic of the oxidized zone of the sandstone. Hematite coats other minerals or it lines fractures or cleavage planes.

In addition to these minerals, the elements molybdenum, arsenic, vanadium, beryllium, cobalt, and copper have distinctive distributions about certain roll fronts. These distributions are represented in Figures 3.7 to 3.12. The mineral and element distribution within and around the roll front best indicates the processes responsible for developing the ore zone and its subsequent modifications.

Figure 3.3 shows that U (primarily in the +6 state) is soluble over a fairly wide range of pH-Eh conditions. As a result, uranium is a poor indicator of the chemical character of the transporting medium and of the processes inherent in roll formation. Harshman (1972), however, describes other factors that restrict the conditions under which the roll-front deposits in the Shirley Basin, Wyoming, could have formed. The Shirley Basin appears to be fairly representative of the typical roll-front depositional environment. The arkosic sandstone contains 1 to 5% acid-soluble material (mostly calcium carbonate), which should equilibrate fairly rapidly with the ground water, producing alkaline (pH > 7) conditions. Pyrite is present in the unaltered zone, but not in the altered zone greater than a few tens of feet from the nose of the roll. Carbonaceous material is present in the unaltered zone but not in the altered zone, and Fe^{2+}/Fe^{3+} ratios are 1:1 in the altered zone and 2:1 in the unaltered zone. This evidence suggests that the transporting fluid was oxidizing relative to Fe^{2+}/Fe^{3+} until it reached the region of ore formation. Alkaline, oxidizing ore-bearing solutions are also suggested by the occurrence of selenium in the roll-front region. Selenium, whether it migrates as the selenate ion or as a complex with sulfur, is soluble in most natural waters only under alkaline, oxidizing conditions. It apparently was transported in ground water with these properties and was subsequently deposited in association with the uranium and other elements in response to a change in geochemical conditions. The uranium pH-Eh diagram (Figure 3.3) shows that uraninite can be precipitated from alkaline, oxidizing conditions by lowering the Eh or pH or a combination of the two factors. The Eh can be depressed by a number of possible reductants (H_2S, methane, organic matter, reduced sulfur minerals), whereas the process that most likely would lower pH is tied to sulfur oxidation. Because oxidation of reduced-sulfur minerals also lowers the Eh, this reaction is considered a likely precursor to ore formation.

Harshman (1972) suggests that the uranium roll-front deposits in the Shirley Basin of Wyoming were formed by the long-term migration and concentration of redox-sensitive elements in a confined sandstone aquifer. Uranium, and associated elements, are mobilized by ingressing alkaline, oxidizing

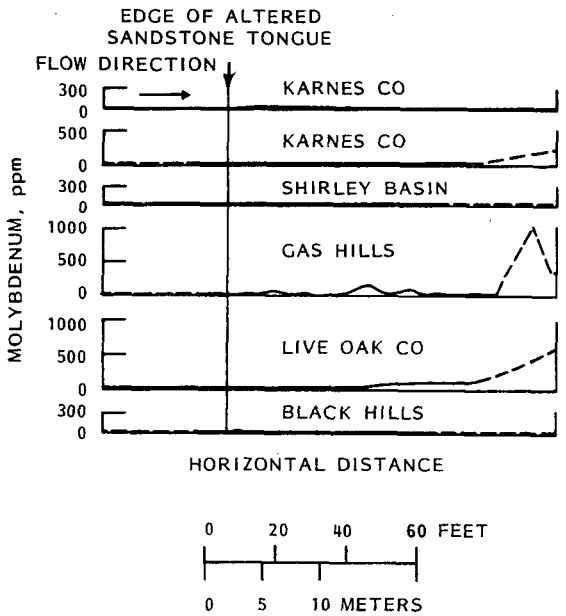

FIGURE 3.7. Distribution of Molybdenum (after Harshman 1974)

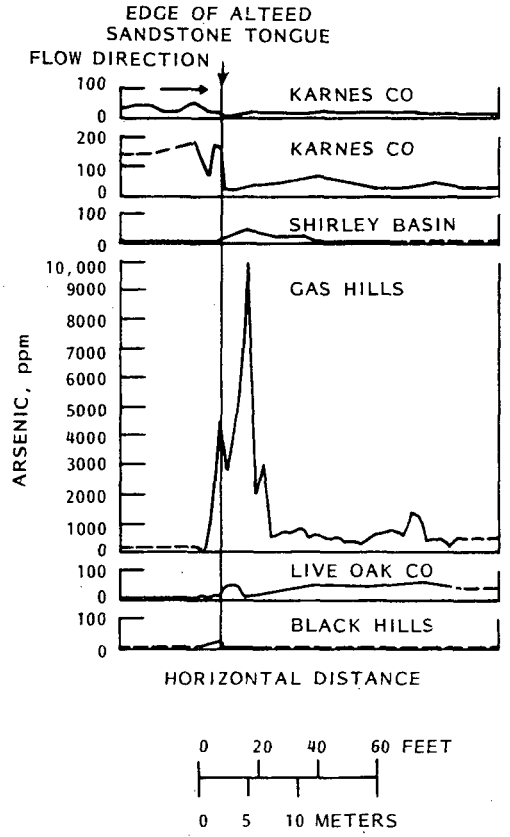

FIGURE 3.8. Distribution of Arsenic (after Harshman 1974)

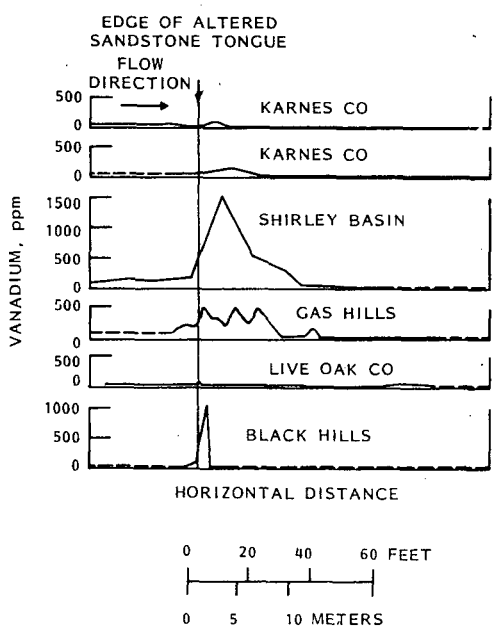

FIGURE 3.9. Distribution of Vanadium (after Harshman 1974)

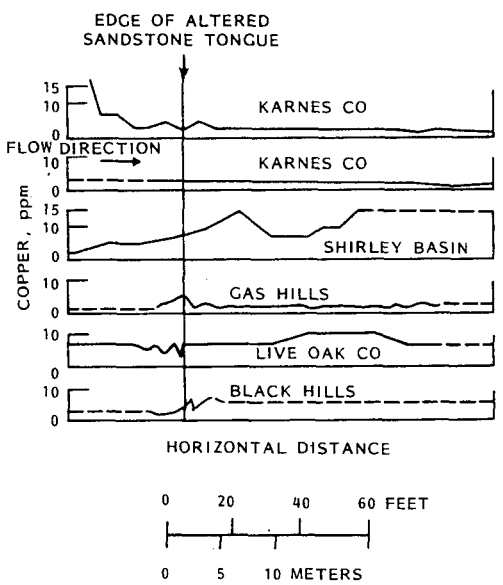

FIGURE 3.10. Distribution of Copper (after Harshman 1974)

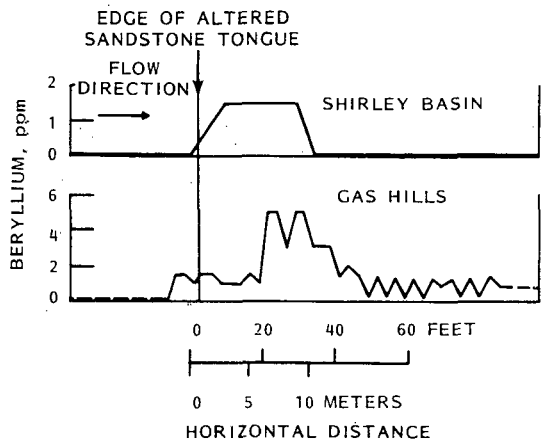

FIGURE 3.11. Distribution of Beryllium (after Harshman 1974)

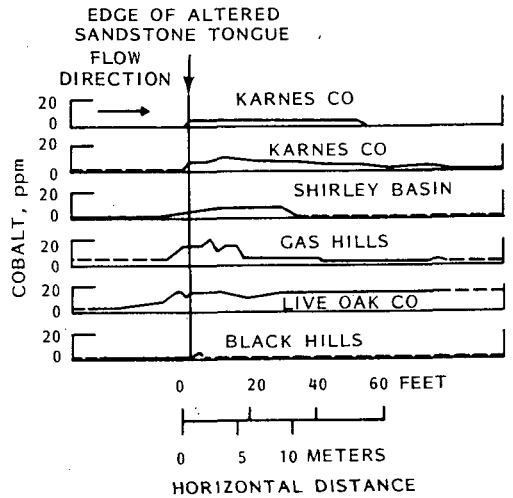

FIGURE 3.12. Distribution of Cobalt (after Harshman 1974)

ground water, which subsequently undergoes an Eh and pH change in response to interactions with reductants 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 accepted and expanded by a number of investigators. Granger and Warren (1974), in order to explain mineralogic variations in roll-type deposits, suggest that soluble ferric thiosulfate [$Fe(S_2O_3)^+$] forms in the alteration zone by oxygenation of authigenic siderite and elemental sulfur. As reducing conditions are reimposed, the ferric thiosulfate precipitates as metastable ferrous carbonate and elemental sulfur. Post ore-forming processes may cause pyrite or limonite to form from the ferrous carbonate or the ferrous carbonate may be removed by leaching. The conditions present in the particular ore zone determine which process occurs, and the variations between deposits. Doi, Hirono and Sakamaki (1975) found that an important concentrating mechanism for uranium in several deposits in Japan was its adsorption onto organic material, ferric hydroxide, clay minerals, and perhaps zeolites. Based on a study of uranium mineralization in the Catahoula Formation of S. Texas, Galloway and Kaiser (1980) state that adsorption of uranium may be the first important step in the concentrating procedure. They note that maximum adsorption of uranium (VI) on a variety of sorbents occurs at approximately pH = 6. This is near the boundary of anionic and neutral species of uranium in carbonate waters and is governed by the fact that the majority of sorbents have a net negative surface charge. Adsorbed U(VI) will desorb if the environment remains oxidizing; therefore, reduction to U(IV) is necessary to fix the uranium in place. Galloway and Kaiser believe that the initial uranium (IV) phase formed by the adsorption/reduction process is probably amorphous UO_2 or $USiO_4$.

The distribution of elements and the probable genesis of the uranium roll-fronts described above provide a great deal of information on the present geochemical environment of the system and suggest techniques for leaching and restoring an ore body. These factors will be considered in subsequent sections of this paper, particularly in the discussion of natural restoration.

3.5 REFERENCES

Amell, A. R., and D. Langmuir. 1978. "Factors Influencing Solution Rate of Uranium Dioxide Under Conditions Applicable to In-Situ Leaching." U.S. Bureau of Mines, Washington DC, Open File Report, OFR 84-79 (NTIS PB-299 947).

Ball, J. W., E. A. Jenne, and M. W. Cantrell. 1981. WATEQ3: A Geochemical Model with Uranium Added. Open-File Report 81-1183. U.S. Geological Survey, Denver, Colorado.

Charbeneau, R. J., et al. 1981. Resource Impact Evaluation of In-Situ Uranium Ground-Water Restoration. CRWR-184. Center for Research in Water Resources, University of Texas, Austin, Texas.

Doi, K., S. Hirono and Y. Sakamaki. 1975. "Uranium Mineralization by Ground Water in Sedimentary Rocks, Japan." Econ. Geol. 70:628-646.

Dyck, W. 1978. "The Mobility and Concentration of Uranium and Its Decay Products in Temperate Surficial Environments." In Uranium Deposits, Their Mineralogy and Origin, Mineral. Assoc. of Canada, Short Course Handbook, Volume 3, ed. M. M. Kimberly, University of Toronto Press, Toronto, Canada.

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 Investigations No. 100. Bureau of Economic Geology, University of Texas, Austin, Texas.

Granger, H. C., and C. G. Warren. 1974. Zoning in the Altered Tongue Associated with Roll-Type Uranium Deposits. IAEA Proceedings. IAEA-SM-183/6, Vienna, Austria.

Harshman, E. N. 1972. "Geology and Uranium Deposits, Shirley Basin Area, Wyoming." Professional Paper 745, U.S. Geological Survey, Washington DC.

Harshman, E. N. 1974. Distribution of Elements in Some Roll-Type Uranium Deposits. IAEA Proceedings. IAEA-SM-183/4, Vienna, Austria.

Hostetler, P. B., and R. M. Garrels. 1962. "Transportation and Precipitation of Uranium and Vanadium at Low Temperatures, with Special Reference to Sandstone-type Uranium Deposits." Ec. Geol. 57:137-167.

Langmuir, D. 1978. "Uranium Solution-Mineral Equilibria at Low Temperatures with Applications to Sedimentary Ore Deposits." Geochim. et Cosmochim. Acta. 42:547-569.

Larson, W. C. 1981. Uranium In-Situ Leach Mining in the United States. U.S. Bureau of Mines Information Circular. No. 8777, Washington DC.

Runnels, D. D., and R. D. Lindberg. 1981. "Hydrogeochemical Exploration for Uranium Ore Deposits: Use of the Computer Model WATEQFC." J. Geochem. Expl. 15:37-50.

Tatom, A., R. S. Schechter and L. W. Lake. 1981. "Factors Influencing the In-Situ Acid Leaching Rates of Uranium Areas," SME-AIME Fall Meeting Paper 81-310.

Texas Department of Health, Radiation Control Branch. 1979a. Environmental Assessment Related to the Everest Minerals Corporation Hobson Solution Mining Project, TRCBEA-1.

Texas Department of Health, Radiation Control Branch. 1979b. Environmental Assessment Related to the Uranium Resources Incorporated Longoria Leach Project, TRCBEA-2.

Thompson, W. E., et al. (Gerahty and Miller, Inc.). 1978. Groundwater Elements of In-Situ Uranium Leach Mining of Uranium. NUREG/CR-0311 (NTIS No. PB 286856), U.S. Nuclear Regulatory Commission, Washington DC.

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 DC.

Tweeton, D. R. 1981. "Restoring Ground Water Quality Following In-Situ Leaching." In In-Situ Mining Research, U.S. Bureau of Mines Information Circular, No. 8852, Washington DC.

Wolery, T. J. 1980. Chemical Modeling of Geologic Disposal of Nuclear Waste: Progress Report and a Perspective. USCL-52748. Lawrence Livermore Laboratory, Livermore, California.

4.0 NATURAL RESTORATION AND SWEEPING

When uranium production ceases the operator is required to restore the ore-zone aquifer and surrounding strata to their pre-mining chemical condition. The topics of this chapter are natural restoration (allowing the natural influx of ground water and the natural capacity of the sediments to restore the production zone via water transport, dispersion and chemical reactions) and ground-water sweeping (withdrawing water via pumping that draws surrounding ground water into and through the production zone to effectively flush the area). Sweep water is disposed of by deep-well injection (in Texas), surface treatment followed by injection, or surface storage and evaporation. Infrequently, surface disposal to neighboring streams is allowed. The surface treatment processes and other induced treatment schemes are discussed in Section 5.0.

This section includes a general discussion of chemical, physical and biological processes which contribute to restoration and a review of available data on the effectiveness of natural restoration and sweeping. In addition, we discuss hydrologic and geochemical models that can be used to simulate the events and processes that occur during restoration.

4.1 RESTORATION MECHANISMS

This subsection describes several natural processes that inhibit the migration of contaminants in ground water or that reduce the concentration of the contaminants in ground water. Reduction-induced precipitation/adsorption of redox-sensitive elements is perhaps the most important retardation mechanism for elements such as V, Cr, As, Se, Mo and U. Reduction of sulfate to sulfide can lower the solution concentrations of Co, Ni, Mn, Cu, Pb, Zn and Mo by forming sulfide minerals. We should note that some scientists believe sulfate reduction requires bacterial mediation to occur at a significant rate under typical aquifer conditions. Reducing conditions can also cause the oxides uraninite (UO_2), V_2O_4 and elemental Se or $FeSe_2$ to precipitate. Roll-front uranium ore deposits exist at the interface of a reducing zone and an oxidizing zone. Thus, the natural condition is a reducing regime with a mineralized zone of UO_2 and the above elemental metals, oxides, and sulfides. After the mining disturbance, the natural reducing conditions can be expected to be re-established over time. Typically, the down-gradient aquifer materials are reduced, so any oxidized spent lixiviant that percolates down-gradient probably will be reduced and solubilized electroactive elements and heavy metals probably will be redeposited. The above re-establishment of reducing conditions will very likely take place in active roll fronts in which metals are being deposited. For those roll fronts that are being naturally oxidized, post in-situ leaching conditions might not re-establish reducing conditions. The status of the ore deposit can be assessed during the baseline studies.

No data were found on the kinetics of reduction in the field but Riding and Rosswog (1979) quote several laboratory studies of the kinetics of iron sulfide formation. Berner (1970) estimates that pyrite formation in the presence of sulfate-reducing bacteria reaches completion in several years at

room temperature. Given the necessary conditions for bacterial growth in the one-zone aquifer and considering the slow rate of ground-water movement (1-10 m/yr), it is possible that contaminants will be removed from the ground water as insoluble sulfides and will not travel far from the leached ore zone.

Conversely, in-situ mining oxidation can also create insoluble precipitates such as manganese and iron oxides that are known as good scavengers for trace metals. Further, oxidation of sulfides to sulfate may precipitate gypsum and the lixiviant addition of total carbonates may induce precipitation of calcite. Both of these slightly soluble calcium salts can scavenge or co-precipitate some trace metals. The oxidation of uranium, vanadium and arsenic that occurs in the leach process may generate high enough concentrations to form insoluble compounds such as carnotite $[K_2(UO_2)_2(VO_4)_2]$ and uranium arsenates. In the roll front, V often occurs with U, but Se usually precipitates up-gradient, Mo precipitates down-gradient, and As patterns are diffuse. The joint occurrence of U and V suggests carnotite as a possible solubility control under oxidizing condition. Thus, during the active leaching period, and as long thereafter as oxidizing conditions occur, some elements may be solubility constrained. Scavenging of trace metals by hydrous iron oxides and perhaps calcite may also be an important retardation mechanism. Formation of hydrous iron oxides is a common water treatment process for waste water (EPA 1977). Uranium scavenging by iron oxides is reduced in the presence of high carbonate concentrations as a result of the formation of the negatively charged soluble carbonate complexes. Thus, scavenging of uranium by hydrous iron oxides may be less important than scavening of other trace contaminants in oxidized regions surrounding in-situ leach sites. Uranyl ion substitution into calcium carbonate has been studied in the laboratory and in field samples (Potter 1976; Lauffenburger and Wey 1966; and Serebrennikov and Maksimova 1977). At natural (low) levels of uranium in solution a calcite-saturated solution will remove about 50% of the uranium upon calcite precipitation. For comparison, hydrous iron oxides often scavenge 90% of selected trace metals (Pb, As(V), Ag) from neutral pH solutions. Iron scavenging for Se(VI), Cr(VI) and Ba is typically less than 20%.

Sandstones in which roll-front deposits are found contain measurable amounts of clay. The clays exhibit significant cation exchange capacities that can interact with soluble contaminants to retard their migration. Further, numerous studies have shown quartz and feldspars contacting neutral pH solutions laden with trace metals can adsorb significant percentages of the metals. Much of the apparently divergent data on trace metal adsorption on oxide surfaces and aluminosilicates has been clarified by recent models (James and Healy 1972; Schindler et al. 1976). In general, trace solution pH and trace metal species distribution followed by solution ligand concentrations, competing macro cation concentrations and adsorbent surface characteristics control trace metal sorption. For in-situ uranium leach environments one can generalize and make the following statements:

- Classical ideal ion exchange constructs do not adequately describe trace metal adsorption. The large concentrations of Ca, Na and perhaps NH_4 present in pregnant lixiviants compete strongly for exchange sites and would yield predictions that minimize trace metal adsorption.

- Adsorption theories based on surface complex formation and electrostatic interaction may better describe adsorption of trace metals. The neutral pH of the lixiviant favors the adsorption of trace metals excepting those likely to be present as anions or soluble anionic carbonate complexes such as As, Se, Mo, V, and U.

- Reaction products such as the hydrous iron oxides may be the most important sorption substrates because the clay content of the sandstone sediments is typically low.

Adsorption of contaminants onto organic matter can significantly retard contaminant migration if significant quantities of organic matter are present. Roll-front U deposits sometimes are associated with coal, oil, or gas deposits; thus, the presence of organics in the aquifer should be evaluated. The adsorptive properties of organic matter may in fact be a reflection of their association with and ability to create reducing conditions. The reduction-induced precipitation process previously discussed may be the driving force behind organic sorption. Bacterial-induced precipitation may also be predominately a reduction process.

For the macro anions (bicarbonate, sulfate and chloride) present in pregnant lixiviant, adsorption reactions are minimal. Precipitation of calcite ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$) can reduce concentrations of carbonate and sulfate, but neither salt is insoluble enough to drop concentrations down to baseline values in potable or near-potable aquifers. Thus, some other mechanism must be available. The only natural process is dispersion/dilution with natural ground waters. Qualitatively, the in-situ U leach system should be significantly influenced by dispersion. At the end of production, the pore volume of spent lixiviant represents a small volume source in the overall aquifer. Dispersion is most effective on point or small-volume sources. Further, the sandstone aquifer is most likely to comprise several horizontal layers with long-range horizontal correlations. Typically, the horizontal permeability of the sandstone aquifers is 100 times greater than the vertical permeability; thus, flow within the sandstone strata versus depth on a small scale should show large variations in horizontal flow rates. Such a physical setting should present a good example of an aquifer with non-Fickian transport. Non-Fickian transport usually implies large dispersion. A good review article and discussion of the dispersion effects in both Fickian and non-Fickian regimes is Simmons (1982). Specific calculations of the ability of dispersion to reduce the concentrations of solutes from a slug of spent lixiviant would require a knowledge of the physical setting, and hydrologic and geochemical data, but a reasonable estimate of the effect of dispersion predicts an order of magnitude reduction in minimally-interacting constituents such as Cl, SO_4, HCO_3 would occur from a 10-to-20-acre commercial in-situ leach site within a few miles down-gradient. For chemically reactive species (those that adsorb, precipitate, etc.) the reduction occurs much sooner. That is, dispersion has an even greater favorable affect on reactive constituents.

In summary, numerous natural processes can remove contaminants from solution, retard their migration from the ore production zone and dilute the concentration of contaminants over space and time. The more important process for

electroactive elements such as As, Se, Mo, V and U and selected trace metals is precipitation down-gradient as insoluble compounds that include sulfides and lower valence state oxides (e.g., UO_2). An important process for some metals and ligands is coprecipitation and scavenging on hydrous iron oxides, gypsum, and calcite. Ion exchange onto clays and chemi-sorption onto quartz, feldspars, and hydrous oxide phases can significantly influence the migration of transition metals, ammonia, alkaline-earth cations, and to some extent, alkali-metal cations. Dispersion is probably the most important process for reducing anionic species like Cl, SO_4 and HCO_3. Potentially mobile trace contaminants are oxidized species of U, Mo, V, As, Se, and Cr.

4.2 AVAILABLE LABORATORY AND FIELD DATA ON THE EFFECTIVENESS OF NATURAL RESTORATION

We located only one report that specifically explores natural restoration via laboratory study (Kidwell and Humenick 1981). The objective of Kidwell and Humenick's study was to determine the quantity of trace elements released to ground water when spent ore was leached, and to what extent down-gradient sediments could remove the leached constituents. This was done by pumping NH_4^+-based lixiviants through ore zone sediments at mining flow rates until U dropped to 10 ppm (normal cut-off value for commercial production); leach mining was then stopped and simulated ground water was pumped through the ore sediments to simulate sweeping. The sweep water was chemically analyzed and pumped through fresh ore zone sediments. The final eluent was chemically analyzed to determine the amount of restoration. The restoration part of the experiment was performed using N_2-gas saturated waters to simulate reducing conditions. An in-line pH/Eh monitoring system measured these parameters after exiting the leached ore sediment column. The elements U, V, Mo, As, and Se were monitored but Se analyses (AA-hydride generation) proved sporadic and were not reported.

For three different ore-bearing sediment types, at the beginning of ground-water sweeping, V, As, and Mo concentrations exiting the leached ore column were below EPA-recommended limits (V < 2 ppm, As < 0.005 ppm, Mo < 1 ppm). Uranium exceeded its 2 ppm limit for up to 25 pore volumes of sweep for one ore, whereas the U concentration fell to 2 ppm in 6 and 9 pore volumes for the other two test cases. Note that these low concentrations for V, As and Mo were observed without additional percolation into unleached ore or down-gradient sediments.

When a second column of unleached ore-bearing sediments is contacted in series with the sweep ground water (1 pore volume of water is flushed out of the first column before connecting the second column in series to remove the residual spent lixiviant), Mo concentrations in solution from the second column peak in the first pore volume at levels below that leaving the first column during active leaching. Uranium peaked between the 7th and 13th ground-water sweep pore volume at 21 ppm, well above the 10 ppm U concentration in solutions from the first column at the end of active leaching. The cause for the uranium release is not explained, but it should be noted that the second column contained ore grade sediment, not down-gradient reduced sediment. Kidwell and

Humenick also caution that as Mo is typically found down-gradient from U, and because Mo appears to rapidly oxidize and mobilize, Mo release from down-gradient sediments may occur.

In a second experiment, two unleached ore sediment columns were attached in series to the leached column. The simulated ground water from column one was sequentially percolated through columns 2 and 3. The uranium effluent concentraton curve of column 3 lagged column 2 by one pore volume and the peak concentration was slightly lower at 29 ppm U versus 31 ppm U. The data suggest no further mobilization of uranium between column 2 and 3 but also show no further removal of leached U. In contrast the third column removed a significant portion of the Mo leaving column 2, but again the highest Mo concentrations occurred in the first pore volume of effluent from each column.

In one leach/sweep experiment the Eh was continuously monitored at the effluent end of the first column. At peak U concentration the Eh measured +480 mv; when the U concentration dropped to 10 ppm the Eh was +450 mv. Sweeping with N_2-saturated, simulated ground water dropped the Eh over 10 pore volumes to +390 mv, and continued sweeping slowly reduced the Eh to +350 mv. [Note, these Ehs are different than those reported by Kidwell and Humenick because they used an incorrect conversion factor to compute Eh from the measured potential.] The data suggest that the leached ore column either flushes spent lixiviant slowly (it took 25 pore volumes of sweep before the effluent Eh remained at the initial value of the N_2-sparged, simulated groundwater) or that the spent ore zone supplies some residual oxidation capacity. Alternatively, the difficulty in maintaining air-tight experiments and difficulty in Eh measurement itself may be causing the observed Eh trend.

This work offers a rudimentary look at natural restoration. Experiments to be performed at PNL will improve upon this work by utilizing actual down-gradient non-ore grade sediments, reducing the velocities of the ground-water sweeps when natural restoration is being examined, filtering column effluents to remove particulates, analyzing a larger suite of elements, using more sensitive and precise measurement procedures, and measuring Fe^{2+}/Fe^{3+} and perhaps As^{3+}/As^{5+} analytical couples as well as Eh. (The Kidwell and Humenick study used flow rates of 300 m/yr during the ground-water-sweep phase. These velocities are about 100 times faster than natural flow rates. Thus, they more correctly investigated induced sweeping of spent lixiviant through non-leached ore sediments as opposed to true natural restoration.)

Our literature review did not identify any field data for natural restoration. Possibly, one could find some short-term, near-field data by collecting water quality data from wells at existing pilot-scale or commercial sites which have been put on standby during this period of depressed uranium prices.

Several sources of field data are available on ground-water sweep for pilot tests and perhaps on one or two commercial enterprises. Review documents (Riding and Rosswog 1979; and Buma et al. 1981) and environmental reports and environmental statements for individual sites (prepared for licensing requests) are available. In general, mining companies currently use ground-water sweeping coupled with deep-well injection or evaporation pond storage to flush the

first pore volume or so of spent lixiviant. Past attempts at relying solely on ground-water sweeping on pilot tests have shown anywhere from 2 to 25 pore volumes are needed to restore baseline conditions for minimally interacting constituents. Strongly interacting species, notably NH_4^+, oftentimes never dropped to baseline. Such large volumes of flush water and the inability to reduce the concentration of strongly interacting species to baseline have necessitated the coupling of ground-water sweeping with other induced-restoration processes. A cursory look at data from individual sites shows that problem constituents (in terms of reduction to baseline values) include NH_4^+, HCO_3^-, UO_2^{2+}, MoO_4^-, SO_4^{2-} and perhaps Ca^{2+}, Mg^{2+} and Na^+ in some cases. Most of the chemical analyses are not complete enough to evaluate trace metals or Ra.

In general, we can state that some amount of sweeping is beneficial in that a large portion of the high total dissolved solids content can be rapidly removed from the production zone. After the initial reduction, complicating processes such as dispersion, precipitation, and adsorption combine to slow the cleansing process. Sweeping by itself would require too much water and generate too large an amount of contaminated water to be practical. On the other hand, results based solely on pilot tests probably underestimate the effectiveness of sweeping when reported on a per pore volume basis. Because of hydrodynamic streaming, the flushing of a small pilot scale site may require 5 to 10 pore volumes to remove the residual lixiviant, but in an actual commercial site with a much larger pore volume, streaming of outside water into the sweep wells would be much less important, and perhaps 2 or 3 pore volumes would be adequate. For a commercial site of 10 to 20 acres, an effective pore volume would be 5×10^7 gal.

4.3 APPLICATION OF GEOCHEMICAL AND HYDROLOGIC MODELS FOR SIMULATING NATURAL RESTORATION

Any theory of roll-front formation is a genetic model for the system. As such, the ideas of Harshman (1972), Granger and Warner (1974) and Galloway and Kaiser (1980) discussed in Section 3.4 on the geochemistry of uranium are conceptual models for the system. These conceptual models can be used with geochemical and hydrologic computer modeling programs to simulate the process of mineralization and to provide estimates of the effectiveness of the natural system in retarding pollutant migration from a leach-mined zone. The models considered here are the available geochemical and hydrologic modeling codes. Examples are included of how the models have been used in studies related to uranium roll fronts.

In essence, geochemical models for aqueous/solid systems consider four separate but interrelated processes: ion speciation, mineral solubility, adsorption/ion exchange, and mass transfer. A schematic of how a model might interrelate these functions is shown in Figure 4.1. The analytical concentration of dissolved constituents is entered into an ion speciation submodel which speciates the elements among their various complexes and computes an activity (effective concentration) for each element and its complexes. The dissolved species equilibrate with the available ion exchange sites and adsorb reversibly onto specified solid phases. The solubility submodel uses the resultant solution data to compute the degree of saturation of the fluid with respect to

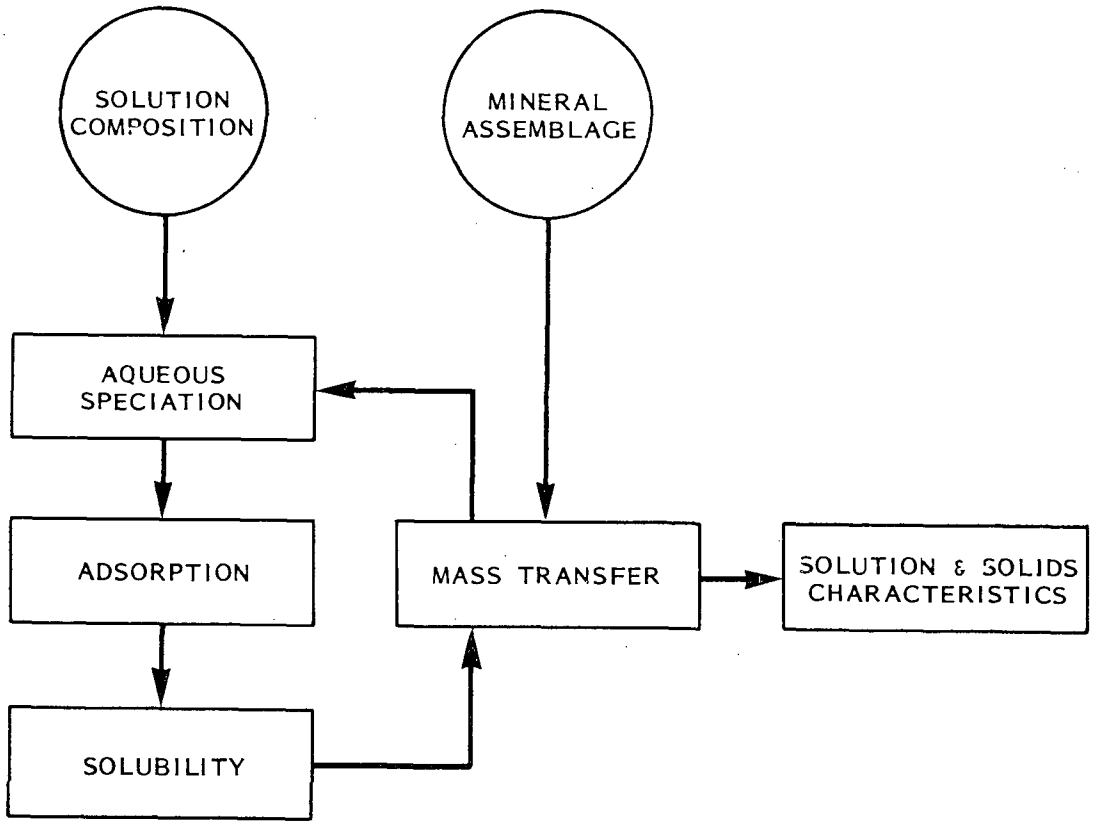

FIGURE 4.1. Flowchart of a Geochemical Model

minerals in the code data base. The mass transfer of constituents between the solid and liquid phases requires respeciation of the elements; consequently, an iteration routine is necessary to cycle through the submodel until all solid phases are in equilibrium or undersaturated. The final product of the geochemical model is a description of the chemistry of the solution and the solid phases with which it is at equilibrium (either partially or complete).

Modeling of natural and polluted waters, as well as laboratory solutions over the last half decade has indicated that a subset of the naturally occurring minerals and other solids have sufficiently rapid kinetics to serve as effective solubility limits. This situation is referred to as partial local equilibrium.

Conversely, many minerals have been identified which are quite generally oversaturated, thus, do not equilibrate with the waters with which they are in contact. Notwithstanding, these minerals may well be forming but at rates which are too slow to limit the concentrations of any of their constituents. As additional geochemical modeling of aquifers and both field and laboratory studies are carried out, some additional minerals and other solids will be added to this subset and more information concerning the exact conditions under which specific minerals form will be developed. Until now, the primary emphasis - of necessity - of geochemical modeling has been the determination of which of the multitude of existing solid phases do in fact form at sufficient

rates to limit the concentration of dissolved constituents. A significant example is the study of the reactions between acidic uranium mill tailings and the associated clay liners.

We observe that certain solids form in various environments and other solids rarely, if ever, form at ambient temperature and pressure. Another subset of minerals appear to form occasionally. The present need is to model a wide enough range of conditions to increase our confidence in the members of these subsets and to delineate the conditions under which certain solids form in one place, but not in another, even though they are oversaturated in both places. Application of reaction path models to low temperature environments generally necessitates removing from the data bank those solid phases which are not known to equilibrate with formation water or experimental solutions under the existing conditions. With the notable increase in geochemical modeling in this decade, we are now on the verge of using the accumulated knowledge in a predictive mode. There is a pressing need to assemble and evaluate the available geochemical modeling data to delineate the conditions under which the various minerals and other solids form at sufficient rates to effectively limit the concentration of dissolved constituents.

Several investigators have used thermodynamic geochemical models as an aid in understanding the processes of roll-front formation. Capuano (1977) used a reaction path code (of the type described by Helgeson et al. 1970) to simulate the interaction of: 1) oxidized, acidic, uranium-bearing ground water with reduced sandstone, and 2) reduced, uranium-bearing, carbonate ground water with a kaolinite and hematite-bearing altered sandstone, or mixing with an acidic ground water. In all cases, Capuano found that the sequence of mineral precipitation/dissolution mimicked that of a roll-front for the minerals considered (uraninite, pyrite, montmorillonite and calcite). Trace elements (As, Se, and Mo) distributions were not modeled because of a lack of thermodynamic data for these elements in the model. A simulation of this type would be useful, with additional thermodynamic data, to test alkaline, oxidizing, ore-bearing solutions. Runnells et al. (1980) and Runnells and Lindberg (1981) have used the aqueous speciation and solubility routines in the WATEQFC model as uranium exploration tools and as a guide to understanding ore genesis. They have shown that plotting uraninite saturation indices on a map of the areal distribution of a roll front clearly delineates the pattern of ore occurrence. This is not the case for the dissolved uranium concentration in the ground water. The uranium concentration may be lower (because of precipitation) in the actual ore zone than in the aquifer surrounding the deposit. These and other geochemical modeling codes can be used with hydrologic codes to simulate mass transport through an aquifer.

Hydrologic codes require physical data on the aquifer's extent, permeability, porosity, transmissivity, hydraulic gradient and storage coefficient. The data are used to develop a ground-water flow model that can be used to simulate natural ground-water movement and response of the system to operational mining and restorative processes. Schmidt et al. (1982) describe a geochemical mass transport model that includes hydrology, solute transport, and uranium dissolution kinetics. The model divides a leachate flow pattern from an in-situ mining operation into discrete hydrologic components (individual

streamlines) and then models the chemistry and mass transport for each of these components separately. The model is capable of predicting the impact of operator-controlled parameters (well configuration, pumping schedule, and oxidant injection concentration) or site-dependent parameters (aquifer permeabilities, ore grade, competing minerals) on individual steamline productivity.

A comparison of sweeping with forward and reverse recirculation using a computer model was presented in Riding and Rosswog (1979). The model was purely hydrologic, and assumed no cation exchange. It defined restoration as the time when the extracted solution was no more than 10% leach solution. The results indicated that restoration was achieved in 24 days, and all the leach solution was removed after 24.4 days of sweeping. Reverse recirculation allowed restoration, as defined here, to be attained in 13.3 days, but only 26% of the leach solution was recovered by that time. The model used hypothetical but typical input parameters.

The computer modeling of aquifer restoration and, in particular, ammonium migration is discussed by Walsh et al. (1979). Ammonium is not a major dissolved constituent of any of the ground waters associated with uranium-bearing sandstone aquifers; consequently, if it is used as the cation in the lixiviant, it will have to be removed almost in total during restoration. This removal will be hindered by the sorption of ammonium onto the cation exchange sites of the clays present in most of the sandstones. The restoration model developed by Walsh et al. (1979) can be used to predict the rate of ammonium migration in ground water as a function of ground-water flow, ground-water composition and the cation exchange capacity of the ore body. Using typical environmental conditions for a South Texas confined aquifer (ground-water velocity = 28 ft/yr, CEC = 5 meq/100g, porosity = 0.3, $K_D, NH_4^+ = 5$), they show that during the first 7 to 14 years of migration the ammonium front can have a high concentration because anion concentration is also high. The ammonium front can move on the order of hundreds of feet during this period of time. After the anion wave has passed, ammonium concentration drops to the ppm level and it moves less than a foot per year in the majority of the simulations.

The modeling studies of solute transport described above consider two of the important chemical aspects of restoration: mineral dissolution and ion exchange. To adequately represent natural restoration, mineral precipitation should be added to these processes and the dissolution of a wider variety of minerals must be considered. Geochemcal models such as WATEQ3 (Ball et al. 1981), WATEQFC (Runnels and Lindberg 1981), and EQ3/6 (Wolery 1979) can be used to determine which elements and compounds must be incorporated into the solute transport model for adequate simulations of restoration processes.

4.4 SECTION SUMMARY

To date, no company has proposed natural restoration nor has any regulatory agency accepted natural restoration as the sole activity to cleanse the contaminants left in the produced ore zone after in-situ leaching. The mechanisms involved in natural restoration are complex, and it is difficult if not impossible to predict the time and distance required for the contaminant removal process to be effective and the degree of contaminant removal possible.

Some people claim that the amount of in-depth site specific data that would have to be collected to evaluate the potential for natural restoration is prohibitive. In defense of natural restoration, the hydrologic (dispersion/dilution) and physiochemical (reduction, precipitation, coprecipitation, scavenging, chemisorption and ion exchange) processes discussed in Section 4.1 appear capable of mitigating the rapid transport of high concentrations of contaminants released from leached sediments or added during the lixiviant or recycle water injection. These processes are identifiable and known to be effective. Mathematical models of the hydrologic and physiochemical processes based on Darcy's Law and the laws of thermodynamics exist and can be used in evaluating and predicting the fate of solubilized trace constituents in in-situ leached sediments. The regional stratigraphy and hydrology of typical roll front U deposits are adequately described by porous media hydrologic models. These porous media models are well-established tools and are accepted by technical, managerial and regulatory bodies. Currently, great strides are also being made in hydrologic modeling of fractured media. Transport along fractures may be important in the case of certain deposits.

Chemical models have in the last five years been used to study U exploration, U waste disposal (Markos and Brush 1981; Peterson and Krupka 1981), and in-situ U leach mining. Details in Section 4.3 support the conclusion that many of the processes that occur in these activities appear to be adequately described by thermodynamic models. Thus, a long term predictive tool (thermodynamic computer codes) is available to evaulate the fate of uranium and associated elements in the geosphere.

The few laboratory data available need to be augmented with more laboratory and field data before definitive predictions on the effectiveness of natural restoration can be made, but tools are available that, given the necessary input data (hydrologic and chemical), should be capable of significantly improving our knowledge.

The effectiveness of natural restoration in reducing mine-induced contaminants is important for several reasons. First, after any induced-restoration activity there is no guarantee that slow reactions may not degrade the system. Regulatory agencies have set very finite time regulations that mining companies must meet. As long as the mining companies meet the restoration requirements within the specified time limit, a final clearance must be granted. Reactions that occur after a site has been officially designated as restored must rely on the capacity of the natural system to mitigate further degradation. In other words, natural restoration is the only practical long-term process available to protect the environment.

Secondly, restoration using active techniques has not been as easily achieved as originally thought. Most mining enterprises are behind schedule and a complete restoration of a commercial in-situ U leach site has never been demonstrated. Cost analyses by Riding and Rosswog (1979) and Buma et al. (1981) show that restoration can represent a significant amount of the cost of U production by in-situ leaching. Thus, if some amount of reliance on natural restoration were possible and advisable, the problems and costs involved in restoration would be significantly lessened.

4.5 REFERENCES

Ball, J. W., et al. 1981. WATEQ3: A Geochemical Model with Uranium Added." USGS Open File Report 81-1183. Denver, Colorado.

Berner, R. A. 1970. "Sedimentary Pyrite Formation." Am. Jour. Sci., 268:1-23.

Capuano, R. M. 1977. "Chemical Mass Transfer and Solution Flow in Wyoming Roll-Type Uranium Deposits." M.S. Thesis U. of Arizona, Arizona.

Environmental Protection Agency (EPA). 1977. Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations. EPA-600/8-77-005, Washington, D.C.

Helgeson, H. C., et al. 1970. "Calculation of Mass Transfer in Geochemical Processes Involving Aqueous Solutions." Geochim. Cosmochim. Acta. 34:569-592.

James, R. O., and R. W. Healy. 1972. "Adsorption of Hydrolyzable Metal Ions at the Oxide/Water Interface. I. Co(II) Adsorption on SiO_2 and TiO_2 as Model Systems, II. Charge Reversal of SiO_2 and TiO_2 Colloids by Adsorbed Co(II), La(III), and Th(IV) as Model Systems, III. A Thermodynamic Model of Adsorption." J. Colloid Interface Sci. 40:42-81.

Kidwell, J. R., and M. J. Humenick. 1981. Assessment of Trace Ground Water Contaminants Released from South Texas In-Situ Uranium Solution Mining, CRWR-179, Center for Research in Water Resources, The University of Texas at Austin, Austin, Texas.

Lauffenburger, I., and R. Wey. 1966. "Incorporation of Uranyl Cations into Carbonates During Formation." Full. Chim. Soc. France 287:1743-1749 (In French).

Markos, G., and K. J. Brush. 1981. Contamination of Ground and Surface Waters by Uranium Mining and Milling, Vol. II. Field Sampling and Empirical Modeling. Geochemistry and Environmental Chemistry Research, Inc. Final Report to U.S. Department of Interior Bureau of Mines, Contract No. J0295033, Washington, D.C.

Peterson, S. R., and K. M. Krupka. 1981. "Contact of Clay Liner Materials with Acidic Tailings Solution II. Geochemical Modeling." In Uranium Mill Tailings Management Proceedings of the Fourth Symposium, pp. 609-626.

Potter, R. W. 1976. Some Geochemical Parameters Effecting the In-Situ Leaching of Uranium. USGS Open File Report 76-835, 24 p.

Riding, J. R., and R. J. Rosswog. 1979. Restoration of Ground-Water Quality After In Situ Uranium Leaching. Ford, Bacon and Davis Utah, Inc., for U.S. Department of Interior Bureau of Mines, Contract No. J0275028, Washington, D.C.

Runnells, D. D., and R. D. Lindberg. 1981. "Hydrogeochemical Exploration for Uranium Ore Deposits: Use of the Computer Model WATEQFC." J. Geochem. Expl. 15:37-50.

Runnells, D. D., et al. 1980. "Applications of Computer Modeling to the Genesis, Exploration, and In-Situ Mining of Uranium and Vanadium Deposits." Memoir 38. New Mexico Bureau of Mines and Mineral Resources, Socorro, New Mexico. pp. 355-367.

Schindler, P. W., et al. 1976. "Ligand Properties of Surface Silanol Groups I. Surface Complex Formation with Fe^{3+}, Cu^{2+}, Ce^{2+}, and Pb^{2+}." J. of Colloid Interface Sci. 55:469-475.

Schmidt, R. D., et al. 1982. "Geochemical Kinetics Model for In-Situ Leach Mining." Presented at 111th AIME Annual Meeting, Feb. 14-18, 1982, Dallas, Texas.

Serebrennikov, V. S., and I. G. Maksimova. 1977. "The Deposition Mechanisms of Uranium from Mineral Waters Containing CO_2." Geochemistry International, 13(5):167-174.

Simmons, C. S. 1982. "A Stochastic-Convective Transport Representation of Dispersion in One-Dimensional Porous Media Systems." PNL-SA-10322, Pacific Northwest Laboratory, Richland, Washington, Accepted for publication in Water Resoures Research.

Walsh, M. P., et al. 1979. "A Model for Predicting the Restoration of an Ammonium Migration from In-Situ Mine Sites." South Texas Uranium Seminar, Corpus Christi, Texas.

Wolery, T. J. 1979. "Calculation of Chemical Equilibrium Between Aqueous Solution and Minerals: The EQ3/6 Software Package." UCRL-52658. Lawrence Livermore Laboratory, Livermore, California.

4.6 OTHER LITERATURE CONSIDERED

Bureau of Mines. 1981. In-Situ Mining Research Proceedings: Bureau of Mines Technology Transfer Seminar, Denver, Colorado, August 5, 1981. IC 8852.

Camp Dresser and McKee, Inc. 1981. Environmental Report Texaco Inc. and Sunoco Energy Development Co. Hobson TEX-1 In Situ Uranium Project. Prepared for Texas Department of Health.

Charbeneau, R. J., et al. 1981. Resource Impact Evaluation of In-Situ Uranium Groundwater Restoration. CRWR-184, Center for Research in Water Resources, the University of Texas at Austin, Austin, Texas.

Cowan, E. W., et al. 1980. Some Implications of In Situ Uranium Mining Technology Development. PNL-3439, Pacific Northwest Laboratory, Richland, Washington.

Hill, A. D. 1978. Restoration of Uranium In-Situ Leaching Sites. SPE 7534 Society of Petroleum Engineers of AIME Proceedings of 53rd Annual Fall Meeting Houston, Texas, Oct. 1-3, 1978.

Hunkin, G. G. 1975. "The Environmental Impact of Solution Mining for Uranium." Mining Congress Jour. 61:24-27.

Nuclear Regulatory Commission. 1980. Draft Environmental Statement Bison Basin Project, Ogle Petroleum, Inc., NUREG-0687.

Thompson, W. E., et al. 1978. Ground-Water Elements of In-Situ Leach Mining of Uranium, NUREG/CR-0311 completed for NRC by Geraghty and Miller, Inc.

Tweeton, D. R., et al. 1979. Geochemical Changes During In-Situ Uranium Leaching with Acid. SME Preprint 99-43, published in In-Situ Uranium Mining and Ground Water Restoration edited by W. J. Schlitt and D. A. Shock.

5.0 INDUCED RESTORATION

5.1 LONG TERM SWEEPING

Sweeping and other restoration techniques are discussed in the Bureau of Mines contract report titled "Restoration of Groundwater Quality After In Situ Uranium Leaching" (Riding and Rosswog 1979). Much of the material in this section is taken from that report.

5.1.1 Process

Sweeping is a process of pumping water from wells in the leach field without any injection of leach solution or recycling of water. The hydrologic cone of depression created by the pumping causes ground water surrounding the leach zone to flow into the zone, so much of the leach solution is replaced by ground water.

5.1.2 Effects on Ground Water

When a comercial site uses only sweeping for restoration much more ground water is consumed than when recycling is used. If plug flow with no mixing or geochemical reactions is assumed, then incoming ground water can replace leach solution fairly rapidly. Riding and Rosswog (1979) calculated a replacement time of 25 days of pumping, using hypothetical but typical site conditions. However, restoration pumping must continue much longer than calculated, assuming no mixing takes place, to allow sufficient cation exchange.

The University of Texas report titled "Resource Impact Evaluation of In-Situ Uranium Groundwater Restoration" (Charbeneau et al. 1981) points out the large consumptive use of ground water if sweeping is employed. Restoration of U.S. Steel's Moser production area is predicted to require nearly a billion gallons of water, and that is assuming only 6.3 pore volumes of flushing will be sufficient.

The water requirements of the south Texas area, an area not densely populated, are now easily met by the existing ground-water supplies. The total ground-water availability is about 80,000 acre-ft/yr; water use is currently at 40,000 acre-ft/yr and is expected to increase to 60,000 acre-ft/yr by the year 2000 (Charbeneau et al. 1981). Calculations in the above report indicate that restorations could use all of the available water, and that while restoration to baseline by ground-water sweep without recharge appears possible, the cost in terms of water use is high. Also, the surface handling of these large quantities of water may present problems.

The effect of ground-water sweeping in areas where ground water is already in short supply will naturally be even more severe. In Texas, the current value of water in the aquifer is zero. In New Mexico and many parts of Wyoming and Colorado, ground water has a significant value, and water rights must be

purchased. Thus, economic factors and regulatory agencies may preclude unrestricted sweeping to be an acceptable restoration technique, especially in areas where ground water has significant value.

5.1.3 Waste Disposal

The ground water consumed by sweeping must be disposed of; usual disposal options are deep disposal wells and evaporation ponds. Deep disposal wells cost less per unit of capacity.

Riding and Rosswog (1979) indicate that the estimated total cost for a pond system of 200,000 and 1,000,000 gpd capacity were $6.23 and $5.98, respectively, per 1000 gal, assuming 40 in./yr net evaporation rate. The costs are almost inversely proportional to the net evaporation rate. In contrast, the total costs for deep disposal wells of corresponding capacities are $3.96 and $2.50 per 1000 gal. The cost per acre of pond reported by operators of several evaporation ponds is somewhat higher than estimated in Riding and Rosswog (1979). Also, the net evaporation rate in many areas of in-situ mining is <40 in./yr. The cost of wells reported by operators was usually similar to that reported in the Riding and Rosswog report. Thus, the cost difference between ponds and wells will often be even greater than indicated in the Riding and Rosswog (1979) report.

Evaporation ponds are used in Wyoming, where permits for disposal wells for in-situ mining are difficult to obtain. Disposal wells are used in Texas. The Crownpoint operation in New Mexico used evaporation ponds, but the required size was reduced by recycling.

A combination of ground-water sweeping with no recycling plus complete reliance on evaporation ponds could be a very expensive disposal technique. Where the evaporation rate is 30 in./yr, an acre of pond surface is required for every 1.5 gpm of solution. Ponds cost $50,000 to $100,000/acre. Thus, handling 600 gpm would require a 400-acre pond costing $20,000,000 to $40,000,000.

5.2 IN-SITU TREATMENT METHODS

In-situ treatment of contaminated ground water has been proposed as a method of restoration. Its major advantages are: 1) surface disposal of large volumes of waste water is not required, 2) treatment is more effective than sweeping or recirculation, and 3) in-situ treatment can be less expensive than surface treatment. Disadvantages of in-situ treatment include: 1) the difficulty of distributing treatment agents uniformly, 2) less control over the in-situ treatment process compared to surface treatment, and 3) our lack of experience using this method.

In-situ treatment has been considered for treatment of ammonia and uranium and other trace elements. Proposed ammonia 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. Uranium may be treated by chemical and biological reduction.

5.2.1 Chemical Oxidation of Ammonium

Chemical oxidation of ammonium has been observed in batch and column laboratory tests in the presence of hydrogen peroxide (Garwacka et al. 1979). Oxidation increased when core material was present. Conceivably, chemical oxidation could be used in-situ to convert ammonium on clays and in ground water to nitrites and nitrates.

Humenick and Garwacka (1982) performed laboratory tests on ammonia-saturated leached uranium ores to determine the feasibility of chlorine oxidation of ammonium. They found calcium hypochlorite, $Ca(HOCl)_2$, completely destroyed ammonium in leached ore samples from Mobil Oil (O'Hern site) and U.S. Steel (Burns Site) in less than one hour. Calcium hypochlorite doses of 8.9 to 9.7 g/g ammonium-nitrogen (3.5 to 3.8 meq chlorine per meq NH_3-N) were required to reach the breakpoint. Reaction products included nitrogen gas, chlorates, chlorides, HOCl, OCl^-, chloramines, nitrates, and hydrogen ions. Because of the large quantities of reagent required, this method would probably be cost-effective only on very low concentrations of ammonium remaining after other restoration methods have been used. Furthermore, nitrogen gas formation may prevent effective penetration of the hypochlorite solution into the formation.

A second problem with chlorine oxidation (and chemical oxidation in general) is the formation of soluble reaction products, which may be less desirable than ammonium. For example, the U.S. EPA Interim Primary Drinking water standard for Nitrate-N is 10 mg/l [40 CFR 252, as reported by Riding and Rosswog (1979)]. Surface treatment to remove nitrate, following the in-situ oxidation of high concentrations of ammonium, may be required. However, this may be more cost effective than ground-water sweeping or recirculation of fifty or more pore volumes.

Chemical oxidants added to destroy ammonium will also react with other compounds that were not oxidized during mining. For example, hypochlorite will oxidize residual Fe(II), Mn(II), and organic matter before oxidizing ammonium. Vogt (1981) performed laboratory studies on oxidation of a uranium ore from Crownpoint, New Mexico using sodium hypochlorite. He found that sodium hypochlorite at the same chlorine concentrations used by Humenick and Garwacka (1982) was as effective as hydrogen peroxide for oxidizing uranium. Thus, hypochlorite added for the purpose of oxidizing ammonia will also increase uranium and other trace element concentrations.

In summary, in-situ chemical oxidation of ammonium has not been tested except in the laboratory. Laboratory studies show that ammonium adsorbed on ores can be successfully oxidized by breakpoint chlorination methods similar to water treatment. Chemical oxidants are not specific to ammonium. Additional ground-water treatment may be required for oxidation products and byproducts.

5.2.2 Biological Oxidation of Ammonium

Biological oxidation of ammonium occurs naturally in soils. Unlike chemical oxidants, nitrifying bacteria are specific to ammonium. In theory, bacteria and nutrients injected into the ore body will oxidize ammonium to

nitrate which can be easily flushed from the aquifer and treated at the surface. The bacterial genera of interest are Nitrosomonas, Nitrosococcus, Nitrospira, and Nitrosolabus which oxidize ammonium (NH_4^+) to nitrite (NO_2^-) and Nitrobacter, Nitrospina, and Nitrococcus, which oxidize nitrite to nitrate (Garwacka et al. 1979). These bacteria successfully oxidized absorbed ammonium to nitrate in batch and column laboratory tests (Garwacka et al. 1979).

The laboratory studies showed that the bacteria are inhibited by hydrogen peroxide and by the high ammonia (NH_3) concentrations typical of lixiviants. Therefore, a preliminary ground-water sweeping or recirculation would be required before the injection of bacteria. Also, injection patterns should be adjusted to prevent the aquifer or injection well from plugging by bacterial growth.

The major problem with in-situ biological oxidation is the bacterial requirement for oxygen, which would have to be injected into the aquifer. Garwacka et al. (1979) compared the rate of oxygen addition (limited by the oxygen solubility) to completely oxidize ammonium to the rate of ammonium elution. They concluded that in-situ biological oxidation is probably not feasible because the ammonium would be eluted before it could be oxidized. Of course, elution and biological oxidation could be performed simultaneously.

5.2.3 Cation Elution of Ammonium

During leach mining with ammonium carbonate, the ammonium ion exchanges with cations on the clays that are usually present in sandstone ore bodies. After mining is completed, the adsorbed ammonium will exchange with cations in ground water. However, removal of the NH_4^+ is very slow because of the relatively low concentration of cations normally present in the ground water. A considerable volume of ground water is required to replace all the NH_4^+ contained in the clays (Braswell et al. 1978).

Ground-water concentrations can be altered to increase the rate of ammonium exchange. In general, ion exchange will proceed faster if cation concentrations in the water are higher (through the law of mass action). Also clays are more selective for divalent cations such a Ca^{++} and Mg^{++} than for monovalent cations such as Na^+ and K^+ (Garwacka et al. 1979). Higher pH solutions are more effective for ammonium exchange (Yan and Espenscheid 1982). The high pH drives the aqueous $NH_4^+ \leftrightharpoons NH_3$ equilibrium toward NH_3, thus reducing the concentration of NH_4^+ concentration in the aqueous phase. This pushes the NH_4^+ (aq) $\leftrightharpoons$ NH_4^+ (surface) adsorption equilibrium toward the aqueous phase, thus reducing the concentration of NH_4^+ on the clay. Theoretically, the best elution water should be a high ionic strength, high calcium concentration, high pH solution. In practice, calcium may react with carbonate in the lixiviant to precipitate calcium carbonate and plug the aquifer. An initial flush with sodium or potassium chloride followed by ammonium elution with calcium chloride may be the best procedure.

Yan and Espenscheid (1982) report that restoration levels of ammonia (3 ppm) were achieved by elution with calcium-saturated brine in laboratory column tests after 25 pore volumes. In the first stage of elution, the aqueous

ammonium concentration was limited by the calcium concentration. Later, at low levels of adsorbed NH_4^+, other cations on the clay compete with NH_4^+ for calcium. Yan and Espenscheid recommend the addition of sodium chloride to the eluting solution to reduce this competition.

Researchers at the University of Texas (Hill et al. 1978, Garwacka et al. 1979) also performed laboratory studies of cation elution. They report that clays are more selective for Ca^{++} than NH_4^+ and that an optimum elution velocity may exist. However, the preference of an ion exchange medium for a divalent cation over a monovalent cation will decrease as the ionic strength of the solution increases (mass action law). Laboratory data matched an ion exchange model based on mass action.

Field tests of cation elution have been performed by Mobil and Wyoming Minerals Corporation (WMC). Mobil used NaCl and NaOH to flush NH_4^+ in a pilot test (two wells in a 20-ft square pattern) at the O'Hern site (Buma et al. 1981). After 6.2 pore volumes, the ammonium concentration was 88 mg/l, significantly above the baseline level of 1.9 mg/l (Tweeton 1981). Mobil also experienced corrosion problems and permeability losses. WMC used a Ca^{++}/Mg^{++} solution to elute NH_4^+ during a pilot test (2 wells in a 25-ft. square pattern) on the Bruni site (Buma et al. 1981). Eluted NH_4^+ was stripped from ground water at the surface. At the conclusion of the pilot test, the NH_4^+ concentration was 17 mg/l and dropping (compared to a baseline of 1 mg/l). WMC performed a similar pilot test (5 spot pattern--25 x 25 ft square) at the Irigaray site using a $Ca^{++}/Mg^{++}/Na^+$ solution. The final ammonium concentration was less than 35 ppm; baseline was less than 1 ppm.

In general, theory and laboratory tests have shown that cation elution can be effective in reducing NH_4^+ concentrations on the clay. However, ammonium concentrations have not been reduced to baseline levels in three pilot tests.

5.2.4 Chemical Reduction of Uranium

In uranium leach mining, uranium is deliberately oxidized from the insoluble +4 state to the soluble +6 state. Once mining is complete, oxidized uranium remains in the ground water--usually at concentrations higher than baseline. Reducing agents injected into the aquifer should reduce uranium to the +4 state, allowing precipitation to occur. Geologists theorize that uranium ore bodies in sandstone formed when oxygenated uranium-bearing ground water reacted with natural reductants, such as pyrites, organic matter, methane, and hydrogen sulfide (Kidwell and Humenick 1981). Possible reductants for injection include hydrogen, hydrogen sulfide, methane, sulfur dioxide, sodium sulfide, and sodium sulfite.

The major problem with using a chemical reductant for restoration will be uniform distribution of the reductant throughout the aquifer. As the reductant spreads out from the injection well, it will react with uranium and other metal ions. The precipitated metal compounds may plug pores near the well, thus preventing reduction of metal ions farther away. Another potential problem is gas blockage of pores by gaseous reductants, although experience with injection

of oxygen and hydrogen peroxide should apply. The precipitated metals may also be reoxidized by upgradient oxygenated ground water or lixiviant as it moves into the restoration zone.

Chemical reductants should also react with other trace elements, particularly those oxidized during mining. Based on thermodynamic data, arsenic, selenium and vanadium should be more easily reduced than uranium, and molybdenum should be more difficult. If molybdenum is present in the ore body, then requirements for molybdenum restoration may determine reductant requirements.

Chemical reduction of uranium and other trace elements is theoretically possible and has been examined in laboratory experiments. Uranium Resource Incorporated (URI) tested hydrogen sulfide on cores from its Benevides site but had problems controlling hydrogen sulfide concentrations (Sergio Garza, February 1982, URI, personal communication). Data on uranium reduction in core samples are not available. URI proposes using sodium sulfide or sulfite instead. Texaco/Sunoco proposed using chemical or biological reductants at the Hobson Tex-1 site (Texas Department of Health 1981). No field tests have been performed.

5.2.5 Biological Reduction of Uranium

Biological reduction of uranium and other trace elements could be used to restore ground water. Sulfate-reducing bacteria produces hydrogen sulfide which could reduce and precipitate uranium. *Desulfovibrio* and *Desulfotomaculm* are anaerobic bacteria which use organic matter as a carbon source (Riding and Rosswog 1979). *Desulfovibrio hydrocarbonoclastia* has been isolated from alkaline ground water and could be used after leaching by alkaline lixiviants. *Desulfovibrio desulfuricans* prefers pHs <4.3 and would be viable after sulfuric acid leaching. Injection of nutrients may be required.

As in chemical reduction, the major problem of biological reduction will be uniform distribution of bacteria throughout the aquifer. Bacterial growth may cause plugging of aquifer pores. The production of hydrogen sulfide will be uncontrolled and may cause gas blockage.

Bacteria exist which could reduce uranium and other trace elements, but their applicability to and effectiveness on uranium-bearing ores and waters has not been determined experimentally. Anaerobic, sulfate-reducing bacteria appear to reduce uranium and molybdenum in a mine wastewater treatment system in the Grants, New Mexico, uranium district (Brierly 1979). Extensive field tests would be required before the feasibility of in-situ reduction could be shown.

5.3 SURFACE TREATMENT

A number of surface treatment processes have been used or suggested to enhance restoration. The techniques are described in this section.

5.3.1 Processes

The waste stream from restoration can be sent directly to the disposal system (evaporation pond or deep disposal well), or it can first be treated to produce two streams. One stream is purified water, and the other is a brine carrying most of the dissolved solids. The advantages of the second method are that the purified water can be reused, thereby reducing the total consumption of water, and the disposal system does not need as large a capacity.

The surface treatment techniques that have been used by in-situ leaching companies are reverse osmosis (RO), electrodialysis (ED), and dual ion-exchange (DIX). Two other methods will be briefly discussed after RO, ED, and DIX. Much of the information is from a contract report by Riding and Rosswog (1979) to the Bureau of Mines.

Reverse Osmosis

Reverse osmosis is a physical means of separating dissolved ions from an aqueous stream. 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 solution's osmotic pressure is a function of the type of constituents, the ionic characteristics of the dissolved solids, and the relative and absolute concentrations of the solutes. A typical operating pressure for RO used for in-situ leach applications is several hundred psi.

Cost estimates are provided in Riding and Rosswog (1979). Estimated 1978 capital costs are $303,000 and $1,228,000 for capacities of 200,000 and 1,000,000 gpd, respectively. A water recovery of 85% was assumed, based on field experience. The 1978 total costs per 1,000 gal are as follows:

	Capacity (Feed Rate)	
	200,000 gpd	1,000,000 gpd
Direct	$ 0.33	$ 0.31
Overhead	0.14	0.10
Fixed	0.73	0.58
TOTAL	$ 1.20	$ 0.99

The fixed charges were calculated assuming a sinking fund at 8% with a 10-year life, and interest at 10%/yr with 50-50 debt equity financing. The fixed costs with current (1982) interest rates would be higher. The basic RO cost data were provided by L. J. Kosarek, Environmining Co., Inc., El Paso, Texas.

The three configurations of RO membranes are spiral wound, hollow fine fiber, and tubular. Riding and Rosswog (1976) recommended the spiral wound design. The tubular system had a high operating cost without the possibility

of high water recovery. The hollow fine fiber was too susceptible to fouling and could not be cleaned. The spiral wound design can be operated at high water recoveries (85%), can be easily cleaned, and is economical.

Concerning membrane materials, the Riding and Rosswog report recommended cellulose acetate derivatives because the polyamide, polyfurance, polysulfone, polyethylene amine, and polybenzimidazolone types were either still in the R and D stage, lacking in either sufficient rejection or water flux, retained little or no successful field operation, or were incompatible with residual oxidants present within the aquifer requiring restoration. The cellulosic type membranes have proved to be very successful.

Electrodialysis

Electrodialysis (ED) has been used successfully in in-situ leaching applications, but has been used less often than has RO. ED 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 end plates much like a plate and frame filter. Spacing is usually about 2.5 mm, and spacers are arranged to provide a tortuous path. Stacks range from 500 to 2500 m^2 of membrane area. A large stack can desalt 150 gpm at 20 to 50% salt removal. Practical systems use two to six stages.

Cost estimates in Riding and Rosswog (1979) indicate that ED is somewhat more expensive than RO. The estimated 1978 capital costs are $571,000 and $1,501,000 for feed rate capacities of 200,000 and 1,000,000 gpd, respectively. The estimated 1978 total cost per 1,000 gal of water are as follows:

	Capacity (Feed Rate)	
	200,000 pgd	1,000,000 pgd
Direct	$ 0.52	$ 0.46
Overhead	0.21	0.16
Fixed	1.38	0.73
TOTAL	$ 2.11	$ 1.35

These 1978 costs were calculated assuming electric power at 2.5 kw/hr with an average of 2500 ppm salts removed, the sinking fund payment was at 8% with a 10 year life, and financing was 50-50 debt-equity with interest at 10%. A different source of information, presented in a following field data section, stated that ED cost about the same as RO.

Riding and Rosswog (1979) indicated that ED has some technical advantages over RO. ED 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. ED membranes are of synthetic ion-exchange materials with service life of up to 20 years, compared

to 3 to 5 years for RO. ED membranes are stable over a pH range of 1 to 14. Cellulose acetate membranes for RO are most successfully operated in a pH range of 4 to 8. Thus, less pretreatment 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 solutions normally found in in-situ leaching, dual ion-exchange (DIX), which consists of replacing solution anions and cations with bicarbonate and hydrogen ions using special resins, may be cost effective in certain cases. This procedure is known as the Desal process, and is described in the Riding and Rosswog (1979) report.

The ion-exchange resins can provide greater selectivity than RO. An example of an application where the selectivity was advantageous was when a leaching company was required to significantly reduce sulfate but not chloride levels. The selectivity for sulfate available with ion-exchange resins led to greater cost-effectiveness than would have been obtained with RO. It was also thought that RO would be more susceptible to fouling. However, it appears that where selectivity is not unusually important, RO will generally be more cost-effective than DIX. Published reports of field experience with DIX are not available.

Other Treatment Methods

Distillation appears to be prohibitively expensive, four to five times the cost of RO. The high cost is partly due to the high energy requirements. Similarly, ion-exchange treatment costs two to five times as much as RO.

Water purification by freezing has not been applied to in-situ leaching, but the process is claimed to have the potential for low costs, high water recovery, and effective contaminant rejection. The process is based on the principle that when ice is frozen from an aqueous solution of salts, the ice is a distinct and purer phase of water. The ice excludes most of the salts from its crystal structure. Costs for freeze separation have been estimated to be 20 to 40% greater than costs for RO for small flow rates, and potentially 20 to 40% less than RO for high flow rates.

5.3.2 Effects on Ground Water

The effect of using a surface treatment system and recirculating the purified water is to decrease the consumptive use of ground water. Both RO and ED allow recovery of 80% of the water from waste solutions, with a corresponding decrease in the consumption of ground water.

5.3.3 Field Data and Experience

The results of restoration attempts using reverse osmosis and electrodialysis are described in this section.

Reverse Osmosis

At least one company has reported some problems with RO, according to Buma et al. 1981. In discussing the restoration at the Pawnee, Texas, site of Intercontinental Energy Company (IEC), the report said that IEC had two 35 gpm RO units equipped with high pH Dupont membranes of the hollow fiber type. The report states (p. 35) "A number of problems were encountered with the RO unit. Its capacity and efficiency were reduced because of plugging over the last three months of use such that replacement of the expensive membranes was necessary. Better pretreatment practices and alternate membrane types are currently being examined.

Analysis of the RO membranes have shown that the fouling has been caused by iron salts, calcium sulfate, magnesium salts, and especially by a uranium calcium silicate or sulfate compound. Plugging varies greatly with the water composition. This makes membrane protection very difficult."

Note, however, the warning in Riding and Rosswog (1979) that hollow fine fiber membranes are unacceptable because of their susceptibility to plugging and incapacity of being cleaned. Thus, reported problems with RO are not necessarily an indication that RO is unsuitable, it may mean only that the wrong type was selected.

Wyoming Mineral Corporation uses a 150 gpm spiral wound unit at Irigaray. No difficulties have been reported. The performance of the RO unit in removing ionic species is given in Table 5.1 (Buma et al. 1981). With the exception of CO_3, greater than 95% of each of the important species were removed.

TABLE 5.1. RO Performance at Irigaray, WMC

Species	RO Feed	RO Permeate	Percent Removal of Species by RO Process
U_3O_8 mg/l	43	1	97.6
$CO_3^{=}$ mg/l	8	4	50.0
Cl^- mg/l	686.8	26	96.2
NH_4^+ mg/l	54.3	2.7	95.0
$SO_4^{=}$ mg/l	641.8	4.3	99.3
Na^+ mg/l	434	10.7	97.5
Ca^{++} mg/l	71.5	2.2	96.9
pH	4.7	4.9	--
Mg^{++} mg/l	23.3	1.0	95.7
Conductivity, µmhos/cm	3237.3	149	--

Electrodialysis

Garling (1981) reported on a field experience with ED, used at the Teton-Nedco Leuenberger R and D in-situ uranium leaching operation in Wyoming. The feedrate was 30,000 gpd. The author stated that "[b]ased on recent quotes from both RO and ED manufacturers, capital equipment costs are comparable and range from $175,000 to $250,000 for 1.26×10^{-2} m^3/s (200 gpm) unit. Operating costs for ED units have historically been equal to or lower than comparably size RO units (when feed TDS remains below 5000 mg/l) and ED feed pretreatment costs are typically lower."

Thus, some disagreement is evident between Garling's article and Riding and Rosswog (1979). When this matter was discussed with an ED manufacturer, he felt that RO might be cheaper for solutions of high ionic strength, but ED is cheaper for low ionic strength. The electrical power costs for ED depend on the concentration. The ED manufacturer thought that for most of the restoration process, the ionic strength of the solutions would be low enough that ED would be cheaper overall.

ED performed well for Teton. A commercial ED unit with a feed capacity of 1.31×10^{-3} m^3/s (30,000 gpd) was operating by February 25, 1981. The dual stage unit was expected to produce 665 mg/l TDS water from a feed of 2650 mg/l with a product water recovery of 80 pct. During the evaluation period, 1.25×10^7 l (3.31×10^6 gal) were fed at an average TDS of 2.35 g/l, and 1.02×10^7 l (2.7×10^6 gal) product at 0.35 g/l TDS and 2.24×10^6 l (5.8×10^5 gal) of brine were generated, representing a salt rejection of 87.5% and water recovery of 81.5%. Chemical results from the final month of testing are shown in Table 5.2.

The ED unit operated 96% of the time available, requiring only four cleaning cycles and no stack dissassembly. The cleaning downtime was necessitated by operator error. Routine direct operating costs averages $1.02/3785 l(1000 gal).

Teton personnel concluded that the ED process had proved amenable to water treatment requirements of carbonate-bicarbonate in-situ leaching operations. They decided to use a larger ED unit for their planned commercial leaching operation.

5.3.4 Waste Disposal

The required capacity of the waste disposal system can be greatly reduced by surface treatment. The waste disposal system needs to receive only the concentrated brine, which will typically have a flow rate of only 20% of the flow rate of the total feed stream to the surface treatment system. For evaporation ponds, the surface area can be reduced in direct proportion to the reduction in flow rate of the waste stream. For disposal wells, the allowed reduction in capacity may be somewhat less because highly concentrated brines may be difficult to inject without causing some plugging. Nevertheless, a significant reduction in capacity, and hence cost, can be obtained.

TABLE 5.2. ED Test/Analytical Means

Parameter	Feed	Brine	Product	Rejection
Major Parameter	-------	mg/l	--------	-- % --
HCO_3^-	573	2,384	106	81.5
Cl^-	432	1,884	61	85.9
$SO_4^=$	363	1,656	23	93.7
Ca^{++}	191	826	16	91.6
Na^+	337	1,464	61	81.9
Mg^{++}	44	208	6	84.6
K^+	20	88	2	90.0
Traces				
As	0.022	0.104	0.009	59.1
Ba	0.15	0.23	<0.1	>50
NO_3+NO_2	1.9	8.0	0.44	76.8
Se	0.11	0.19	0.02	81.8
U	9.15	21.4	1.80	80.3
Radiometrics	--------	pCi/l	--------	-- % --
Ra 226	667	2,904	64	90.4
Th 230	54	415	10.0	81.5
Gross α	735	3,294	149	79.7
Gross β	2,182	4,390	379	82.6

5.4 REFERENCES

Braswell, J., et al. 1978. Literature Review and Preliminary Analysis of Inorganic Ammonia Pertinent to South Texas Uranium In Situ Leach. Technical Report CRWR-155, EHE 78-01, Center for Research in Water Resources, University of Texas, Austin.

Brierl, C. L. 1979. "Microbiology and Uranium Mining: Practices and Problems." Third Annual Uranium Seminar, Wyoming Mining and Metals Section of AIME, Casper, Wyoming.

Garling, R. A. 1981. "Evaluation of Electrodialysis for Process Water Treatment for In-Situ Mining." In Fifth Annual Uranium Seminar, Albuquerque, New Mexico.

Garwacka, K., et al. 1979. Investigation of the Fate of Ammonia from In-Situ Uranium Solution Mining. Technical Report EHE 79-01, Bureau of Engineering

Research, University of Texas, Austin.
Hill, A. D., et al. 1978. "Restoration of Uranium In Situ Leaching Sites." SPE Fall Meeting, Paper 7534.

Humenick, J. M., and K. Garwacka. 1982. "Oxidative Destruction of Ammonia for Restoration of Uranium Solution Mining Sites." Paper 82-105, SME-AIME Annual Meeting, Dallas, Texas.

Potter, R. W., et al. 1979. "Equilibrium, Kinetic and Chromatographic Controls of Solution Composition Obtained During In Situ Leaching of a Uranium Orebody." In Chemical Modeling in Aqueous Systems, E. A. Jenne, ed., American Chemical Society.

Riding, J. R., and F. J. Rosswog. 1979. Restoration of Ground-Water Quality After In Situ Uranium Leaching. Ford, Bacon and Davis Utah, Inc., for U.S. Department of Interior Bureau of Mines, Contract No. J0275028, Washington, D.C.

Schmidt, R. D. 1980. "Computer Modeling of Fluid Flow During Production and Environmental Restoration Phases of In Situ Uranium Leaching." Report of Investigation 8479. U.S. Bureau of Mines, Washington, DC.

Texas Department of Health. 1981. "License Application and Supplemental Information for Uranium Recovery Facility." Texaco Inc. and Sunoco Energy Development, Co., Hobson Tex-1 In Situ Uranium Project.

Tweeton, D. R. 1981. "Restoring Ground Water Quality Following In Situ Leaching." In In-Situ Mining Research, U.S. Bureau of Mines Information Circular IC 8852.

Vogt, T. C. 1981. "In-Situ Leaching of Crownpoint N.M., Uranium Ore., Phase III Laboratory Study of Strong Leaching Systems: Sodium Hypochlorite," AIME Annual Meeting, Paper 81-348.

Yan, T. Y., and W. F. Espenscheid. 1982. "Removal of Ammonium Ions from Subterranean Formations by Flushing with Lime Saturated Brines." Paper 82-02, SME-AIME Annual Meeting, Dallas, Texas.

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In-situ leach uranium mines and pilot-scale test facilities are currently operating in the states of Wyoming, Texas, New Mexico and Colorado. This report summarizes the technical considerations involved in restoring a leached ore zone and its aquifer to the required level. Background information is provided on the geology and geochemistry of mineralized roll-front deposits and on the leaching techniques used to extract the uranium.

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