

FC
USGS
OFR
76-835

GLOO292

UNIVERSITY OF UTAH
RESEARCH INSTITUTE
EARTH SCIENCE LAB.

(204)
R29s

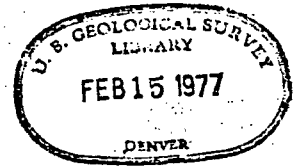
UNITED STATES DEPARTMENT OF THE INTERIOR

Geological Survey

Some Geochemical Parameters Effecting the
In-Situ Leaching of Uranium

by

Robert W. Potter II



Open-File Report

76-835

This report is preliminary
and has not been edited or
reviewed for conformity with
Geological Survey standards.

FEB 17 1977

The geological features which effect the in-situ leaching of uranium have been capable reviewed by Brooks (1976). The purpose of this paper is to review some of the geochemical parameters which effect the in-situ leaching of uranium. The objectives of in-situ leaching of uranium are to dissolve all of the uranium-bearing minerals in place and to carry the dissolved uranium back to the surface in a fluid that was injected into the ore-bearing horizon. In its simplest form, the chemical process consists of: (1) oxidizing the uranium-bearing species, (2) putting the uranium into solution in the form of a complex which can be recovered at the surface, and (3) having no reactions occur between the injected leaching solution and the ore-bearing horizon which are detrimental to the extraction of the uranium. In practice, however, interactions between the injected fluid and rock lead to detrimental effects with respect to uranium recovery.

These detrimental lixiviant rock interactions can be generally divided into four categories.

- 1./ Reactions which decrease the porosity-permeability of the formation.
- 2./ Reactions with non-uranium-bearing minerals which consume either the oxidizing agent and/or the complexing agent.
- 3./ Reactions which cause a phase to precipitate that coprecipitates the uranium.
- 4./ Reactions which form or activate a phase which removes uranium by ion exchange.

These four categories are not totally independent of each other, e.g., a phase that coprecipitates uranium may also serve to reduce the permeability

and porosity in the ore-bearing formation. Numerous examples of deleterious fluid-rock reactions could be cited in each of the above four categories. For the sake of brevity, only four examples will be discussed.

Hydrolysis of Feldspars:

It is important to examine the breakdown of feldspars under leaching conditions because these reactions exert a major control on other interactions between the formation and the lixiviant. Many detrimental processes are directly related to the hydrolysis of feldspars.

During in-situ leaching the hydrolysis of feldspar is not likely to be an equilibrium process. Rather, it will be a process strongly influenced by kinetic factors. Hence a strict equilibrium approach to the alteration of feldspars would not accurately predict the course of the chemical reactions.

One of the rate-controlling parameters of the hydrolysis of feldspars is the lixiviant pH. Figure 1 illustrates the rate of orthoclase breakdown as a function of pH as shown by the concentration of SiO_2 in solution at specific time intervals. The most rapid decomposition occurs in the low pH region, and the minimum rate of feldspar alteration is at pH's near neutral.

The initial feldspar composition is another parameter effecting the rate of feldspar alteration. Figure 2 shows the amount of silica released by the hydrolysis of various plagioclases in equal times as a function of anorthite content. In general, the higher the anorthite content of a plagioclase, the more rapidly it breaks down. Andesine (An_{50}) is a notable exception, as it was found to break down more slowly than other plagioclases

(Fig. 2). Plagioclases also tend to break down faster than orthoclase; e.g., after 27.8 hours 1.39×10^{-10} moles/cm² of SiO₂ is released to the solution by orthoclase versus 4.42×10^{-10} moles/cm² of SiO₂ for oligoclase. Note that less SiO₂ should be released by the same amount of hydrolysis for Ca-rich feldspars than for K-rich feldspars. These kinetic factors result in the solution becoming enriched in Ca with respect to Na and K. The consequences of this phenomena will be discussed later in connection with the precipitation of calcite. Any attempt to model the chemistry of the hydrolysis of feldspars during the leaching process, in order to predict and control scaling problems, must take into account these kinetic factors.

Eventually a computer model based on an equilibrium calculation scheme heavily modified for kinetics should be able to describe the feldspar-lixiviant interactions. However, at present there are insufficient kinetic data available to apply computer codes to the in-situ leaching situation. The direct applicability of the kinetic factors is limited because: 1./ the rate of breakdown is a strong function of grain size and most of the kinetic data has been determined only for very fine-grained materials, and 2./ the studies generally are done with slurries of 5% suspended solids, but increased concentrations of solids affect the reactions (Fig. 3). Also, before a computer model would be applicable to natural systems, a prohibitive amount of information about the physical and chemical nature of all of the minerals in the solution flow path would be required.

Oxidation of Pyrite:

The oxidation of pyrite can cause several problems: 1./ it consumes oxidant, 2./ it consumes complexing agent, 3./ it generates sulfate, which in turn promotes the precipitation of gypsum, thereby decreasing permeability, 4./ it causes the precipitation of Fe-oxyhydroxides which plug the formation and also coprecipitate uranium, and 5./ it may locally dissolve calcite, adding to the Ca-scaling problem elsewhere in the flow path. Pyrite is an ubiquitous mineral in sandstone uranium deposits. The environment encountered in the uranium deposits is generally such that pyrite is stable (stippled area of Fig. 4). Solutions which are injected to leach uranium will have pH and Eh values incompatible with pyrite, e.g. point A in Fig. 4. On contact with pyrite the lixiviant is reduced and the pyrite is oxidized. If the pH buffer capacity of the solution is large enough to absorb the acid produced by the oxidation of pyrite, a pH-Eh path such as A-B (Fig. 4) will be followed during the reaction. If the buffer capacity is not large enough to handle the oxidation products, there are several paths which the solution can follow, e.g., the path A-C (Fig. 4). If the $H_2CO_3-HCO_3^-$ buffer is encountered, the Eh of the solution will decrease at a constant pH fixed by the $H_2CO_3-HCO_3^-$ buffer until either all the HCO_3^- is consumed, graphite precipitated, or the oxidant is consumed (a new equilibrium situation is established). In either case the uranium solutioning and complexing capacity of the solutions will be greatly reduced. The foregoing discussion has assumed that there are significant amounts of pyrite such that the pyrite in the formation is not completely oxidized.

If enough oxidant and leaching solution are put into the pyritic formation to oxidize all of the pyrite, then the preceding discussion applies only until the last pyrite crystal oxidizes. This results in a lixiviant that still has the capacity to move uranium. Experimental studies have shown that the most effective oxidant for uranium is Fe^{3+} , which is one of the breakdown products of pyrite. Given a condition where the solutions become stratified with respect to Eh and pH, the oxidizing pyrite could be a very effective mobilizing agent for the uranium. In general, however, the overall effect of the oxidation of the pyrite is a costly consumption of oxidant and complexing agent. Because of the conditions necessary to leach the uranium, it is improbable that the oxidation of pyrite can be totally prevented; however, because the process is a kinetic rather than an equilibrium process, it may be possible to adjust the chemical parameters of the lixiviant to take advantage of the kinetics to reduce the consumption of oxidant and complexing agent. Hence, an understanding of the parameters effecting the kinetics of the oxidation of pyrite in typical leaching solutions is quite important.

Essentially all of the experimental studies on the oxidation of pyrite have been done in acidic media and a detailed discussion of the kinetic controls of pyrite oxidation in basic media is not possible at the present time. However, a few generalizations can be made on the basis of the studies in acidic media. It is generally agreed that the rate-controlling step in pyrite oxidation is the formation of Fe^{3+} . But, another significant factor is the grain size of the pyrite. Three series of experiments were

conducted to illustrate the effect of size and Fe^{3+} on the oxidation rate (Fig. 5). The pH of the solution is lowered as a result of the oxidation of pyrite. Therefore, the rate of oxidation can be monitored in an experiment by monitoring pH changes as shown in Fig. 5. One would expect that the size of pyrite crystals in the formation would still be a controlling factor in the oxidation of pyrite in basic media; however, the effect of Fe^{3+} is less certain due in part to the instability of this ion in the basic pH region.

Another critical area of investigation is the specificity of various oxidants for pyrite versus uranium-bearing species. Figure 6 illustrates the reaction of three common oxidants with fine-grained pyrite. Hydrogen peroxide has the strongest oxidizing capacity for pyrite; however, the specificity of the oxidizers for uranium vs. pyrite has not been determined. Hence, before any conclusions can be drawn about the advisability of using or not using hydrogen peroxide, the specificity of the various oxidants for uranium, pyrite, and other materials needs to be evaluated.

Precipitation of Calcite

The precipitation of calcite should be avoided in uranium by in-situ leaching operations for several reasons: 1./ the precipitated calcite reduces the porosity-permeability of the formation, 2./ the precipitated calcite plugs the well screens, pumps, ion exchange columns, etc., and 3./ calcite will co-precipitate uranium. For these reasons an understanding of the precipitation of calcite under conditions encountered during in-situ leaching is of great importance. More information also is needed about

the mechanism by which calcite coprecipitates uranium and the amounts of uranium which can be coprecipitated by calcite.

Lauffenburger and Wey (1966) studied the coprecipitation of uranium by calcite precipitating from CaCl_2 solutions containing $\text{UO}_2(\text{NO}_3)_2$. Using 10% excess Na_2CO_3 to precipitate the calcite, they found that the amount of uranium coprecipitated depended on the uranium concentration in solution and reached a limiting high concentration of about 1 part U for 80 parts of Ca precipitated. With an order of magnitude more $\text{CO}_3^{=}$, the amount of coprecipitated uranium was found to be significantly less. Hence the amounts of uranium precipitated appear to be a function of the degree of supersaturation with respect to calcite and the concentration of uranium in the solution. No attempt was made to determine the effect of various types of uranium complexes on the coprecipitation of uranium by calcite. This is another area which needs to be investigated experimentally.

In order to precipitate calcite from the alkaline carbonate lixivants, a source or sources of calcium must be provided. There are many possible sources of calcium in the formation:

- 1./ ion exchange reactions involving clays,
- 2./ dissolution of calcite in response to pyrite oxidation and movement of calcium to a new chemical environment,
- 3./ zeolite transformations induced by the lixiviant, and
- 4./ hydrolysis of feldspars and clays.

However, based on reasonable chemical reactions and exchange mechanisms, the most likely sources of calcium are the hydrolysis of feldspars and

clays and reactions involving zeolites. It was previously noted that the calcium-bearing feldspars tend to decompose more rapidly than potassic feldspar so that the lixiviant becomes selectively enriched in calcium.

Theoretically the kinetic data for the breakdown of the feldspars (keeping in mind the limitations of the data with respect to direct application in the natural system field) can be used along with equilibrium data for calcite to predict a time and place at what pH and carbonate concentration will allow precipitation of calcite. Using the kinetic data of Busenberg and Clemency (1976) for the hydrolysis of oligoclase and anorthite and the equilibrium solubility data for calcite of Christ et al. (1974), a diagram for the precipitation of calcite as a function of pH and total carbonate was calculated (Fig. 7). The assumptions used to calculate figure 7 are as follows:

- 1./ The feldspar mixtures are in the solution as a slurry where the solids compose 5% of the system by weight.
- 2./ The diagram is calculated for 400 hours (except for anorthite which is calculated for 24 hours).
- 3./ Calcite precipitates when it has become slightly supersaturated (~ 0.1 of a log k unit).
- 4./ The Ca contribution is a linear function of the amount of the phase present. The lower oligoclase concentrations were obtained by assuming that non-reactive solids composed the remainder of the reactants.

These calculations indicate that calcite precipitation could be controlled by adjusting the pH and carbonate concentrations of the lixiviant provided

the mechanism for Ca release of the formation was understood and could be quantified.

The Exchange of Uranium by Clays and Other Phases:

Ion exchange reactions involving uranium are generally not well known. There have been a limited number of investigations of the exchange and adsorption capacity of clays for uranium. Ukai et al. (1958) found that in general the exchange capacity of the clays was greater for uranium than for Na, Ca, K and NH_4 . In the case of montmorillonite a possible exchange reaction would replace calcium in the clay with uranium from the solution. This would lead to two harmful consequences, i.e. the removal of uranium from the solution and the release of calcium to the solution promoting precipitation of calcite.

Unfortunately the study by Ukai et al. (1958) does not specify the pH of the solutions used to ion exchange the clays. Presumably, however, the solutions were in the acidic pH range because the chloride and sulfate salts of uranium were used. Not only should the ion exchange capacity of the various clays for uranium in alkaline carbonate media be determined, but also the specificity of the clays for uranium versus Na, K, Ca, and NH_4 in alkaline carbonate solutions.

The recovery of uranium held in clays has not been overly successful. Figure 8 illustrates the results of trying to leach a clay containing 0.087% uranium with various lixiviants at different concentrations. Because these tests were done on finely-powdered suspensions of the clay in the lixiviant, the extraction of uranium from clays under field conditions, particularly in

alkaline carbonate solutions, does not look too promising. If uranium is indeed significantly fixed in clay minerals by ion exchange, this may well prove to be the limiting factor in uranium extraction by in-situ leaching.

The ion exchange of uranium by other phases such as zeolites is even less well-known. Presently this can only be described as a pertinent area for research. It should be noted that clinoptilolite is a very common constituent of the ore-bearing horizons in Texas (Brooks, 1976). The ion exchange capacity of zeolites for uranium, their specificity for uranium exchange, and their ability to adsorb uranium from alkaline carbonate solutions needs to be investigated.

Summary and Suggestions for Further Study

There are many lixiviant-rock interactions which can lead to the reduction of the porosity-permeability of the ore-bearing formation. These include reaction involving phase changes such as clay transformations, zeolite transformations, feldspar alteration to zeolites, feldspar alteration to clays, and alteration of various accessory minerals. There are a plethora of phases which can precipitate from solution as a result of lixiviant-formation interactions, but in general the most common phases are Ca-carbonates, Fe-oxyhydroxides, Al-oxyhydroxides, and silicates.

A uranium-bearing formation is likely to contain many phases that can consume oxidant and complexing agent from a lixiviant. The most significant reactions involve the oxidation of pyrite, oxidation of organic materials, and the dissolution and precipitation of calcite. Other oxidation-reduction

and precipitation reactions also could cause problems; however, the problems would generally be minor unless some unusual lixiviant was employed or exotic mineralogy encountered.

The coprecipitation and exchange reactions of uranium with various phases are the most poorly understood aspects of lixiviant-formation interactions. Uranium, and thorium to a lesser extent, can be coprecipitated by calcite, gypsum, Fe-oxyhydroxides, Al-oxyhydroxides, silicates, arsenates, phosphates, and vanadates. Exchange and adsorption of uranium can be done by clays, zeolites, calcite, Fe-oxyhydroxide, Al-oxyhydroxide, and organic materials.

Thus far this report has emphasized the detrimental aspects of lixiviant-rock interactions. However, in some places it may be possible to take advantage of these interactions to improve the recovery of uranium. For example, formation waters with low Eh values that contain ferrous iron will rapidly precipitate Fe-oxyhydroxides where they mix with an oxidizing water and the pH after mixing is greater than 3.5. This precipitation can effectively seal and prevent further mixing of the two waters as has happened numerous times in natural regimes. Hence it might be possible, by adjusting the formation water chemistry, to effectively seal off the ore horizon from the remainder of the formation. This could be beneficial where porous and permeable horizons surround the ore. Another advantage which might be gained from such sealing is that less volumes of lixiviant would be required to completely leach the ore, because only the ore-bearing portion of the formation would be soaked in the lixiviant.

The lixiviant-formation interactions that occur are wholly dependent on the mineralogy of the formation, the chemical composition of the lixiviant, and the residence time of the lixiviant in the formation. Because the lixiviant-rock reactions are dominantly kinetic, a purely equilibrium model for describing the system will not accurately predict what will happen. The chemical reactions that occur entirely in the fluid phase will closely approach equilibrium conditions and hence could be described with an equilibrium model. The dissolution and hydrolysis reactions of the solid phases will be kinetic processes, and hence can only be accurately described via a kinetic model. The most practical method for modeling the system would be a model which combined both an equilibrium and kinetic approach and applied it to the appropriate phases. Considering the many difficulties in directly applying the kinetic data, it is not likely that this approach can be implemented in the near future.

Although a direct theoretical approach to modeling the in-situ leaching system is presently impractical, an empirical model could be erected. Kinetic studies of the leaching of samples of "representative" uranium ores with various lixiviants coupled with the appropriate equilibrium data for the solutions would provide data for such a model. The model may not be fully satisfying from a theoretical and scientific viewpoint, but it is one that could effectively allow an operator to adjust the physiochemical parameters of the lixiviant so that the kinetics of the various reactions could be used to obtain the maximum uranium recovery.

The data obtained by such an approach would serve as the base for a more comprehensive model explaining the intricate details of the chemistry of the leaching of uranium.

Bibliography

Brooks, R. A., 1976, The geological features effecting the in-situ leaching of sandstone uranium deposits *

Busenberg, E. and Clemency, C. V., 1976, The dissolution kinetics of feldspars at 25°C and 1 atm. CO₂ partial pressure: *Geochim Cosmochim. Acta*, v. 40, pp. 41-49.

Christ, C. L., Hostetler, P. B., and Siebert, R. M., 1976, Stabilities of calcite and aragonite: *Jour. Research U.S. Geol. Survey*, v. 2, pp. 175-184.

Lauffenburger, I. and Wey, R., 1966, Incorporation of uranyl cations into carbonates during formation: *Bull. Soc. Chim. France*, v. 1966, pp. 1743-1749.

Ukai, Y., Nishimura, S., and Yokoi, T., 1958, On the uranium exchange of clay minerals: *Memoirs Col. Sci, Univ. Kyoto, Ser. B.*, v. 24, pp. 353-357.

Wollast, R., 1967, Kinetics of the alteration of K-feldspar in buffered solutions at low temperature: *Geochim. Cosmochim. Acta*, v. 31, pp. 635-648.

* Released as USGS open-file report 79-1238, "Geologic parameters effecting the in-situ leaching of uranium deposits" in 1980.

Figure Captions

- Figure 1: A pH-silica concentration diagram showing the breakdown of K-Feldspar as a function of pH. The contours are drawn for equal time in hours. Data from Wollast (1967).
- Figure 2: Moles of SiO_2 contributed by feldspars to a solution as a function of anorthite content after 27.8 hours. Data from Busenberg and Clemency (1976).
- Figure 3: Percent solids in suspension versus amount of dissolved SiO_2 contributed by the K-feldspar to the solution. The contours are equal time in hours. Data from Wollast (1967).
- Figure 4: Eh-pH diagram at 25°C illustrating possible Eh-pH paths for lixiviant-pyrite interactions, calculated assuming $\text{EC} = 100 \text{ mg/l}$. Solid lines are Fe equilibria while the dashed lines are CO_3 equilibria.
- Figure 5: A pH-time diagram illustrating the oxidation of pyrite as a function of grain size and Fe^{3+} . The squares represent $\frac{1}{4}$ mm size fragments of pyrite in oxygenated water, the circles represent less than 200 mesh pyrite in oxygenated water, and the triangles less than 200 mesh pyrite in oxygenated water with 100 ppm ferric sulfate.
- Figure 6: A pH-time diagram showing the interaction between less than 200 mesh pyrite and 100 ml of oxidants (1.5 wt. % concentration).
- Figure 7: A pH-total carbonate diagram illustrating the calcite precipitation curves for oligoclase and anorthite suspensions.

Figure 8: A per cent extraction (E) versus log normality (N) diagram for extraction of uranium for various lixiviants. Data from Ukaï et al. (1958).

