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*Granite Immobilization and
Nuclear Waste*

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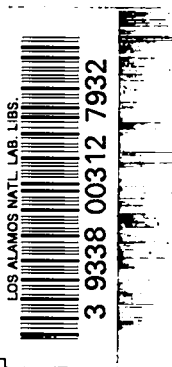
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Uraninite Immobilization and Nuclear Waste

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URANINITE IMMOBILIZATION AND NUCLEAR WASTE

by

C. J. Duffy and A. E. Ogard

ABSTRACT

Considerable information useful in nuclear waste storage can be gained by studying the conditions of uranium ore deposit formation. Further information can be gained by comparing the chemistry of uranium to nuclear fission products and other radionuclides of concern to nuclear waste disposal. Redox state appears to be the most important variable in controlling uranium solubility, especially at near neutral pH, which is characteristic of most ground water. This is probably also true of neptunium, plutonium, and technetium. Further, redox conditions that immobilize uranium should immobilize these elements.

The mechanisms that have produced uranium ore bodies in the Earth's crust are somewhat less clear. At the temperatures of hydrothermal uranium deposits, equilibrium models are probably adequate, aqueous uranium (VI) being reduced and precipitated by interaction with ferrous-iron-bearing oxides and silicates. In lower temperature roll-type uranium deposits, overall equilibrium may not have been achieved. The involvement of sulfate-reducing bacteria in ore-body formation has been postulated, but is uncertain. Reduced sulfur species do, however, appear to be involved in much of the low temperature uranium precipitation.

Assessment of the possibility of uranium transport in natural ground water is complicated because the system is generally not in overall equilibrium. For this reason, Eh measurements are of limited value. If a ground water is to be capable of reducing uranium, it must contain ions capable of reducing uranium both thermodynamically and kinetically. At present, the best candidates are reduced sulfur species.

I. INTRODUCTION

Immobilization of uraninite in natural environments is a phenomenon that needs to be studied because it can provide a model for the deposition of certain minerals. More importantly, it will display the conditions that might be suitable for immobilization of nuclear fission products and other radionuclides. By comparing the chemistry of uranium, neptunium, plutonium, americium, rare earths, and technetium, it may be possible to show how these more troublesome nuclear waste materials would behave under the same conditions that caused uraninite immobilization. This could be true whether the waste products are still associated with UO_2 , as in a spent fuel element or mill tailings, or are separated out and fabricated into some other waste form.

Uranium has an average crustal abundance of about 2 ppm. However, because of its relatively large size and high charge, it is present in only trace amounts in most rock forming minerals. It is, however, found in appreciable amounts in such accessory minerals as fluorite, zircon, and apatite. It is also found sorbed on iron hydroxides, clays, zeolites, and organic matter. In the hexavalent state, it is found in a variety of relatively rare minerals such as the vanadate, carnotite, and the phosphates of the autunite group. Uraninite, however, is the most abundant uranium mineral. It is also the only commonly occurring U(IV) mineral.

II. THERMOCHEMISTRY OF URANIUM

The thermodynamics of uranium and associated compounds and aqueous species to be considered here are moderately well known only at 25°C. However, because nuclear wastes will probably spend most of their lifetime below 200°C and much of it at considerably lower temperatures, many useful things can be learned from these data.

Langmuir¹ suggests that uraninite formed at low temperature contains less than 1% ThO_2 , La_2O_3 , and rare-earth oxides; and although some radiogenic lead is always present in natural uraninite, it can be well approximated as uranium oxide. The oxygen content of natural uraninite is somewhat more uncertain. Palache et al.² list uraninite analyses ranging from $\text{UO}_{2.16}$ to $\text{UO}_{2.64}$. However, Schaner³ found that nearly stoichiometric UO_2 coexists with a phase very

slightly less oxygen rich than U_4O_9 at temperatures less than $200^\circ C$. Van Lierde et al.⁴ confirmed this finding and found that U_4O_9 coexists with U_3O_8 . Van Lierde et al.⁴ also noted the metastable existence of an oxygen-rich phase with uraninite structure.

The structure of U_4O_9 has been examined by Masaki and Doi.⁵ The basic unit cell is very similar to that of UO_2 but with a superlattice structure with a cell dimension 4 times that of UO_2 . There are few analyses of natural uraninite known to have formed at low temperature, but it seems likely that such uraninite has a composition near UO_2 or U_4O_9 . Deviations from these compositions probably are caused by secondary oxidation.

Figure 1 illustrates phase relations in the system $U-O-H_2O-CO_2$. It can be seen that uraninite cannot be expected to form above an oxygen fugacity (fO_2) of about $10^{-4.5}$ bar at $25^\circ C$, whereas stoichiometric UO_2 requires an even lower fO_2 . The field labeled $UO_2 + C$ is not actually attainable because conditions in this field should cause crystallization of graphite and a change of conditions to those of the $UO_2 + C, UO_2$ boundary. This line does, however, indicate the reducing power of graphite. Phase relations in the system $Fe-O-S$ at $25^\circ C$ are shown in Fig. 2. The FeS field is calculated for troilite but should correspond to the field for pyrrhotite reasonably well. It is obvious

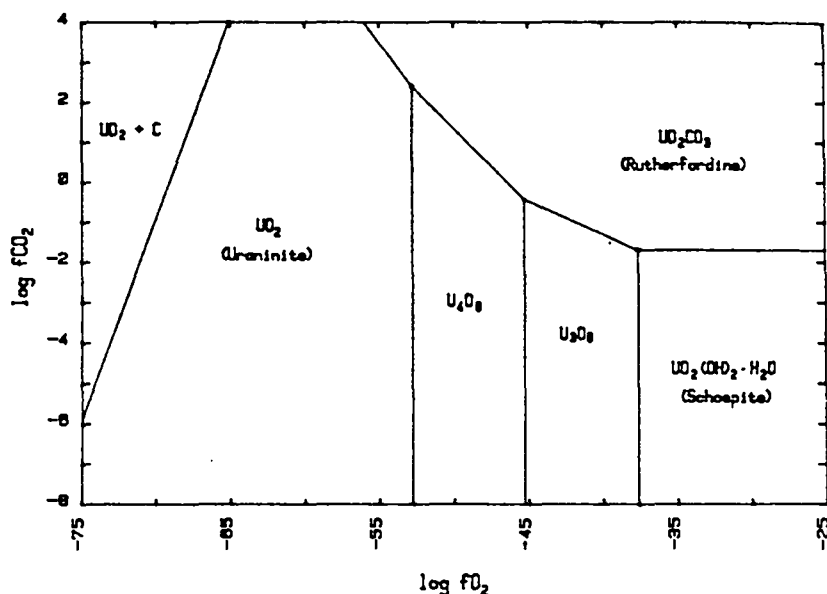


Fig. 1. Phase relationships among idealized stoichiometric phases in the system $U-O-CO_2-H_2O$ as a function of fO_2 and fCO_2 . Equilibrium conditions in the UO_2+C region cannot be achieved because graphite should crystallize under these conditions.

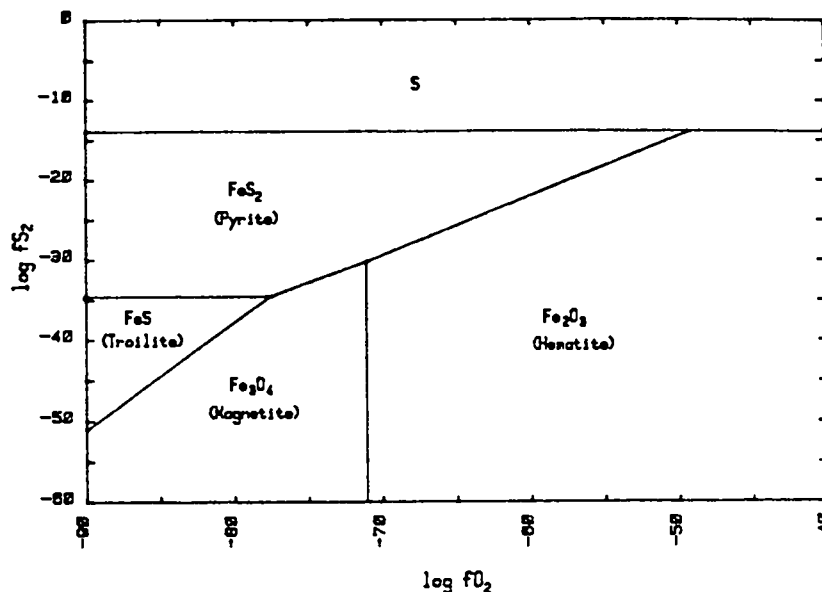


Fig. 2. Phase relationships in the system Fe-O-S as a function of f_{O_2} and f_{S_2} at temperature = 25°C. Sulfur will crystallize under conditions in the field denoted by S.

that uraninite is stable in the magnetite, pyrite, and pyrrhotite or troilite stability fields. This is also true for ferrous-iron silicates such as fayalite and the ferrous-iron amphiboles and biotites. The extent to which ground waters may equilibrate with these phases will be discussed later.

Using the data of Langmuir,¹ the solubility of UO_2 can be calculated as a function of pH, f_{O_2} , and concentration of complexing agents. Figure 3 shows the solubility of uraninite and amorphous UO_2 in the system $U-O_2-H_2$. Ground waters seldom exceed 100 ppb uranium.^{1,6,7} Amorphous UO_2 with the Gibbs energy suggested by Langmuir¹ could precipitate from a 100 ppb uranium solution only under conditions of quite low f_{O_2} and then only over a rather limited pH range. However, most natural UO_2 , even that called pitchblende, is at least finely crystalline and probably has a Gibbs energy very near that given for uraninite. (Reduction of f_{O_2} below 10^{-80} bar does not significantly affect UO_2 solubility because all the uranium in solution is in the +IV state.)

Figure 4 may be compared to Fig. 3 to see the result of carbonate complexing on the solubility of uraninite. Figure 4 shows that, in the pH range

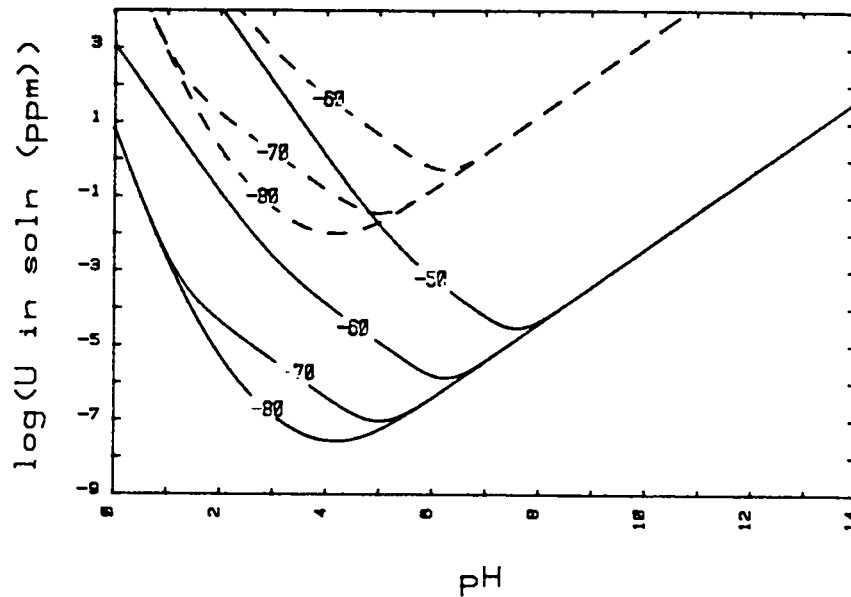


Fig. 3. Solubility of uraninite (crystalline UO₂), solid lines, and amorphous UO₂, dashed lines, in pure water at 25°C and 1 bar as a function of pH and fO₂. Labels on lines are log fO₂.

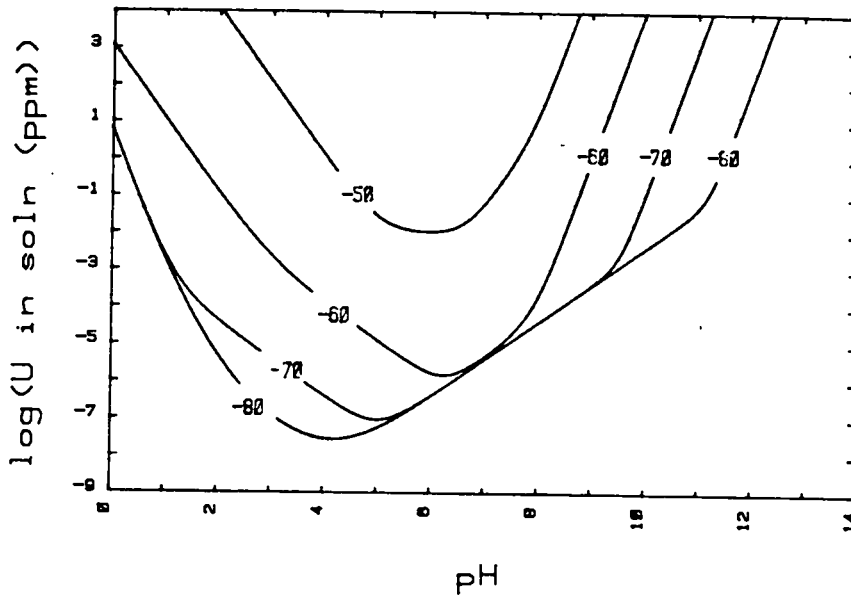


Fig. 4. Solubility of uraninite in aqueous solution as a function of pH and fO₂ with fCO₂ = 0.01 bar. Labels on lines are log fO₂. Temp. = 25°C. Pressure = 1 bar.

from 7 to 8, a $f\text{CO}_2$ of 10^{-2} bar has little effect upon uranium solubility at $f\text{O}_2$'s below 10^{-60} bar. However, with increasing pH the solubility of uranyl carbonate complexes becomes important at increasingly lower $f\text{O}_2$'s. In a similar manner, Fig. 5 shows the effect of phosphate complexing on uraninite solubility for total PO_4^{3-} equal to 0.1 and 1.0 ppm. Langmuir¹ indicates that ground water seldom exceeds 1 ppm PO_4^{3-} . Most of the ground waters in sediments are below 0.1 ppm, whereas granite ground waters often exceed 0.1 ppm. At 0.1 ppm PO_4^{3-} , phosphate complexing is also of minor importance below an $f\text{O}_2$ of 10^{-60} bar. At higher $f\text{O}_2$'s it is primarily important in the intermediate to moderately acid pH range. The effect of F^- at 2 ppm as illustrated in Fig. 6 is restricted to pH's below 7. Although F^- appreciably increases uranium solubility in quite acid environments, it is unimportant at intermediate and alkaline pH's. Figure 7 shows the effect of dissolved sulfur on uranium solubility. At a total sulfur concentration in solution of 0.1 mol/l, which is slightly oversaturated with respect to native sulfur at low pH and slightly undersaturated at high pH, sulfate complexing is important only below pH 7 and at $f\text{O}_2$'s higher than about

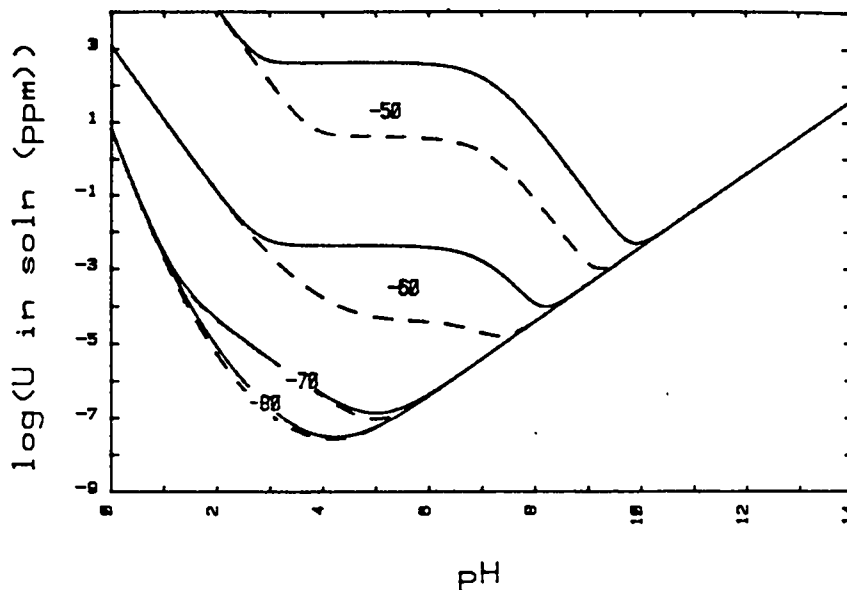


Fig. 5. Solubility of uraninite in aqueous solution as a function of pH and $f\text{O}_2$ with total $\text{PO}_4^{3-} = 1$ ppm (solid lines) and 0.1 ppm (dashed lines). Labels on lines are $\log f\text{O}_2$. Temp. = 25°C . Pressure = 1 bar.

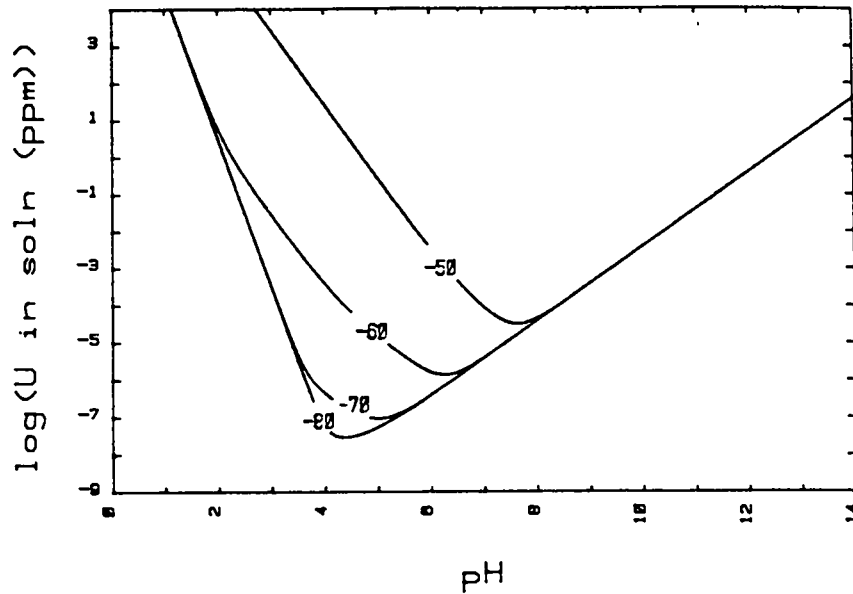


Fig. 6. Solubility of uraninite in aqueous solution as a function of pH and fO_2 with $F = 2$ ppm. Labels on lines are $\log fO_2$. Temp. = $25^\circ C$. Pressure = 1 bar.

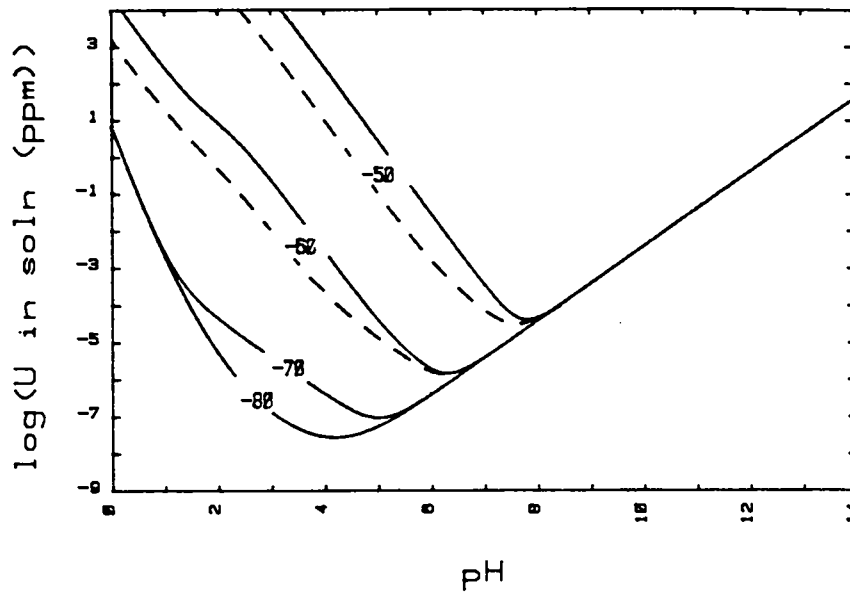


Fig. 7. Solubility of uraninite in aqueous solution as a function of pH and fO_2 with total sulfur equal to 0.1 moles/liter (solid lines) and 0.01 mol/l (dashed lines). Labels on lines are $\log fO_2$. Temp. = $25^\circ C$. Pressure = 1 bar.

10^{-65} bar. When total sulfur is 0.01 mol/l, sulfate complexing is relatively unimportant. Finally, Fig. 8 shows the effect of Cl^- complexing. The diagram is drawn for 1 mol/l Cl^- . Even at this concentration Cl^- has little effect on uranium solubility.

The above calculations have been made assuming ideal solutions. For most ground waters this is probably a very adequate approximation; although the trends would probably remain the same, actual uranium concentrations in concentrated solutions such as brines might vary somewhat. Furthermore, the calculations can only be presumed correct in so far as all important species in solution have been considered. The compilation of Langmuir¹ on which these calculations have been based is probably reasonably complete. However, some solubility experiments at intermediate pH would be very desirable.

From Figs. 4-8 it is obvious that, of the complexing agents considered, only carbonate and phosphate can be expected to increase the solubility of uranium in most ground waters at intermediate pH's. If the $f\text{O}_2$ is below 10^{-70} bar, none of the complexing agents are important in the intermediate pH range.

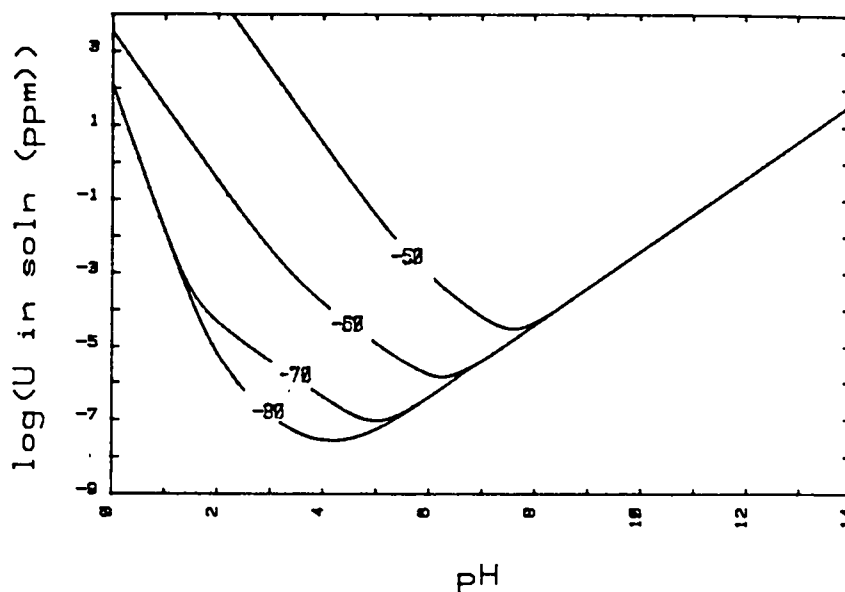


Fig. 8. Solubility of uraninite in aqueous solution as a function of pH and $f\text{O}_2$ with $\text{Cl}^- = 1.0$ mol/l. Labels on lines are $\log f\text{O}_2$. Temp. = 25°C . Pressure = 1 bar.

Such fO_2 's are found in equilibrium with magnetite. In fact, most ferrous-iron silicates are probably capable of reducing aqueous solutions to such levels if given the time to equilibrate. It is interesting to note that in the pH range from 6 to 9 the uranium solubility at fO_2 's less than 10^{-70} bar ranges from approximately 10^{-6} to 10^{-3} ppm. Uranium concentrations in natural waters compiled by Rogers and Adams⁶ range from less than 10^{-4} to $4.6 \cdot 10^{-1}$ ppm. Certainly uraninite maintained within the above ranges of pH and fO_2 in the Earth's crust would be essentially immobile. The question now to be explored is the extent to which these conditions are achieved.

III. URANIUM ORE DEPOSITS

In hydrothermal uranium ore deposits, there is considerable evidence that uranium was deposited as a result of reduction of the hydrothermal fluid by the wall rock of the deposit. The evidence is well summarized by Rich et al.⁸ Hematite, which is rare in other hydrothermal ore deposits, is quite common in hydrothermal uranium deposits where it generally precedes or occurs with pitchblende. It seems probable that hematite is a product of wall-rock oxidation by oxidized, uranium-bearing solutions. Pitchblende is often followed by base-metal sulfides. Deposition of hematite followed by pitchblende and then base-metal sulfides appears to represent a depositional sequence from increasingly reducing solutions.

An excellent example of depositional control by wall-rock reduction of the ore fluid noted by Rich et al.⁸ is the Union Pacific Mine in Golden Gate Canyon, Colorado. Here pitchblende mineralization is confined to a narrow band of hornblende gneiss where it is cut by faults. The ferrous iron previously present in the hornblende has been largely oxidized to hematite in the ore zone.

Although other mechanisms such as loss of CO_2 from the ore solution may sometimes control pitchblende deposition in hydrothermal deposits, it appears that at the temperatures of these deposits, which fluid-inclusion data indicate to be from 100-500°C with values clustering around 200°C, reducing material in the host rock is effective in reducing the hydrothermal fluid. However, at lower temperatures, equilibration between host rock and pore fluid may be quite slow. At the lower temperatures of concern in a nuclear waste repository, the existence of reducing material in the host rock may not assure reducing conditions in the pore fluid.

The conditions of deposition of uranium deposits in sedimentary rock and in particular in Wyoming-type roll deposits may be more applicable to nuclear waste disposal. The roll-front deposits were deposited at the ends of altered tongues in permeable, dipping, sandstone units. The host sandstones are predominantly reduced arkosic or siliceous sandstones. The altered material is clearly oxidized. Analyses of closely spaced samples across several ore bodies by Harshman⁹ indicate a progressively more reducing environment moving from the oxidized sandstone across the ore zone and into the unoxidized sandstone.

The oxidized zone contains little or no pyrite and generally less carbon, both mineral and organic, than the reduced zone. Pyrite is most abundant in the reduced zone near the redox interface and gradually decreases with distance into the reduced zone. Iron minerals remaining in the oxidized zone are generally limonite, hematite, or corroded pyrite rimmed by limonite.

Uraninite precipitation to form the ore body is caused by the interaction of relatively oxidizing uranium-bearing solutions with the reduced sandstone. However, there are two credible hypotheses that may lead to uranium precipitation. The first hypothesis relies on bacterial activity to catalyze the reduction of sulfate, which is known to be a very sluggish reaction at low temperature. Oxidizing ground water reacts with pyrite at the roll front to produce sulfate and ferrous iron. This reaction may proceed either inorganically or with the help of aerobic bacteria. As this solution proceeds into the ore zone, the sulfate is reduced by anaerobic bacteria such as *Desulfovibrio desulfuricans* using the organic matter present as food. One of the products of the bacterial metabolism is H_2S or HS^- , which functions as a reductant to precipitate uraninite. Pyrite is also precipitated by recombining the sulfide with the available ferrous iron in solution.

That the appropriate bacteria may be present in such deposits is confirmed by Lisitsyn and Kuznetsova.¹⁰ They were able to grow a variety of aerobic and anaerobic bacteria cultures by inoculating with well waters, taken under carefully controlled conditions from a sandstone strata containing a uranium roll. A particularly varied and active set of bacteria was found in the vicinity of the redox interface.

Sulfur isotopic data have also been used as an argument for bacterial involvement in the formation of these uranium deposits. Jenson¹¹ found that sulfur in sandstone-type uranium deposits was generally enriched in lighter isotopes and considered this suggestive of sulfides produced by sulfate reducing

bacteria. Harrison and Thode¹² have shown bacteria to be capable of isotopically fractionating sulfur. Thode et al.¹³ measured the sulfur isotopic compositions of sedimentary sulfides and sulfates of varying ages and found little fractionation in specimens older than 700-800 million years and increasing fractionation at younger ages. They took this as evidence of the appearance of sulfur-reducing bacteria 700-800 million years ago. Ault and Kulp¹⁴ consider bacterial reduction of sulfate to be the most important cause of isotopic fractionation of sulfur, but they note that inorganic processes may be locally important.

Granger and Warren^{15,16} have proposed an alternate mechanism for roll formation in which the oxidation of pyrite produces sulfite and thiosulfate. These ions are metastable and quite reactive. They react with iron in solution to produce ore-stage pyrite and sulfate that is unreactive and leaves the system with the ground water. The intermediate sulfur species may also be effective in reducing and thus fixing uranium. They may also react with water decomposing to H_2S or HS^- and SO_4^{2-} , thus producing even stronger reducing agents.

Because sulfur is isotopically fractionated by exchange reactions involving different oxidation states of sulfur,¹⁷ the repeated oxidation of sulfur at the roll front and its reduction in the interior of the roll provide a mechanism for sulfur fractionation even in the absence of bacteria. Warren¹⁸ has even argued that the observed distribution of sulfur isotopes favors the abiogenic hypothesis. Warren¹⁹ has also presented models of pyrite distribution in roll-type deposits that favor abiogenic formation. At the present time it seems uncertain whether or not bacteria are essential to the formation of uranium roll-type deposits.

IV. REDOX STATE OF NATURAL GROUND WATERS

Most ground waters are not in overall equilibrium and therefore cannot be described by a single oxidation potential (Eh). In the recharge area of an aquifer, the ground water generally contains dissolved oxygen and oxidized species such as NO_3^- , SO_4^{2-} , and Fe^{3+} and dissolved organic carbon (DOC). Such is clearly not an equilibrium assemblage because DOC is capable of reducing all of the above. Further, Stumm and Morgan²⁰ note that "because many redox processes do not couple with one another readily, it is possible to have several different apparent oxidation-reduction levels in the same local." On these grounds alone, it is obvious that platinum-electrode measurements of Eh

cannot give a quantitative measure of the redox state of a ground water. A single redox state will, in general, not exist. Moreover, lack of electrochemical reversibility at the electrode and electrode contamination lead to additional ambiguity in platinum-electrode measurements of redox potential²¹.

Nevertheless, platinum-electrode measurements do appear to yield a qualitative measure of the redox state of ground waters. Champ et al.²² cite three examples of closed ground water systems in which Eh decreases away from the recharge area. This decrease is accompanied by a decrease in dissolved oxygen to below detection limits and decrease in sulfate and increase in sulfide concentration.

The reduction of ground water appears to be catalyzed by bacterial activity. Stumm and Morgan²⁰ emphasize the importance of bacterial activity in catalyzing redox reaction in natural waters. The waters considered by Stumm and Morgan²⁰ are chiefly surface waters, but it seems probable that bacteria are also important in aquifer systems. Champ et al.²² note the presence of denitrifying and sulfate-reducing bacteria in ground water systems, and as noted above, Lisitsyn and Kuznetsova¹⁰ have identified a large number of bacteria in ground water. Most ground waters may be expected to provide the requirements of bacterial activity. The average DOC content of uncontaminated ground waters in the United States was found by Leenheer et al.²³ to be 0.7 mg/ℓ. According to Zobell and Grant²⁴ this should be adequate for bacterial growth. Champ et al.²² argue that nitrogen, phosphorus, sulfur, and trace metal concentrations should also be adequate.

Closed aquifer systems, that is those aquifers which are closed to the addition of oxidizing material except from their recharge areas, appear to become increasingly reducing away from the recharge area as bacterial activity promotes the reaction between DOC and oxidized material in solution in the aquifer.

V. IMMOBILIZATION OF URANIUM IN NATURAL WATERS

The primary mechanism of uranium removal from natural waters is through reduction of soluble U(VI) to quite insoluble U(IV) and precipitation as uraninite (usually the pitchblende variety at low temperature) or more rarely as coffinite.

At elevated temperatures experienced during the formation of hydrothermal uranium deposits, reaction with the wall-rock controls the redox state of the

solution. Uranium is deposited in this environment when the solution is reduced by interaction with ferrous-iron-bearing minerals or other reduced solids. These systems can be well modeled with equilibrium thermodynamics. However, in low-temperature ground water systems, disequilibrium is generally the rule. Reaction nevertheless tends to proceed toward an equilibrium state. The chief reductant in these systems is DOC, although some reaction also occurs with the more reactive minerals of the enclosing rock. Uraninite precipitation in these systems is generally associated with precipitation of iron sulfides, primarily pyrite. In terms of the ground water chemistry, pyrite precipitation will not occur until reduction of the ground water has been sufficient to produce appreciable H_2S or HS^- (pH determines which will be most abundant) at the expense of SO_4^{2-} . It seems likely that H_2S and HS^- are the most important reductants for uranium in low-temperature aqueous environments. The two most probable sources of H_2S and HS^- are the reduction of more oxidized sulfur species by sulfate-reducing bacteria and the oxidation of pyrite by ground waters free of dissolved oxygen.

What characteristics are desirable in a nuclear waste disposal site? Certainly the ground water should contain an appreciable amount of its sulfur as H_2S or HS^- . The presence of a moderate amount of DOC (perhaps 0.5 mg/l) and sulfate-reducing bacteria would be encouraging. The presence of at least a small amount of pyrite might also help to assure that the ground water would remain reducing.

It might also be tempting to use platinum-electrode measurements of Eh to identify reducing ground water. Although Eh measurements do tend to be lower in more reduced waters, the large number of uncertainties associated with such measurements make them difficult to interpret. Langmuir and Chatham²⁵ used Eh measurements in calculating saturation uranium concentrations in several uraninite-, coffinite-ore bodies. They found that the actual measured concentrations were sometimes several orders of magnitude higher than calculated. They attributed this to the finely crystalline nature of the pitchblende present in the ore bodies, which would tend to make it more soluble than the uraninite used in the model. An alternate explanation would be that the ground water is more oxidizing than the Eh measurement indicates. Langmuir and Chatham²⁵ note evidence that the pyrite in the ore bodies may be oxidizing. Further, the higher uranium concentrations observed in the ore bodies are higher than are generally found in ground waters except where associated with oxidizing

uraninite ore bodies. Finally, some wells in the ore bodies contained as little as 1 ppb uranium, which is relatively close to the predicted value. The use of Eh to predict uranium concentrations in ground waters is, at best, suspect.

The evidence from hydrothermal uranium deposits suggests that it may be useful to include reducing materials in the packing material around waste canisters. During the high temperature portion of the repository's lifetime, magnetite would probably act as an effective reductant as might other simple oxides and sulfides. The quantity of packing material is probably its most severe limitation. If it is to be effective over an extended period, either the oxidizing capacity of the incoming ground water must be low or the total amount of water must be limited.

VI. FISSION PRODUCT AND ACTINIDE IMMOBILIZATION

In the previous sections we have discussed the conditions that may have resulted in the immobilization of uraninite in nature because of its extreme insolubility. By comparing uranium chemistry to the chemistry of selected nuclear wastes, it may be possible to predict under what conditions these nuclear wastes may also be immobilized. Laboratory experiments can be used to verify the conclusions.

A. Conditions for Minimum Solubility

In any kind of system, especially a geologic setting with its many mineral assemblages, the processes associated with the formation of the crystalline oxides must be considered. Reactions that need to be considered are hydrolysis of the metal ions, adsorption, and finally, precipitation and crystal growth. R. O. James and T. W. Healy²⁶ studied the adsorption of hydrolyzable metal ions on substrates of low dielectric constant such as SiO_2 . They observed, as many other researchers have done, that the adsorption of the metal ions was qualitatively, but not simply, related to the formation of hydrolysis products of the metal ions. For each metal ion there was a very narrow pH range of about 1 unit where the percentage adsorbed changed from 0 to 100%. In their model, James and Healy related this adsorption and eventual precipitation to the hydrolysis products of the metal ions, where the second hydrolysis product appeared to be the dominant variable.

The model of James and Healy should apply to a description of the adsorption of actinides and rare earths on minerals. The actinides and rare earths are known to hydrolyze, and the minerals in the ground are of low dielectric constant similar to SiO_2 used in developing the model. B. Allard et al.²⁷ produced diagrams of the concentrations of the various oxidation states of the light actinides, uranium, neptunium, and plutonium, and their hydrolysis products as a function of pH. Qualitatively, uranium, neptunium, and plutonium exhibit similar diagrams for each particular oxidation state. The second hydrolysis product for each oxidation state reaches a high percentage concentration at pH 8 for oxidation state III, pH 2 for IV, pH 10 for V, and pH 4 for oxidation state VI. By comparison to the model, adsorption would be expected to set in strongly at 1 to 2 pH units below the pH at which the second hydrolysis product is prominent; that is, pH 6-7 for oxidation state III, pH 1 for IV, pH 8-9 for V, pH 2-4 for oxidation state VI. At the pH 8 of naturally occurring waters, only the +V oxidation state may not be strongly adsorbed. Oxidation states IV and VI may have even precipitated depending on their concentration in solution at the adsorption sites.

Very little is known about the hydrolysis of the rare earth ions such as europium and cerium and other actinides such as americium. As listed in the review by Baes and Mesmer,²⁸ the +III oxidation state is the most stable, and hydrolysis and precipitation occur almost simultaneously with a minimum solubility of $\sim 10^{-8}$ mol/l at pH 9. It would, therefore, be expected that adsorption would abruptly increase at \sim pH 7-8. The relatively abrupt changes in adsorption as a function of pH found by Beall et al.²⁹ for americium at \sim pH 5 and neptunium at \sim pH 8 on granites fit reasonably well with the discussion above. In air-saturated solutions at pH 8, americium exists as the +III oxidation state and neptunium most likely as the +V oxidation state.

T. W. Newton, et al.³⁰ has calculated the solubilities of the various hydrous oxides and crystalline oxides of uranium, neptunium, and plutonium as a function of Eh and pH. In these calculations he used the thermodynamic data and estimates from a review by B. Allard et al.²⁷ This compilation contains a great many estimates, although the chemistry of uranium, neptunium, and plutonium are some of the most studied systems in chemistry, especially uranium. The concentration of ions at minimum solubility of the various oxides and the pH at which the minimum solubility occurs are obtained from these calculations. These results together with the concentrations at pH 8 are listed in Table I.

TABLE I
SOLUBILITIES OF HYDROUS OXIDES
(mol/l)

<u>Oxidation State</u>	<u>Solubility</u>	<u>Minimum Solubility</u>	
	<u>pH 8</u>	<u>pH</u>	<u>Solubility</u>
U (VI)	10^{-5}	8-10	10^{-5}
U (IV)	10^{-6}	4-7	10^{-7}
Np(VI)	10^{-4}	5-10	10^{-4}
Np(V)	10^{-3}	8-10	10^{-3}
Np(IV)	10^{-6}	4-8	10^{-6}
Pu(VI)	10^{-5}	6-9	10^{-5}
Pu(IV)	10^{-6}	4-6	10^{-8}

SOLUBILITIES OF CRYSTALLINE OXIDES
(mol/l)

U (VI)	10^{-5}	8-10	10^{-5}
U (IV)	10^{-10}	4-7	10^{-11}
Np(VI)	10^{-4}	5-10	10^{-4}
Np(V)	10^{-3}	8-10	10^{-3}
Np(IV)	10^{-12}	4-8	10^{-12}
Pu(VI)	10^{-5}	6-9	10^{-5}
Pu(IV)	10^{-14}	4-7	10^{-15}

A pH of 8 was chosen for special consideration because it is the pH generally considered representative of deep ground waters.

Each of the elements exhibits multiple oxidation states. For each particular oxidation state, there is a range of pH over which the solubility of the oxide is a minimum. The +IV oxidation state exhibits the lowest solubility, and its minimum solubility occurs at a pH of 4 to 7 for each of the light actinides. Among the oxides, the highest minimum solubility is noted for Np(V) oxide at pH 8 to 10, a higher pH than noted for the other oxidation states. Uranium and plutonium, by these calculations, do not have a stable +V oxide, and therefore, +V oxides for uranium and plutonium are not listed in Table I. In addition, Table I shows that the solubilities of UO_2 , NpO_2 , and PuO_2 under

certain conditions are indeed extremely low (10^{-11} to 10^{-15} mol/l), and the solubility of the metastable hydrous oxides is very much higher than the crystalline oxides.

The rare earths and other actinides are different from uranium, neptunium, and plutonium. They do not exhibit as many oxidation states, the +III oxidation state is the most stable in solution, and the +III hydroxide has a minimum solubility of $\sim 10^{-8}$ mol/l at \sim pH 8-10.²⁸

B. Importance of Oxidation State

It is apparent that the oxidation state of the actinide or rare earth is the most important variable property in the process of adsorption, hydrolysis and precipitation, especially if maximum adsorption and precipitation and minimum solubility are the goal.

Referring to the calculations and figures by Allard et al.²⁷ for the concentrations of ions in solution as a function of Eh, various estimates related to geologic settings can be made. A pH of 8 is assumed because that pH seems representative of natural waters of geologic burial. From these calculations the oxidation-reduction potentials of the water would have to be reduced to < -0.100 V for uranium, $< +0.100$ V for neptunium, and $< +0.400$ V for plutonium to have the +IV oxidation state of these elements as the predominant species and, therefore, have the highest adsorption and lowest solubility. A further conclusion, important, but somewhat redundant, is that any pH 8 water that is sufficiently reducing to immobilize uranium will also immobilize neptunium and plutonium.

The importance of oxidation state is apparent also for the nuclear waste element technetium. At an Eh above 0.00 V at a pH 8, the oxidation state of technetium is probably +VII as the TcO_4^- ion. As an anion in a stable configuration, the TcO_4^- would not be expected to hydrolyze to any extent nor would it be expected to absorb. When the Eh is reduced below 0.00 V and TcO^{+2} is formed, hydrolysis, adsorption, and finally low solubility of a precipitated oxide will be seen. Again, the conditions that will immobilize uranium should immobilize technetium also.

C. Plans for Laboratory Control of Eh

The importance of Eh control in the immobilization of uraninite, fission products, and other actinides raises the question of what is achievable in the laboratory. Of the many methods used in attempts to achieve anaerobic conditions,

the most extensively used is the bubbling of an inert gas such as nitrogen or a reducing gas such as hydrogen through a solution for a period of time. The oxygen concentration in equilibrium with such a situation can be calculated by assuming the oxygen in the inert gas is ~ 0.1 ppm, a realistic figure if no special precautions are taken to purify the tank gases. This figure of 0.1 ppm oxygen is also realistic for the oxygen content of a good inert-atmosphere glove box. Water at pH 8 in equilibrium with these gases at the Los Alamos, New Mexico, altitude would then contain 3.5×10^{-6} ppm oxygen or 2.5×10^{-9} bar of oxygen. This is not a very low oxygen fugacity if one looks at Figs. 3 through 8, where oxygen fugacities of 10^{-50} to 10^{-80} bar are needed for minimum solubility of uraninite. A corresponding Eh value of 0.63 V at pH 8 can be calculated by use of the Nernst equation. This is too positive an Eh value to reduce any of the light actinides, uranium, neptunium, or plutonium, to the +IV oxidation state, where maximum adsorption and minimum solubility of the oxide are observed. At this Eh, the concentration of particular oxidation states would be U(VI) exclusively: Np(V) 100%, Np(VI) <0.1%, Pu(VI) 50%, Pu(IV) 50%, and Pu(V) 1%. The use of a reducing gas such as hydrogen to react with the oxygen in solution also has its problems. C. J. Duffy^{31,32} has shown quite clearly that, although a water solution being purged with hydrogen gas registers a negative Eh indicative of almost complete absence of oxygen, the solubility of uraninite is quite high demonstrating the opposite conclusion on oxygen content. At room temperature the reaction between hydrogen and oxygen in solution is quite slow without a proper catalyst.

A low oxygen content of $< 10^{-70}$ bar can be obtained in solution by first bubbling the inert gas through a scrubber containing Cr^{+2} solution and then through the solution of interest. However, it must be absolutely certain that no leaks are present in the equipment and that no materials are used as gas lines or containers that allow diffusion of oxygen into the solutions. Although this procedure can eliminate the oxygen from solution, it does nothing to maintain the Eh at a particular level. A potentiostat and/or Eh buffer are needed for this. Some of the Eh buffers may also be helpful in reacting with any oxygen still in solution.

As stated earlier, solutions that are sufficiently reducing to immobilize uraninite will also be suitable for immobilizing neptunium, plutonium, and technetium. Therefore, waters of pH 8 with Eh < -0.1 V will be sought. The steps to be taken are as follows.

- 1) All experiments will be carried out in an inert-atmosphere glove box filled with nitrogen with <0.1 ppm O_2 . This will insure that the maximum oxygen content of any solution would be 2.5×10^{-9} bar even if the solution were accidentally equilibrated with the glove-box atmosphere.
- 2) All equipment used inside the glove box will be designed and assembled as if it were to be used for high-vacuum experiments because exposure of solutions to glove-box atmospheres can lead to oxidation of the solutions.
- 3) A reference deoxygenated solution of \sim pH 8 will be prepared by either or both of two methods: a) a pure nitrogen gas will slowly be bubbled through a Cr^{+2} scrubber and then into the reference solution, or b) the reference solution will be degassed by passing hydrogen through it in the presence of palladium black or activated-palladium sponge as a catalyst.
- 4) This reference deoxygenated solution will then be used as a make-up solution for the Eh buffer and solubility experiments.
- 5) A group of organic redox indicators and inorganic couples has been selected because of their low Eh at pH 7-8, solubility in H_2O , and stability in the pH range 6 to 10.

The selection was made on the basis of the description in the book Indicators by J. M. Ottaway.³³ The suitable Eh indicators are listed in Table II along with their calculated Eh at pH 7 (E_m^7) and the pH range of usage.

These redox indicators will be used in conjunction with a potentiostat to set and maintain the Eh of the solution. Each of the indicators will be investigated to determine if it is stable over long periods of time, is soluble in the

TABLE II
Eh REDOX INDICATORS AND COUPLES

<u>Name or Couple</u>	<u>E_m^7 (v)</u>	<u>pH Range</u>
Indigo Carmine	-0.125	<9
Lissamine Blue BF	-0.253	1-11
Rosinduline 2G	-0.281	4.8-11.4
Induline Scarlet	-0.299	3.0-8.6
N,N'-dimethyl Viologen	-0.446	8.4-13
$Fe^{+3} - Fe^{+2}$	-0.185	7-10
As(V) - As(III)	-0.1	3-11
$SO_4^{2-} - HS^-$	-0.45	1-11

required pH range, exhibits relatively rapid oxidation-reduction reactions with the ions of interest, exhibits reversible reactions at the working electrodes of a potentiostat, does not form complexes or precipitates with the ions of interest, and is stable in the presence of mineral assemblages.

The quantities of oxygen in solution that we are concerned about are too small to measure directly. Commercial oxygen probes have a detection limit of ~0.5 ppm or 10^{-9} bar. Oxygen probes, therefore, are not useful in our problem except to indicate a leak into the inert-atmosphere glove box.

Eh measurements on natural waters have been shown to be difficult to interpret. M. Whitfield³⁴ presents a theoretical discussion in which it appears that platinum electrodes could give meaningful results between +0.300 and -0.100 V at pH 8. However, this remains to be proved experimentally. It has been shown by C. J. Duffy^{31,32} that very misleading Eh measurements can result if the solution is in a nonequilibrium condition. Nevertheless, Eh is still a very useful mathematical concept for comparing oxidation-reduction reactions.

The best measurement of oxygen content of the solutions may be from the measured solubility of crystalline UO_2 . Using the potentiostat and a negative Eh buffer, the Eh of a solution can be set for the experiments on UO_2 solubility. Solution concentrations of natural-isotopic-abundance uranium can be experimentally determined at concentrations of 1 to 5 ppb by counting the delayed neutrons emitted after neutron activation of the solution in a thermal reactor. Sensitivity can be increased a factor of 100 by using ~70% enriched $^{235}\text{UO}_2$ as the uranium source. From Fig. 3 the minimum solubility of UO_2 in a solution of 10^{-80} bar oxygen increases from $10^{-4.5}$ ppb to 1 ppb in changing the pH from 4 to 9. By holding the Eh constant with the potentiostat and Eh buffers, varying the pH, and measuring the UO_2 solubility, we should be able to show the trend of solubility versus pH even at these extremely low solubilities. An analysis of the uranium isotopic composition in the solid and the solutions would also be an indication of any contamination from other uranium sources such as the container vessel.

Once Eh control of pH 8 solutions has been established, these solutions can then be used to verify in the laboratory the expected immobilization of various nuclear wastes in geologic media.

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