

Geochemistry of Radioactive Waste Disposal

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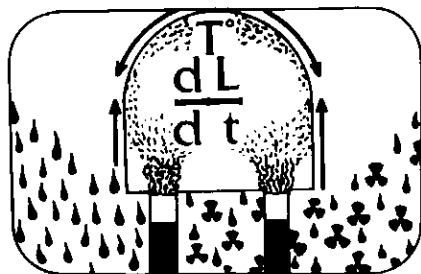
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Résumé de l'article

Safe, permanent disposal of radioactive wastes requires isolation of a number of elements including Se, Te, I, Sr, Cs, Pd, U, Np, Pu and Cm from the environment for a long period of time. The aquatic chemistry of these elements ranges from simple anionic (I^- , 10^{-3}) and cationic (Cs^+ , Sr^{++}) forms to multivalent hydrolyzed complexes which can be anionic or cationic ($Pu(OH)^+$, $Pu(OH)_2$, $PuO_2(CO_3)(OH)^+$, $PuO_2C_1^+$ etc.) depending on the chemical environment. The parameters which can affect repository safety are rate of access and composition of groundwater, stability of the waste container, stability of the waste form, rock-water-waste interactions, and dilution and dispersion as the waste moves away from the repository site. Our overall research program on radioactive waste disposal includes corrosion studies of containment systems, hydrothermal stability of various waste forms, and geochemical behaviour of various nuclides including solubilities, redox equilibria, hydrolysis, colloid formation and transport, ion exchange equilibria and adsorption on mineral surfaces, and irreversible precipitation reactions. This paper discusses the geochemistry of I, Se, Te, Cs, Sr and the actinide elements and potential mechanisms by which the mobility could be retarded if necessary.



Geochemistry of Radioactive Waste Disposal

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Abstract

Safe, permanent disposal of radioactive wastes requires isolation of a number of elements including Se, Tc, I, Sr, Cs, Pd, U, Np, Pu and Cm from the environment for a long period of time. The aquatic chemistry of these elements ranges from simple anionic (I^- , 10^{-3}) and cationic (Cs^+ , Sr^{++}) forms to multivalent hydrolyzed complexes which can be anionic or cationic ($Pu(OH)_2^+$, $Pu(OH)_3^+$, $PuO_2(CO_3)(OH)^-$, PuO_2Cl^+ etc.) depending on the chemical environment. The parameters which can affect repository safety are rate of access and composition of groundwater, stability of the waste container, stability of the waste form, rock-water-waste interactions, and dilution and dispersion as the waste moves away from the repository site. Our overall research program on radioactive waste disposal includes corrosion studies of containment systems, hydrothermal stability of various waste forms, and geochemical behaviour of various nuclides including solubilities, redox equilibria, hydrolysis, colloid formation and transport, ion exchange equilibria and adsorption on mineral surfaces, and irreversible precipitation reactions. This paper discusses the geochemistry of I, Se, Tc, Cs, Sr and the actinide elements and potential mechanisms by which the mobility could be retarded if necessary.

Introduction

Safe, permanent disposal of radioactive waste requires isolation of a number of diverse chemical elements from the environment for a long period of time. The Canadian approach to nuclear waste management is disposal in vaults mined deep into crystalline rocks of the Precambrian Shield (Boulton, 1978). A repository will consist of a mined chamber some 500-1000 metres below the surface, the shaft leading to it and any other underground facilities. After disposal operations have been completed, the design criteria require backfilling and sealing of the entire repository in such a manner as to return the land to a natural condition where no further maintenance or supervision is necessary. The backfilling and sealing of the repository will limit physical access to the vault save by deliberate intrusion of man. This means that the safety of the vault will depend on the geological features of the site, and on engineered features added at the time of development.

In the post-closure period, the repository and surrounding rocks will become heated from the decay of the radioactive waste. The maximum temperature reached is an engineering variable and will depend on the amount of radioactivity emplaced per unit area. Our present reference design limits this temperature increase to $100^\circ C$ (Boulton, 1978). The elevated temperature period will last from tens to several hundreds of years depending on the waste form.

After closure has been completed, the only failure mechanism which can be identified is the prospect that deeply circulating groundwater may penetrate to the waste, leach out the radionuclides, and carry them back to the surface. A number of protective barriers will be used to minimize this. These barriers are illustrated in Figure 1. They are: the waste form itself, its container, the buffer material surrounding the container, the backfill and sealing material, the massive geological barrier, and finally dilution, dispersion and retention in the environment. It is our intention to design the waste form as a principle barrier, with the other barriers being successively redundant.

To evaluate the safety of the entire repository, we must understand how each component will behave in the geological environment and show that all components are compatible. Our research and development program consists of a number of interacting scientific and technological studies and includes waste form development, corrosion of various engineering materials which might be used for waste containment, development of buffers to protect the containers and restrain the movement of radionuclide should the containers be breached, development of backfill and sealing materials with suitable chemical and physical properties, hydrothermal alteration of silicate minerals, interaction of waste nuclides with rocks and minerals, transportation of radionuclides in groundwater, and behaviour of various radionuclides in biological ecosystems. A major proportion of the geochemical research will be devoted to understanding the behaviour of radionuclides in groundwater in order that we can create waste forms and containment systems which will limit radionuclide transport. Another part of the geochemical research must be devoted to ensuring that the results of

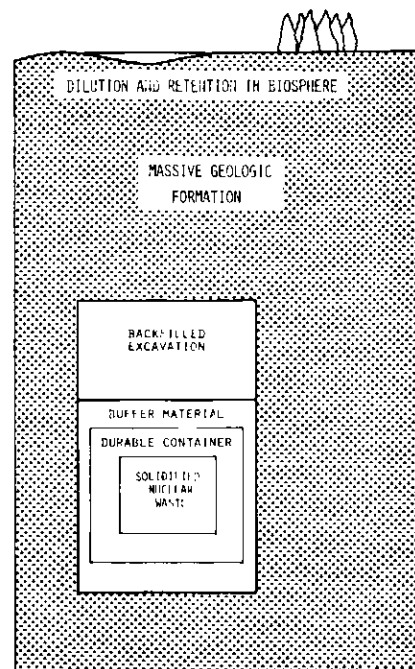


Figure 1
Features protecting man from nuclear waste.

all other investigations are relevant to the geological conditions. This paper discusses the geochemistry of some of the radionuclides and shows why a nuclear waste repository is not expected to present any hazard to the biosphere.

Discussion

Table I lists a number of radionuclides which are of interest for detailed research. Three radionuclides, ^{129}I , ^{79}Se and ^{99}Tc go into solution as simple anionic species. Once dissolved, these anions will not interact significantly with silicate minerals (Neretnieks, 1977) and they would move with the same velocity as the groundwater. This means that we should not rely entirely on the geological barrier to provide retardation and must seek alternative means of immobilizing these anions in the repository. One possibility is to place materials in the buffer which will prevent the I, Se and Tc from being released.

Copper in the metallic state and some copper minerals could be useful for this purpose. We have shown in laboratory experiments that Cu metal will react directly with I^- and SeO_4^{2-} in solution to precipitate low solubility compounds. Copper metal, Cu_2O (Cuprite) and CuFeS_2 (chalcopyrite) adsorb I^- from solution (Haq *et al.*, 1979). Cupric oxide (CuO) on the other hand, does not adsorb I^- , which is compatible with known chemistry of Cu_2^+ (Ekbom, 1977). It has been suggested that Cu metal might have two uses in a waste repository: 1) as a container metal; and 2) as an investment material for filling any free volume of the waste form inside the container. If copper is to retard the movement of I^- , then we must maintain the redox conditions in water near the waste container such that copper remains as the metal or +1 oxidation state. Some relevant redox equilibria are shown in Figure 2. One of the important features to note in Figure 2 is the position of the magnetite (Fe_3O_4) - hematite (Fe_2O_3) redox equilibrium relative to that for $\text{Cu}-\text{Cu}_2\text{O}$. Iron is ubiquitous in rocks and in unaltered plutonic rocks is mainly in the Fe^{2+} oxidation state. Hence, deeply circulating water which remains in equilibrium with the rocks should have

Table I

List of important radionuclides for geochemical study. This list is not comprehensive and not all isotopes are listed. Selection was based on a nuclide

having a half-life of tens of years and being present in significant quantity in the irradiated fuel (see Boulton, 1978 for more detail).

| Isotope | Half-Life (Years) | Probable Form in Groundwater |
|--------------------------|--------------------------|---|
| ^{79}Se | $\leq 6.5 \times 10^4$ | SeO_3^- , SeO_4^{2-} |
| ^{99}Tc | 2.1×10^5 | TcO_4^- |
| ^{129}I | 1.6×10^7 | I^- , IO_3^- |
| ^{90}Sr | 29 | Sr^{2+} |
| ^{137}Cs | 30.2 | Cs^+ |
| ^{107}Pd | 7×10^6 | Pd^{2+} , hydrolysed complexes likely |
| ^{238}U , etc. | 4.5×10^9 , etc. | variable, most soluble as UO_2^{2+} or U(VI) fluoride, phosphate or carbonate complexes; research in progress |
| ^{239}Np | 2.1×10^6 | variable, most mobile as NpO_2^{2+} or Np(VI) complexes; research required |
| ^{239}Pu , etc. | 87.7, etc. | variable, several oxidation states can co-exist, many hydrolysis complexes possible; forms polymers in all oxidation states; research in progress |
| ^{241}Am | 432 | variable, research required |
| ^{244}Cm , etc. | 18.1, etc. | variable, research required |

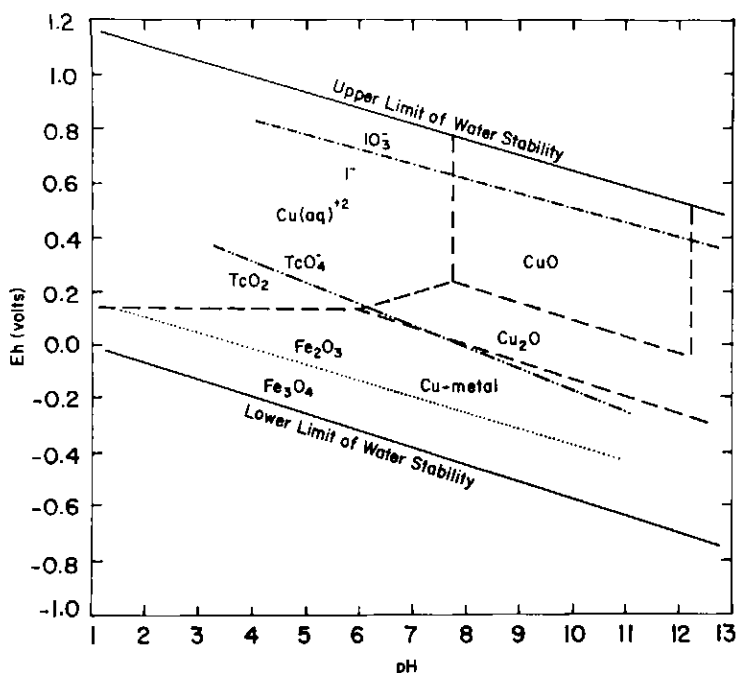


Figure 2

Eh-pH diagram showing some of the equilibria in the Fe-O, Cu-O, I-O, and Tc-O systems. The Fe-O and Cu-O equilibria are from Garreis and Christ (1965). The Fe-O

system assumes pure H_2O , the Cu-O system is calculated for $\Sigma \text{Cu}^{2+} = 10^{-6}\text{M}$. The TcO_2 , TcO_4^- and IO_3^- equilibria are from Pourbaix (1963), and were calculated for $\Sigma \text{Tc} = 10^{-6}\text{M}$, $\text{I} = 10^{-6}\text{g/L}$

a redox potential somewhere near that of the magnetite-hematite buffer, and should prevent the oxidation of copper.

Technetium is another nuclear product requiring special attention. It has a long half-life and goes into solution as the highly mobile pertechnetate anion (TcO_4^-). However, as a metal or as the oxide TcO_2 , it is practically insoluble. The $\text{TcO}_2/\text{TcO}_4^-$ redox boundary is shown in Figure 2. The potential required to oxidize TcO_2 to TcO_4^- is very close to the $\text{Cu-Cu}_2\text{O}$ boundary and we cannot expect copper to prevent oxidation. This has been our experience in the laboratory. The magnetite-hematite buffer potential is well below that of $\text{TcO}_2/\text{TcO}_4^-$ (Fig. 2) and if the water remains in equilibrium with the rocks, technetium should be immobilized.

Lead metal also has been suggested for waste management use. It would be used as a container lining to serve as a radiation shield to make handling easier and as an investment material to fill any free volume (Ekbohm, 1977). In the natural environment, Pb corrodes to the oxide PbO or to basic lead compounds such as hydrocerrusite ($\text{PbCO}_3 \cdot \text{Pb(OH)}_2$) (Shrier, 1976). Coatings of these materials will inhibit further corrosion in many natural waters. We have been studying reactions of PbO and hydrocerrusite with the radioactive waste anions I^- , SeO_4^{2-} and TcO_4^- and have found that low solubility compounds form and remove these anions from solution. Some of our results are shown on Figure 3. Greater than 95 per cent of the I^- , TcO_4^- and SeO_4^{2-} anions were removed from solutions as dilute as 10^{-12} molar.

We have concluded from these studies that several mechanisms exist which could be used to retard the movement of the radioactive waste anions in a repository. We are continuing this research to further quantify our results.

Radionuclides which go into solution as simple cations or cationic complexes constitute a second group of radionuclides. Three of these are listed in Table I. None of these radionuclides are considered major problems in nuclear waste management. ^{90}Sr and ^{137}Cs have relatively short half-lives and so should largely

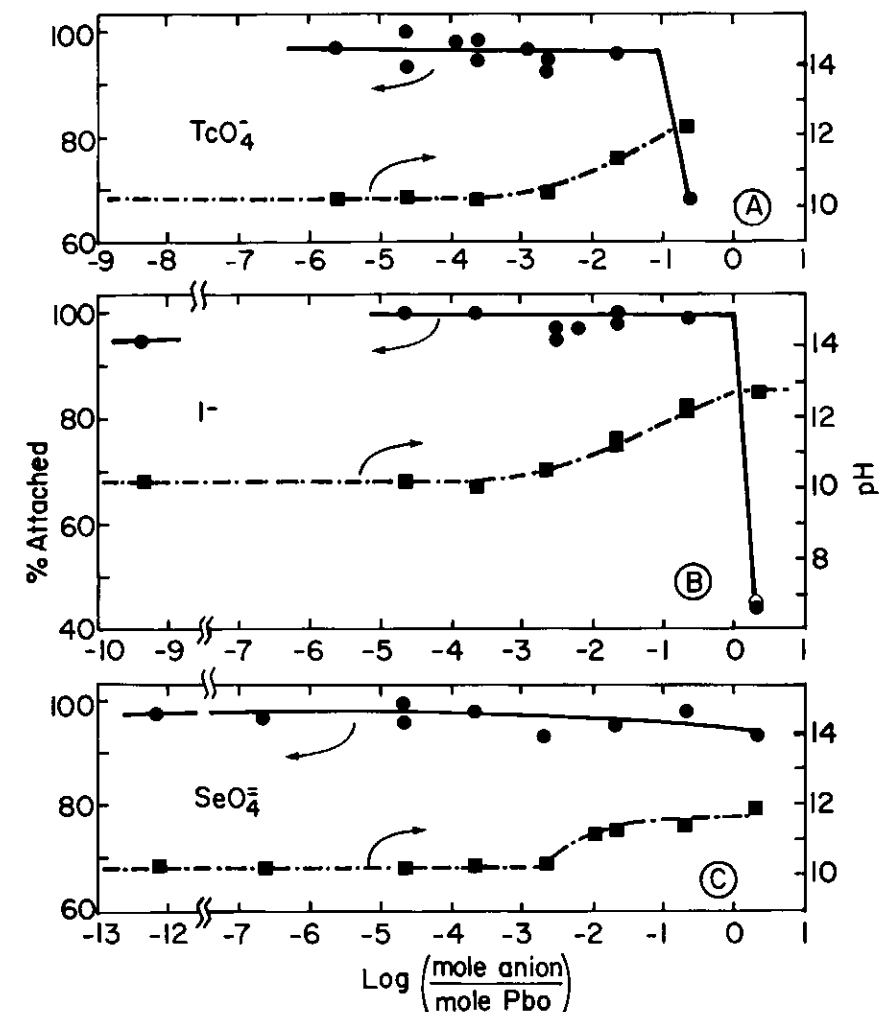


Figure 3

Sorption of TcO_4^- , I^- and SeO_4^{2-} on PbO for a range of molar ratios. The solid circles are measured attachments, the squares are the measured pH of the solution in equilibrium

with the solid. The open circle on B is the calculated I^- sorption assuming all the PbO has been converted to PbI(OH) . (G. W. Bird and V. J. Lopata, to be published)

decay in situ before the waste containers are breached. ^{107}Pd is very low in total contribution to the waste. Should the containers be breached, these cations will interact significantly with the geological barrier and move outward much more slowly than the groundwater. This occurs because cations ion-exchange on silicates such as feldspars and micas, and under some conditions react to form new minerals of very low solubility. In the natural environment, concentration of these elements is largely controlled by interaction with clays, or hydrated mineral oxides, which form as ambient temperature alteration products of silicate minerals (Kronberg *et al.* 1978).

Dilution by the stable isotopes of the elements in the rocks and water will also lessen the hazard from Sr and Cs. Both are common trace or accessory elements in feldspars and groundwaters.

Radionuclides from the actinium series constitute a third group for study. Some longer-lived isotopes from this series are listed in Table I. U, Np, Pu, Am and Cm are the most important actinides. All of these elements have very complex chemistry, can exist in solution in several oxidation states, and are capable of forming a large number of cationic or anionic complexes, colloids and polymers in solution.

The chemistry of uranium is probably

the best understood (Langmuir, 1978). Figure 4 is an Eh-pH diagram for U at a total concentration of 10^{-6} moles/litre in distilled H_2O . In such carbonate-free water, oxide and hydroxide complexes predominate at all geologically realistic pHs (4-9). Most are positively charged and can be expected to ion-exchange on silicates. Figure 5 outlines the same equilibria for U in a carbonate solution with a P_{CO_2} of $10^{-2.0}$ kPa, i.e., above atmospheric pressure but geologically reasonable. In this case, oxidizing conditions result in the formation of negatively charged or neutral carbonate and hydroxide complexes. These would be expected to be highly mobile in the geological environment. Thermodynamic data suggest that all U dissolved in natural water will be complexed, not only by carbonate and hydroxide but also by phosphate, fluoride, sulphate, and perhaps silicate and organic materials. These complexes will greatly increase the solubility of uranium minerals and hence the transport in ground water. To properly evaluate the role of complexes in natural waters, we must know the relative stabilities of the various complexes with the amount of the ligands which could be expected to be present. In this paper it is not possible to look at all possible combinations but we can compare two. Figure 6 shows the effect of 0.1 $\mu g/g$ PO_4^{3-} on the μ solubility of UO_2 as a function of redox potential at room temperature, $P_{CO_2} = 10^{-2.0}$ kPa, pH 6, $\Sigma UO_2 = 10^{-6}$ molar. This amount of PO_4^{3-} in solution increases the solubility of uraninite by one to two orders of magnitude in oxidizing solutions. Under reducing conditions near the magnetite-hematite boundary there is no effect. Figure 7 shows the solubility of uraninite for P_{CO_2} of $10^{-2.0}$ and $10^{-3.5}$ kPa (atmospheric pressure) at pH 8. The increased CO_2 pressure has a similar effect to 0.1 $\mu g/g$ PO_4^{3-} , i.e., it increases the solubility of UO_2 by an order of magnitude under oxidizing conditions. At pH 8, the magnetite-hematite boundary lies at about -0.2 volts and the PO_4^{3-} ligand would also not increase the solubility. These points are stressed for two reasons: 1) to show that U solubility is limited in a reducing environment; and 2) reducing redox potentials are probable in deeply circulating groundwater.

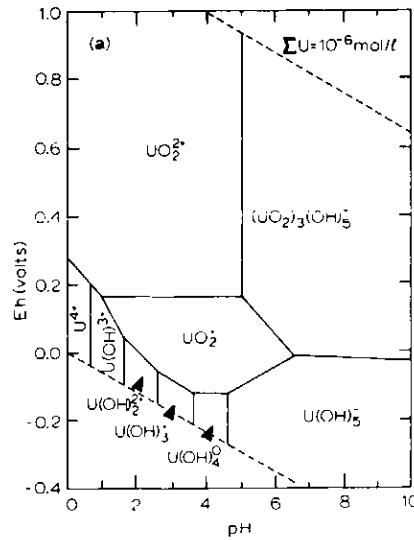


Figure 4
Eh-pH diagram showing the relative importance of +4, +5 (as UO_2^+), and +6 valent uranium species at $25^\circ C$ for $\Sigma UO_2 = 10^{-6} M$. (Redrawn from Langmuir, 1978)

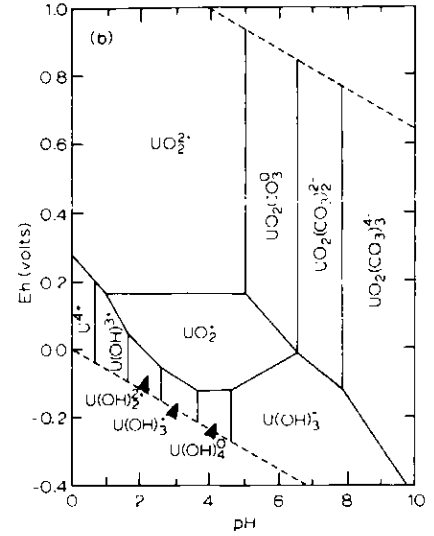


Figure 5
Eh-pH diagram similar to Figure 4 but with a typical groundwater CO_2 pressure of 10^{-2} kPa. (Redrawn from Langmuir, 1978).

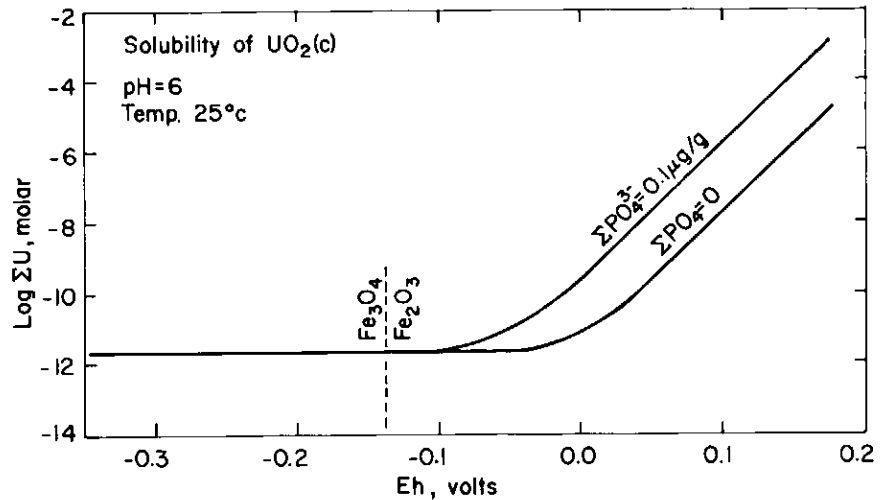
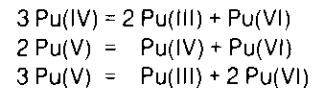


Figure 6
The solubility of uraninite, $UO_2(c)$ at pH 6, and $25^\circ C$ as a function of Eh for $P_{CO_2} = 10^{-2.0}$ kPa with PO_4^{3-} absent, and $\Sigma PO_4^{3-} = 10^{-6} M$

($\approx 0.1 \mu g/g$). The magnetite-hematite redox equilibrium (Garrels and Christ, 1965) is shown for reference. Uraninite solubility is from Langmuir, 1978).

A few comments are necessary on the chemistry of plutonium. These are given in spite of the fact that our current knowledge of plutonium is very limited because most chemical research on plutonium has been done at geologically unrealistic pH's. There are two additional factors which complicate the solution chemistry. First, all four common oxidation states for Pu can coexist in the same solution as there is a tendency for disproportionation reactions such as:



to occur spontaneously at all concentrations of Pu (Silver, 1971).

Second, there is a marked tendency for Pu(IV) species to polymerise at practically all concentrations. This is detrimental as the polymerised species have been noted to move faster than ionic species. The pH at which polymerisation will occur increases as concentration decreases, but even for

a Pu(IV) concentration of $\approx 10^{-8}$ molar, polymerisation begins by pH 7.5. The presence of complexing ions in solutions decreases the tendency of Pu to polymerise.

Figure 8 shows an Eh-pH diagram for Pu species at Pu concentration of 10^{-6} molar (Silver, 1971). The magnetite-hematite boundary is shown on the diagram for reference. It is clear from this diagram the Pu(IV) will be the major oxidation state in most geological environments. Because of the tendency of Pu to polymerise, we must increase our understanding of Pu chemistry in groundwater conditions.

Conclusions

1) The movement of nuclear waste in plutonic groundwater can be effectively prevented. This is most important in assuring that disposal can be done safely and permanently.

2) To do this we probably have to maintain reducing conditions in the waste vault. Redox values near the magnetite-hematite buffer are adequate and these are achievable in a waste repository. Figure 9 shows some redox conditions for natural waters with the magnetite-hematite boundary shown for reference (Garrels and Christ, 1965). Most deep waters are reducing and if we place suitable buffers in the repository we can maintain the reducing conditions.

3) There remain a number of problems requiring further research particularly on actinide chemistry at elevated temperature and/or the effects of groundwater composition and radiolysis. This research is in progress or is planned. By the time we have finished the concept verification stage of our research program (end of 1982) the data base should be adequate for an evaluation of repository safety and the development of a test facility. At the current time, there is no reason to suspect we will not be able to safely dispose of nuclear wastes in a geological repository.

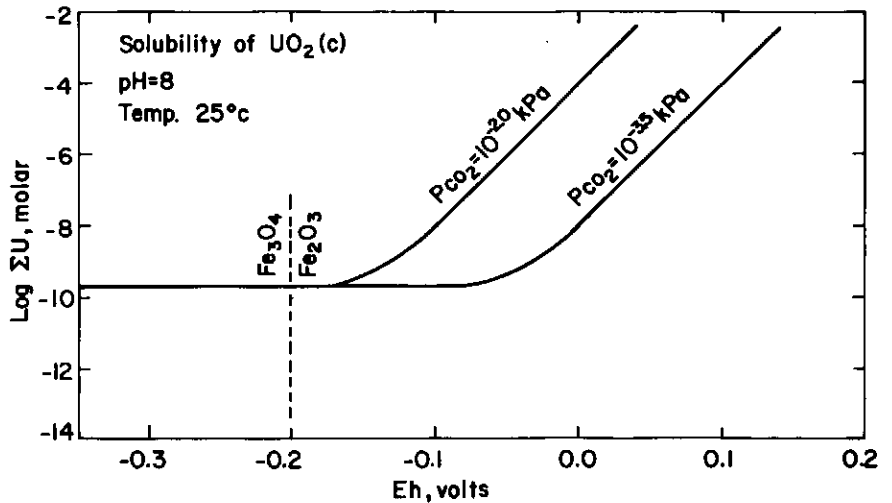


Figure 7

The solubility of uraninite, $UO_2(c)$ at pH 8, 25°C as function of Eh and P_{CO_2} . The magnetite-hematite redox equilibrium

(Garrels and Christ, 1965) is shown for reference. Uraninite solubility is from Langmuir, 1978.

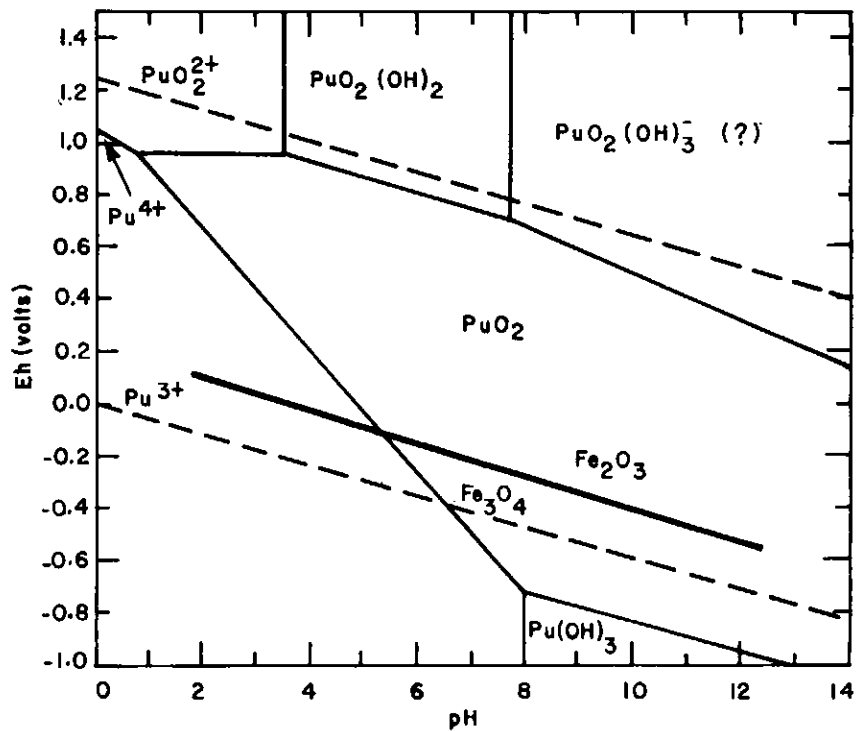


Figure 8

Eh-pH diagram for aqueous plutonium species at 25°C, 0.01 M concentration of dissolved species. Potentials are with

respect to standard hydrogen electrode. Base on data in Silver (1971). The diagram has not been confirmed experimentally and will be subject to modification.

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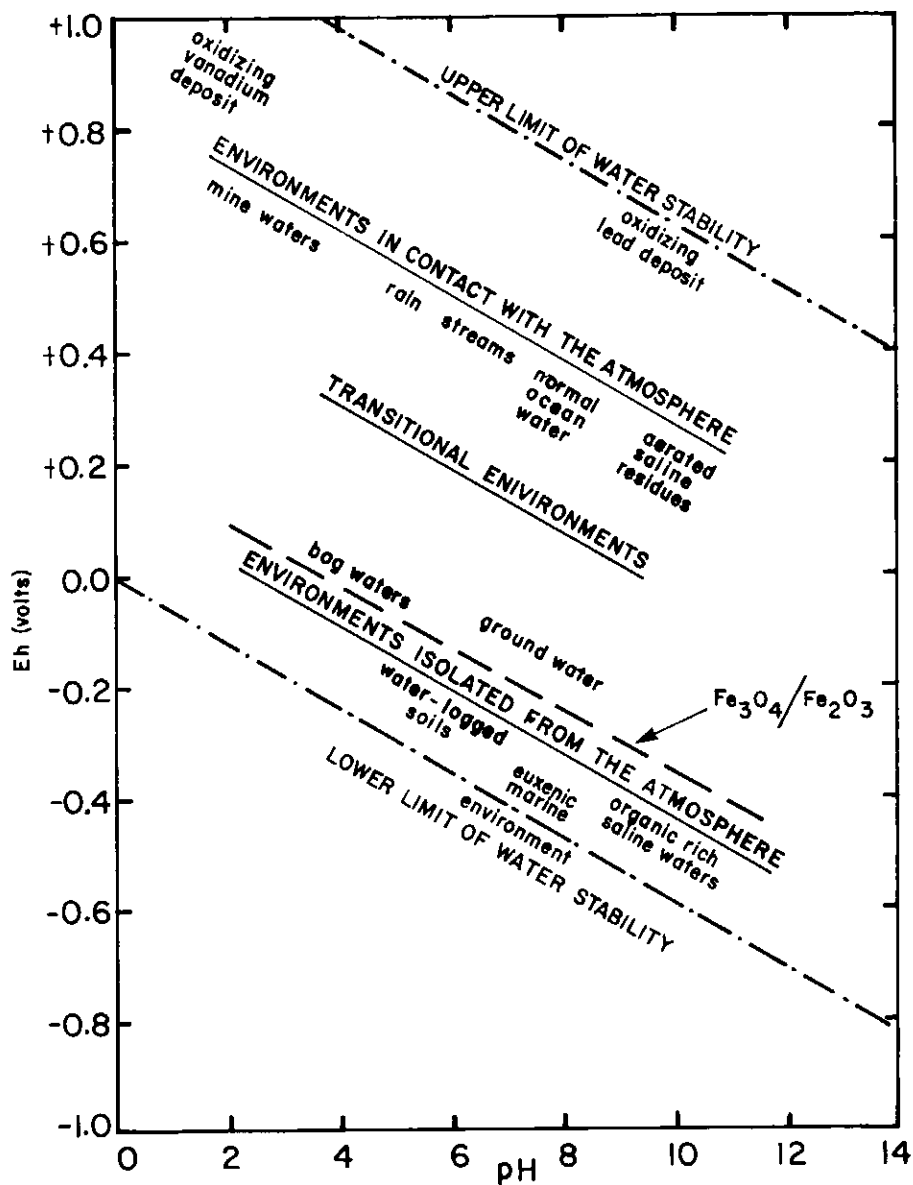


Figure 9
Eh-pH diagram for a number of natural environments (from Garrels and Christ,

1965). The magnetite-hematite equilibrium has been added for reference.