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## GEOCHEMISTRY AND RADIONUCLIDE MIGRATION

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### INTRODUCTION

Effective isolation of nuclear waste in a deep geologic depository can be described in terms of interacting multiple barriers. The simplest to describe is the geometric barrier or physical isolation of the waste as defined by the size of the buffer zone around the repository, the thickness of the rock layers, and the area of the fracture zone around the depository due to construction of the tunnels and shafts.

Of greater complexity is the hydrologic barrier, that is, the group of parameters that determines the waste dilution factor (dispersion) and groundwater flow rates; for example, permeability, heads, gradients, etc. In general, the hydrologic and geometric barriers control waste migration by determining both the resaturation time of the depository after decommissioning and the time it takes for groundwater to flow from the depository to the biosphere.

The least understood is the geochemical barrier, identified as a series of waste/water/rock interactions involving sorption (ion exchange), ion filtration, hydrolysis, precipitation, complexing, and the leach resistance of the waste form. The following scenario demonstrates how these chemical processes can interact to control waste migration.

We begin sometime after decommissioning when the depository resaturates. Eventually, groundwater reaches the waste and dissolution occurs. The dissolution rate of the waste and the solubility of individual radionuclides establishes the maximum concentration

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-2-

in the groundwater leaving the depository. In some cases, the composition of the groundwater will result in the formation of soluble radionuclide complexes (e.g., chloride complexes in briny groundwater). In other cases, the waste may react with the groundwater constituents causing precipitation (e.g., the formation of insoluble sulfides). As the groundwater moves through the rock, changes in pH or oxidation potentials will determine which radionuclide species are stable and whether new compounds or complexes may form. For some radionuclides, hydrolysis and the formation of insoluble oxides is certain. As the groundwater flows along interstitial grain boundaries and through fractures, cationic adsorption on mineral surfaces will retard waste migration to some fraction of the groundwater velocity. For repositories with shale layers acting as semi-permeable membranes, ion filtration with the retention of both cations and anions is possible. With each variation of groundwater composition, new chemical reactions will tend towards equilibrium. Whether equilibrium is reached depends on the groundwater flow velocity and reaction rates--will there be sufficient time for equilibrium to occur?

Clearly, such a complicated scenario involves many assumptions and much uncertainty. Of the processes cited above, only sorption can be expressed in quantitative terms based on experimental evidence. Theoretically, we can calculate the solubility of most radionuclides from thermodynamic data, but we know very little about their actual solubilities in natural waters. A few radionuclide complexes have been identified, but nothing is known of their reaction rates. Future research needs are obvious. For the present, geochemistry related to the study of deep geologic disposal of high level waste is limited by an information base which relies heavily on theory.

46

### ION EXCHANGE

The primary geochemical control on radionuclide migration is ion exchange. The ion exchange capacity of a rock is generally attributed to the clay mineral content, however, most common silicate minerals have at least some sorption capacity. As the dissolved waste moves slowly through the rock barrier, sorption will occur, but because the strength of the force holding the adsorbed ions is a function of the ion's charge density, each ion will adsorb to a different degree.

The extent to which sorption takes place for a particular ion is measured by the ion exchange distribution coefficient,  $K_d$ . This assumes that the ion exchange reaction is reversible and that near equilibrium conditions exist.

$$K_d = \frac{\left( \frac{\text{mass of nuclide}}{\text{in solid phase}} \right) / \left( \frac{\text{weight of}}{\text{solid}} \right)}{\left( \frac{\text{mass of nuclide}}{\text{in liquid phase}} \right) / \left( \frac{\text{volume of}}{\text{liquid}} \right)} = \frac{\text{ml}}{\text{g}}$$

Of the many factors that affect the distribution coefficient, the groundwater composition is probably the most important. Ions already present in the groundwater will compete with radionuclides for exchange sites thus reducing the amount of waste that can be adsorbed by the rock. A theoretical approach describing distribution coefficients for monovalent-monovalent competition (e.g.,  $\text{Cs}^+$  and  $\text{Na}^+$ ), shows  $K_d$  will be independent of the trace ion concentration (i.e., the radionuclides), but inversely proportional to the concentration of the competing ion<sup>1</sup>. For monovalent-divalent competition (e.g.,  $\text{Sr}^{++}$  and  $\text{Na}^+$ ),  $K_d$  is inversely proportional to the square of the univalent cation concentration. This relationship shows good qualitative agreement with experimental results for those minerals in which exchange is truly a surface phenomenon.

While the above theoretical approach assumes simple solutions containing only two cations, groundwaters are complex solutions containing many competing ions. Distribution coefficients as a function of groundwater composition will be difficult to predict. In theory, we can say that more dilute groundwaters will maximize the ability of the rock barrier to inhibit radionuclide migration.

#### RETARDATION FACTORS

For modeling radionuclide migration from a nuclear waste repository, a more useful measurement of sorption is the retardation factor, ( $R_f$ ); that is, the relative velocity of the nuclide to the groundwater velocity. Retardation factors are based on the rock's physical properties and the ion exchange distribution coefficient where<sup>2</sup>:

$$R_f = 1 + \frac{\rho}{\theta} K_d$$

$\rho$  = bulk density  
 $\theta$  = porosity

When there is no sorption,  $K_d$  equals 0 and the minimum value for the retardation factor is 1 (Fig. 1).

Generally, retardation factors are determined from the  $K_d$  values rather than a direct measurement of the factor itself. Distribution coefficients are easily measured in the laboratory as is the porosity and density of the rock. Unfortunately, it is not known how well laboratory measurements of  $K_d$ 's represent in situ values. Since the retardation factor is primarily defined as a function of the ion exchange distribution coefficient, other controls (e.g., low solubilities) are not accounted for in the retardation factor and will be discussed later.

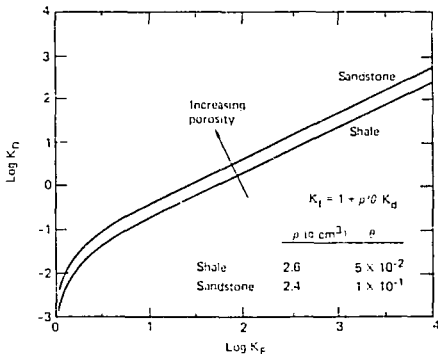


Figure 1 - The Retardation factor ( $K_r$ ) is a function of the distribution coefficient ( $K_d$ ).

In Lawrence Livermore Laboratory's (LLL) hydrologic modeling of radionuclide migration from a geologic repository, retardation factors were derived from the existing data on distribution coefficients<sup>3</sup>. An estimated range of 1 to  $10^3$  for the fission products (primarily  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ ), and  $10^2$  to  $10^5$  for the actinides (e.g.,  $^{239}\text{Pu}$ ,  $^{230}\text{Th}$ ,  $^{243}\text{Am}$ ) reflect the wide variation in  $K_d$  values found in the literature.

It's easy to understand the important effect retardation has on migration when we consider that a radionuclide with a retardation factor of  $10^4$  moves at one-ten thousandth the groundwater

velocity; that is, for groundwater that has moved 1 km, the radionuclide will have moved only 10 cm.

An example from LLL's modeling efforts shows the effect on  $^{239}\text{Pu}$  concentrations at a point 300 m from a hypothetical repository when retardation factors were varied from  $10^2$  to  $10^4$  (Fig. 2, Table I). The time at which peak concentration occurred changed by 2 million years. Radioactive decay and dispersion during that time account for the decrease in concentration by a factor of  $10^9$ .

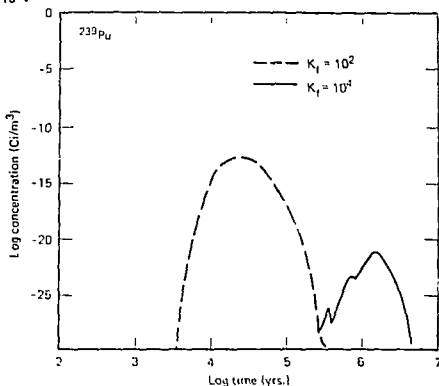


Figure 2 - The change in  $^{239}\text{Pu}$  concentrations with a mass transport hydrologic model shows the importance of retardation factors on radionuclide migration.

TABLE I  
 $^{239}\text{Pu}$  CONCENTRATIONS VS RETARDATION FACTORS

$^{239}\text{Pu}$	Max Conc in Aquifer	$\left(\frac{Ct}{H^2}\right)$	Time (Yrs)	Sensitivity
$K_f = 10^4$	$2.2 \times 10^{-22}$		$2 \times 10^6$	
$k_f = 10^2$	$1.3 \times 10^{-13}$		$3 \times 10^4$	$10^9$

A major problem in estimating the retardation factors from  $K_d$ 's is their dependence on the laboratory conditions under which the  $K_d$ 's were measured. Most  $K_d$  measurements involve crushed rock or soil equilibrated with trace amounts of radionuclides in solution.

The  $K_d$  found will depend on the particle size of the sample, pH, time of equilibration, temperature, etc. We don't know how  $K_d$ 's measured in static experiments relate to retardation factors for groundwater constituents that could flow either interstitially along grain boundaries or through fractures. Various workers have suggested that a  $K_d$  calculated on the basis of surface area rather than mass be used<sup>4</sup>. In fracture flow, a retardation factor related to a surface distribution coefficient and fracture aperture has been suggested<sup>5</sup>. Even with these "improvements", the problem stated earlier of relating laboratory measurements to in situ conditions is unresolved.

#### ION FILTRATION

Clays in shale beds act as semi-permeable membranes, retarding to varying degrees the passage of dissolved species with respect to water. The membrane properties of shales result from negative



charges on the surface and edges of the clay particles. As the clays are forced together during compaction of formation, anions in the pore space are excluded, thereby creating a positively charged barrier. Later, as groundwater moves through the pore space, anions are attracted and cations repulsed, but electrical neutrality must be maintained, thus neither cations nor anions can move readily through the field. Neutral water molecules do move, thus increasing the concentration of the charged ions on the input side of the shale.

Ion filtration differs from ion exchange in that both positive and negative species are retained. Because anion exchange materials have limited distribution in rocks and soils, ion exchange in geologic media usually involves only the cations. With nuclear waste, the ion filtration process of anion retention is important in predicting the behavior of  $^{99}\text{Tc}$  and  $^{129}\text{I}$  which exist as the negatively charged species,  $\text{I}^-$  and  $\text{TcO}_4^-$ , in natural waters.

The degree of retention in shale beds is a function of the exchange capacity of the rock, charge density of individual species, temperature, concentrations in solution and compaction pressure. However, even under ideal experimental conditions, ion filtration is far less effective than ion exchange. In an extensive study of the parameters that affect the membrane properties of shales and clays, Kharaka and Berry<sup>6</sup> reported maximum filtration ratios for iodide of less than 2. (Filtration ratios are analogous to the retardation factors described earlier.) A filtration ratio that small hardly compares with an actinide retardation factor estimated at  $10^2$  or more, but nevertheless may double the time required for  $^{129}\text{I}$  or  $^{99}\text{Tc}$  to reach the biosphere.

#### SOLUBILITY

There are a number of radionuclides whose theoretical solubilities are below the maximum permissible concentrations in water

(MPC<sub>w</sub>) permitted by the Federal Government (10CFR20 App. B) (See Table II). If the theoretical solubilities are correct, the groundwater concentrations of these radionuclides leaving the repository will be below the MPC<sub>w</sub> limits. The combined effects of isotopic dilution, dispersion, retardation, and radioactive decay will further reduce the amount actually reaching the biosphere.

Solubility as a geochemical control on radionuclide migration involves: (1) the hydrolysis and precipitation of relatively insoluble oxides and hydroxides; (2) oxidation-reduction reactions which result in the formation of insoluble products; and, (3) the precipitation of insoluble compounds from reactions with groundwater constituents. Using Eh-pH diagrams constructed from the available thermodynamic data, we can make rough predictions of how the first two processes will contribute to the geochemical barrier; however, almost nothing is known about the interaction of radionuclide species with ions already present in a groundwater system which may cause precipitation or complexing.

TABLE II  
RADIONUCLIDE CONCENTRATIONS (MPC<sub>w</sub><sup>\*</sup>)  
EXCEEDING SOLUBILITY\*\*

	MPC <sub>w</sub> ( $\frac{Ci}{m}$ )	Solubility ( $\frac{Ci}{m}$ )
<sup>129</sup> Sr	$2 \times 10^{-5}$	$3 \times 10^{-12}$
<sup>229</sup> Th	$7 \times 10^{-6}$	$1 \times 10^{-8}$
<sup>230</sup> Th	$2 \times 10^{-6}$	$1 \times 10^{-9}$
<sup>239</sup> Pu	$5 \times 10^{-6}$	$4 \times 10^{-8}$
<sup>240</sup> Pu	$5 \times 10^{-6}$	$2 \times 10^{-7}$

\*Maximum permissible concentration in water from 10CFR20 App. B

\*\*Maximum theoretical solubility in groundwater (pH=5-8, Eh=0); no isotopic dilution

TABLE III  
COMPARISON OF THEORETICAL SOLUBILITY  
AND CONCENTRATIONS IN NATURAL WATERS

	Solubility (M)		Solubility (pH = 6.8)	Fresh Water (M)
	(pH = 8.15)	Sea Water (M)		
Sn	$2 \times 10^{-15}$	$8 \times 10^{-9}_{(8)}$	$4 \times 10^{-16}$	$2 \times 10^{-9}_{(9)}$
Th	$7 \times 10^{-25}$	$3 \times 10^{-11}_{(10)}$	$2 \times 10^{-20}$	?

8. Heide and Reichardt, 1975

9. Hamaguchi, et al., 1964

10. Kaufman, 1969

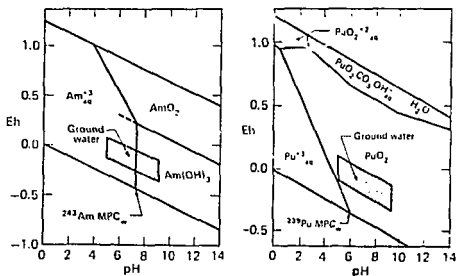


Figure 3A-B: Stability fields for plutonium and americium compounds in an aqueous system at 25°C and 1 atmosphere. Total dissolved carbonate species =  $10^{-3.5}$ . Maximum dissolved Am and Pu activities equal  $MPC_w$  for  $^{243}\text{Am}$  and  $^{239}\text{Pu}$  (see text).

Figure 3A is a stability field or Eh-pH diagram of a hypothetical system containing  $\text{PuO}_2$ , dissolved plutonium and a constant activity of aqueous carbonate species. The redox potential (Eh) is a measure of the oxidizing or reducing conditions in the system and is related to the proportion of oxidized and reduced forms present at equilibrium. The boundaries were computed by chemical equilibrium calculations and indicate the conditions at which the various aqueous plutonium species are stable. The stability field for solid  $\text{PuO}_2$  shows the area where the activity of plutonium in solution is less than  $\text{MPC}_w$  for  $^{239}\text{Pu}$ . The shaded area represents the range of Eh and pH conditions that cover most groundwater environments<sup>7</sup>. This area lies entirely within the stability field for  $\text{PuO}_2$ . Thus, at equilibrium, the concentration of aqueous  $^{239}\text{Pu}$  will be less than its  $\text{MPC}_w$  at normal groundwater Eh-pH conditions. The term "equilibrium" must be emphasized for Eh-pH diagrams tell us nothing about the rate of reaction. If the oxidation of  $\text{Pu}^{+3}$  to  $\text{Pu}^{+6}$  or the precipitation of  $\text{PuO}_2$  is relatively slow compared to the dissolution rate of the waste form, plutonium concentrations in groundwater could be much higher than predicted.

In the second example (Fig. 3B), the concentration of  $\text{Am}^{+3}$  in equilibrium with  $\text{Am}(\text{OH})_3$  is greater than  $\text{MPC}_w$  for  $^{243}\text{Am}$  in slightly acidic groundwater. For both Am and Pu, solubility controls are more effective with increasing pH. This is also true for  $^{229,230}\text{U}$  and many other nuclides (excluding those with amphoteric properties, e.g.,  $^{126}\text{Sn}$ ).

An important source of error in using theoretical solubilities to predict radionuclide behavior is the presence of unidentified aqueous species. Eh-pH diagrams of necessity contain only those ions or compounds for which we have thermodynamic data. The theoretical solubilities in Table II are based on the formation of relatively insoluble oxides and hydroxides. The formation of soluble inorganic

complexes was not considered because there is limited or no available data on them. To have confidence in our predictions, we must learn more about radionuclide solubility in natural waters. The importance of unknown complexes in determining solubility can be illustrated by comparing the theoretical solubility of concentrations found in natural waters for Sn and Th (Table III). For example, the solubility of Sn at pH 6.8 (a common value for fresh water) is  $4 \times 10^{-18}M$ . Yet, the values reported for the Saale River in Germany are  $2 \times 10^{-9}M$ . Until we can identify the actual species likely to exist in natural water systems, theoretical solubilities must be used with caution.

#### SUMMARY

Theoretically, the geochemical barrier can provide a major line of defense in protecting the biosphere from the hazards of nuclear waste. The most likely processes involved are easily identified. Preliminary investigations using computer modeling techniques suggest that retardation is an effective control on radionuclide concentrations. Ion exchange reactions slow radionuclide migration and allow more time for radioactive decay and dispersion. For some radionuclides, solubility alone may limit concentrations to less than the maximum permissible now considered acceptable by the Federal Government.

While the theory behind the above conclusions is sound, the level of uncertainty in the supporting data remains high. The present emphasis on laboratory measurements of  $K_d$ 's is not the answer. We need a more complete "shopping list" of research objectives to reduce this uncertainty. We need to establish whether laboratory measurements have any relationship to in situ values for retardation. The basic relationship between retardation and  $K_d$ 's should be tested. Are the same retardation factors appropriate when evaluating both interstitial and fracture flow? To predict the solubility limits

with confidence, we must measure solubilities and rates of reaction in waters simulating the natural environment. Unfortunately, there are today no reliable in situ measurement techniques for studying waste/water/rock interactions. Even the laboratory approach is fraught with confusion - a standard methodology is non-existent.

The effectiveness of the geochemical barrier is ultimately related to the repository site characteristics. Theory alone tells us that geochemical controls will be most efficient in an environment that provides for maximum ion exchange and the precipitation of insoluble compounds. In site selection, consideration should be given to rock barriers with high ion exchange capacity that might also act as semi-permeable membranes. Also important in evaluating the site's potential for effective geochemical controls are the oxidation potentials, pH and salinity of the groundwater.

#### REFERENCES

1. Sallach, R., 1967, Model for Estimating the Distribution of Cations in Multi-component Ion Exchange Reactions, Sandia Laboratories, SC-RR-67-061, Albuquerque, New Mexico.
2. Duguid, J., and M. Reeves, 1976, Material Transport Through Porous Media: A Finite-element Galerkin Model, Oakridge National Laboratory, ORNL 4928, Oakridge, Tennessee.
3. Isherwood, D., 1977, Preliminary Report on Retardation Factors and Radionuclide Migration, Lawrence Livermore Laboratory, UCID 17551, Livermore, California.
4. Borg, I., R. Stone, H. Levy, and L. Ramspott, 1976, Information Pertinent to the Migration of Radionuclides in Ground Water at the Nevada Test Site, Part 1: Review and Analysis of Existing Information, Lawrence Livermore Laboratory, UCRL-52078, Livermore, California.
5. Burkholder, H., 1976, "Methods and Data for Predicting Nuclide Migration in Geologic Media," BNWL-SA-5822 and presented at the Intl. Symp. on the Management of Waste from the LWR Fuel Cycle, Denver, Colorado, July 1976.

6. Kharaka, Y., and F. Berry, 1973, "Simultaneous Flow of Water and Solutes Through Geological Membranes I. Experimental Investigation," Geochem. Cosmochim. Acta, 37, pp. 2577-2603.
7. Garrels, R., and C. Christ, 1965, Solutions, Minerals and Equilibria, (Harper and Row) New York.
8. Heide, F., and J. Reichardt, 1975, "Tin Content in the water of the Saale River," in Recent Contributions to Geochemistry and Analytical Chemistry, A. Tugarinov, Ed., (Wiley) New York, pp. 371-3d2.
9. Hamaguchi, H., R. Kuroda, N. Onuma, K. Kawabuchi, T. Mitsubayashi, and K. Hosohara, 1964, "The Geochemistry of Tin," Geochim. Cosmochim. Acta, 28, pp. 1093-1093.
10. Kaufman, A., 1969, "The <sup>232</sup>Th Concentration of Surface Ocean Water," Geochim. Cosmochim. Acta, 33, pp. 717-724.

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