282
5-30-78

ANL-78-22

GR-112

ANL-78-22

MASTER

**MIGRATION OF URANIUM PROCESS WASTES
FROM THE URANIUM-233—THORIUM-232 CYCLE**

by

**Sherman Fried, Carmen Sabau,
John Hines, and Arnold Friedman**

MASTER

UdC-ANA-USOE

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

**Prepared for the U. S. DEPARTMENT OF ENERGY
under Contract W-31-109-Eng-38**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MIGRATION OF URANIUM PROCESS WASTES FROM THE URANIUM-233--THORIUM-232 CYCLE

by

Sherman Fried, Carmen Sabau,
John Hines, and Arnold Friedman

ABSTRACT

With the advent of fuel loadings of ^{233}U in the Shippingport Reactor, it has become important to understand the migratory behavior of uranium. The purpose of this study is the determination of the parameters influencing the migration of U(VI) , the most likely chemical form of uranium to be mobilized from a repository. Samples of rhyolite tuff were used to measure the absorption coefficients of solutions of U(VI) in ground waters. In addition, columns of tuff were used to measure the elution behavior of U(VI) at various conditions of pH, U(VI) concentration, and flow saturation.

These results indicate that there are several elution peaks with values of K_d between 35 and 120. This behavior is not the same as that of Pu(VI) on tuff; and the experimental results to date have not revealed the reason for this difference.

Values of K_d in this range imply that geological containment would be difficult in strata of this type. It may be possible to find more retentive strata than tuff. Rocks containing reducing components are the most likely candidates and further investigation is urgently needed if the ^{233}U -Th cycle is to be widely used.

At the end of August 1977 the Shippingport reactor became critical after having been refueled with ^{233}U and a ^{232}Th blanket and became the first breeder on a commercial scale designed to avoid the production of ^{239}Pu .

If this is one of the courses the breeder reactor program may take in this country, a completely new aspect of waste isolation-disposal must be considered; namely the immobilization of ^{232}U , ^{233}U (and their daughters) as contrasted with the present problem of isolation and disposal of the trans-uranium wastes (Np, Pu, Am, and Cm) resulting from operation of LWR or plutonium breeders.

The occurrence of uranium in the process-wastes from an LWR or LMFBR is of little consequence because of the very long half lives of ^{235}U and

^{238}U . The process wastes from the Shippingport breeder however will contain short lived uranium i.e., the high specific activity ^{232}U ($T_{1/2} = 71.7$ years) and ^{233}U ($T_{1/2} = 1.6 \times 10^5$ years) which are environmentally significant.

It is implicit in this work that ground water will be the only agent capable of mobilizing wastes from a repository. In the presently proposed dry land deep geologic repository, rock strata form the ultimate barrier to migration of radionuclides into the environment and at the same time may be conduits bringing them into the biosphere. It is therefore important to determine the migration characteristics of uranium in the same manner as has been carried out for the trans-uranium nuclides.¹ Necessary measurements include "capacities" of various rocks as well as the "binding"* of the various oxidation states of uranium that might exist in the process solutions or in the solutions that may be leached from its immobilizing matrix.

It was decided to work first with U(VI) in the set of experiments to be described here because it was deemed the most likely oxidation state to occur in either wastes or leachates. Obviously it will also be necessary to examine the behavior of the other oxidation states of uranium but they will not be discussed here. In addition, several "representative" rocks will have to be examined because of the lack of knowledge about the particular stratum in which a repository will be built. These limited experiments will have to serve to outline the kind of reactions to be expected when uranium migrates through a rock stratum under the mobilizing influence of ground water. It was also proposed to compare the migration rates and capacities of a rock for uranium at two different pH's.

Three aspects of rock-uranium reaction were examined. The first was to measure the capacity under saturated flow conditions. That is, the rock sample was completely saturated with water before application of the uranium. The second was to measure migration in an unsaturated rock sample simulating the conditions under which certain repositories have already been operated.³ The third aspect was to attempt to determine the batch " K_d " or "binding" with crushed samples of this rock at two different pH's.

In the latter two cases, where only tracer amounts of uranium was employed; it was found to be advantageous to employ the isotope ^{237}U using the 210 keV γ for detection. This technique allows measurement of the uranium in the presence of large amounts of inert material (rock) without the necessity of elaborate, time consuming uranium separations such as would be necessary with the long lived α emitting ^{233}U .

*It is felt that "binding" is a more appropriate term than " K_d " for the description of the reaction of actinides (or perhaps other nuclides) with rocks. Our work has shown² that the behavior of these ions on rocks is not the same as on a well behaved ion-exchange medium. It would appear that solubilities, hydrolysis, and kinetics play an important role and the sum of these behaviors is too complicated to be expressed as a K_d . Much of our work has been expressed as a relative migration rate; i.e., the rate of migration of the ion in question compared to the rate of migration of the water responsible for its mobilization.

The particular rock used in these experiments was Los Alamos tuff, which was chosen because it has been used in this Laboratory for the study of the migration of other actinides¹ and a great deal of experience in its use has been accumulated. This material has been described as a highly siliceous rhyolite tuff. It consists of a siliceous matrix with phenocrysts of quartz + (K, Al -- Na-SiO₃) sanadine with the addition of hematite phenocrysts. It is also very porous (30%) and thus conducts water easily. Consequently an experiment requiring large amounts of flow can be carried out in a practical length of time. In addition, some small amounts of liquid actinide bearing waste has already been disposed of in trenches in this rock over a period of years. Thus comparisons can be drawn between laboratory experiments and a "real" repository³ and with the addition of the experiments to be described here will permit comparisons of the behavior of the several actinides.

The determinations to be described here were made largely with "massive samples" of Los Alamos tuff rather than with crushed, powdered,

Fig. 1. Assembly of Waxed Cylinder of Tuff to Measure Uranium Migration

or granulated samples. It was felt that measurements on "disassembled" rock do not accurately reflect the migration of the nuclides in a real rock stratum but instead are perturbed by exposure of new and possibly more reactive surfaces. Therefore samples of Los Alamos tuff were shaped into cylinders approximately 2 cm in diameter and 3.5 cm long and assembled into a column as shown in Fig. 1. Coating the cylindrical surface of the tuff with wax prevented lateral movement of the solution carrying the nuclide and ensured that the only vertical movement of the uranium through the tuff would be observed. The application of liquid solutions was controlled by a metering pump and the rates of thru-put arbitrarily adjusted to approximate the flow of water in the range of 50-100 meters per year -- a typical rate

in real aquifers. Obviously the relationship of this experiment to migration in a real stratum will depend not only on the rate of flow of the ground water but on the kinetics of the nuclide-rock interaction.

We measured the capacity by applying a solution of ²³³U(VI) chloride at a determined pH. This was applied until the concentration of the effluent rose to that of the input as determined by alpha counting of aliquots of eluate. The desired oxidation state was produced electrolytically by an anodic oxidation of the ²³³U stock solution in 0.1 M HCl. The (VI) state was verified by

spectrophotometric examination of a sample in an absorption cell as well as its behavior on a Dowex A-1 anion column in 5 M HCl.⁴

The unsaturated flow experiment was carried out on a large block of Los Alamos tuff similar to that described in other work.^{1,2} The samples of uranium were in this case ^{237}U ($T_{1/2} = 6.7$ days) and were subjected to varying amounts of total water application with drying periods in between the successive applications. This procedure simulated the conditions occurring at Los Alamos and for comparison with the behavior of plutonium under these conditions.

Finally it was also important to determine the existence of any difference between the behavior of an undisturbed piece of rock and the powdered or granulated material. This experiment was performed to determine the extent of change in properties caused by refracturing the grains.

EXPERIMENTAL

Capacity of Los Alamos Tuff for U(VI)

Los Alamos tuff, whose composition is given in Table I, is the rock used in these experiments. It is very easily shaped and drilled. Cylinders of tuff were shaped by cutting and filing to form columns approximately 3.5 cm long by 2 cm in diameter. The cylinders were weighed and then placed in an oven at 55-60°C. A dish of Cenco Tacki-Wax was also warmed at the same time. It was possible to knead the warmed wax onto the surface of the rock cylinder and press it in so that the surface was effectively sealed. Thus any liquid introduced to the top of the cylinder could only move downward--not laterally. It is crucial to use the wax at its plastic stage rather than as a liquid. If a liquid is used it is drawn completely into the pores of the rock by capillary action destroying its usefulness for a migration experiment.

TABLE I

Constituent	Percentage Composition
SiO ₂	73.6
Al ₂ O ₃	13.6
K ₂ O	4.6
Fe ₂ O ₃	1.9
CaO	0.51
MgO	0.32
FeO	0.25
TiO ₂	0.26
P ₂ O ₅	0.06

When the "rock column" is complete it is immersed in a beaker of water which in turn is placed in a vacuum desiccator. The system is then

evacuated, the air is pumped from the pores of the rock and on reestablishment of atmospheric pressure the water completely saturates the rock. This process is carried through several cycles of evacuation and repressurization.

The water saturated "rock column" is connected to the metering pump as shown (Fig. 2) and the saturation with uranium and subsequent elution with water commenced. The concentration of the uranium (^{233}U) was $2.8 \times 10^2 \mu\text{g/ml}$ or $1.23 \times 10^{-3} \text{ M}$.

Fig. 2. Metering Pump for Tuff Column Apparatus

The concentration of the uranium in both the feed and eluate was determined by counting the alpha particles in a gas proportional counter or liquid scintillation counter. The scintillation counting was carried out on a Beckman LS-100 Liquid Scintillation Spectrometer System using Beckman Ready-Solv GP as the scintillator. All water used was first "equilibrated" with granulated tuff and had a pH ~5.8. Its composition with respect to detectable cations was Al = 0.05, Ba = 0.02, Ca = 1.5, K = 0.07, Mg = 0.03, Mn = 0.1, Na = 0.2, Sr = 0.008 where all quantities are in micrograms per milliliter. The rate of flow through the rock column was controlled by the metering pump and was adjusted so that the linear rate of flow was about 50 to 100 meters/year. The specifications of the column [C] are:

wt = 15.04 g. 2.09 diam x 3.55 cm long, volume = 12.17 cm^3 .
 Free column volume @ 30% porosity = 3.65 cm^3 . Rate of
 flow = 43 meters/year. The ^{233}U solution contained $3.067 \times 10 \times 10^6 \text{ ac/ml} = 1.23 \times 10^{-3} \text{ M}$. The pH of this solution was 5.42 as applied to the column.

When saturation had been achieved the excess ^{233}U solution was removed from the top of the rock by a pipette and the uranium was eluted with tuff-equilibrated-water (TEW) pH = 5.8. As can be seen from the curve in Fig. 3 the uranium was eluted in several peaks at 32, 91, and 110 free column volumes (f.c.v.). Normally this behavior would be interpreted as indicating that the uranium was being eluted as different compounds or complexes.

Fig. 3. Elution of U(VI) at pH 5.8 from Los Alamos Tuff Saturated with Uranium

The oxidation state of the uranium in each peak was determined by the behavior on an anion column. Aliquots were evaporated to dryness in HCl, taken up in 5 N HCl and applied to the top of a column of A-1 x 10, 200 mesh anion resin in a bed 0.3 x 4.8 cm. Uranium IV is not retained by anion resin under these conditions while U(VI) tightly bound but may be eluted with 1 M HCl. In this manner the anion column was used to show that the uranium was administered as U(VI) and was transported and eluted as U(VI).

The experiment described above was repeated but this time the eluant was maintained at pH = 3.87. The uranium feed was applied at a pH = 4.08. The specifications of this column [D] were:

wt = 17.43 g, diam = 2.01 cm, height = 3.95 cm, vol = 12.53 cm³, free column volume = 3.76 ml. The concentration of the ^{233}U solution was 4.013×10^6 c/m/ml = 0.375 g/liter = 1.61×10^{-3} M, rate of flow = 60 meters/year.

The samples were collected in tubes containing 1 f.c.v. each and the contents assayed by mixing 100 microliter aliquots with the scintillator. The performance of this column is shown in Fig. 4 and the differences between the two experiments may be seen. In general the peaks eluted earlier at lower pH.

The capacity of each column is arbitrarily given as the sum of the activities eluted by water between the points A and F as indicated in Figs. 3 and 4. For column C (pH = 5.8) the capacity is 1.6×10^{-3} millimoles U(VI) per gram of rock. For column D (pH = 3.87) the capacity was 7.8×10^{-4} millimoles U(VI) per gram. As can be seen from Figs. 3 and 4 the rates of elution

Fig. 4. Elution of U(VI) at pH 3.87 from Los Alamos Tuff Saturated with Uranium

also differ; with the peaks being at 31, 91, 110, and 116 f.c.v. and 12, 54, 64, and 78 f.c.v. for columns C and D, respectively.

The total number of f.c.v. of water used in the elution of the uranium from each column is shown in Figs. 3 and 4 and was continued until only a small nominal amount of uranium was eluted in each f.c.v. (usually a few hundred counts/minute).

After the water elution was complete the remainder of the uranium still bound to the tuff (a few percent) was stripped with acid washes. The washes consisted of various molarities of HCl and HNO₃ and 25 f.c.v. removed an additional 4-6% uranium.

In order to determine the effect of crushing or disassembling the rock, a column of tuff was prepared by crushing and made into a column by pouring into a glass tube in the usual manner of preparation of conventional ion exchange

column. The specifications of this column [E] are wt = 13.26 g, 2.13 cm diam, 3.82 cm long, volume = 13.26 cm³. Rate of flow $\approx$ 20 meters/year the pH of the uranium solution was 3.98 as applied on the column and the pH of the water elution was carried out at 3.82. The elution curve with water can be seen in Fig. 5. Using the same criteria as for columns C and D the capacity was 3.1×10^{-3} millimoles U(VI) per gram of rock. No definite or prominent elution peaks were observed.

Migration of Uranium through Los Alamos Tuff under Conditions of Unsaturated Flow

A block of Los Alamos tuff approximately 30 x 23 x 20 cm was set up in a manner shown in Figs. 6, 7, and 8. Three small separate notches were made in the upper surface; each at several cm distance from its neighbor. A solution of ²³⁷U in distilled water (approximately 100 λ), containing about 1×10^6 d/m was pipetted into each notch and allowed to dry. "Rain" was administered by a perforated polyethylene bottle. A total of 7 liters of water was added in 1 liter doses uniformly covering the 690 cm² surface. Between each dose the system was allowed to dry.

Fig. 5

Elution of U(VI) at pH 3.82 from Column of Crushed Los Alamos Tuff Saturated with Uranium

Fig. 6. Apparatus for Coring and Collecting Samples. ANL Neg. No. 122-2443.

Fig. 7. Detail of Coring and Locating Assembly. ANL Neg. No. 122-2406.

Fig. 8
Detail of Sample Collection Arrangement from Coring of Block of Tuff

After the final "rain," coring was commenced on one of the sites with cores being removed at successive 0.5 cm depths to a distance of 15-18 cm. Each core was collected in its own weighed bottle and the ^{237}U content determined with a NaI gamma ray spectrometer by counting the 210 keV gamma. The ^{237}U content of each bottle was corrected for differences in weight of each core sample by determining the counts per minute per gram and the data corrected for decay.

The "rain" was continued and a second set of 7 liters of water was applied. The coring sequence was repeated on the second site. This site, of course, experienced twice as much rain as the previous one.

Fig. 9. Penetration of U(VI) Into Tuff as a Function of Total "Rain"

The third site was treated in the same manner as described above and its uranium distribution, after having "seen" three times as much rain, is shown together with the previous two experiments in Fig. 9.

All data are corrected for ^{237}U decay ($T_{1/2} = 6.75$ d) and are directly comparable.

Experimental Batch K_d Determination

In order to round out these experiments, it was felt proper that a "classic" static K_d determination be made. It is realized that this static experiment may not permit definite conclusions to be made with respect to the dynamic situation occurring in leachings from a real repository into a real aquifer where the kinetics may be of paramount importance.

The ^{237}U was purified by anion column separation using 9 M HCl to wash out impurities. The ^{237}U was stripped from the Dowex A-1 by 1 M HCl. It was taken up in HNO_3 , evaporated to dryness to convert it to

the VI state. The HNO_3 solution was evaporated to dryness and the ^{237}U taken up in HCl which in turn was evaporated to dryness. The dried " $^{237}\text{UO}_2\text{Cl}_2$ " was taken up in water that had been contacted with ground tuff. This solution was used in the batch " K_d " determinations.

A solid piece of tuff placed in tared "Bio-vial," crushed in place, and weighed. Tracer-tuff water solution was adjusted to desired pH and 2.00 ml aliquot added to each vial which was then sealed and equilibrated by end over end rotation. After mixing for 70 hr, samples were centrifuged 1/2 hr at full speed in a clinical centrifuge. A 1.00 ml aliquot was withdrawn from each sample and placed in a clean vial for counting. Three radiometric assays were made on each sample using the NaI well counter and analyzer used for the coring experiments described previously.

- A. Rock plus remaining 1.00 ml of liquid and tracer adsorbed on vial wall.
- B. 1.00 ml of liquid withdrawn.
- C. Empty vial from A after rinsing out rock and liquid.

$$K_d = \frac{(A-B-C) \div \text{wt of sample (g)}}{B} \quad (1)$$

The results are shown in Table II.

TABLE II

	1	2	3	4	5	6
wt of tuff	0.4613 g	0.4688	0.3977	0.5167	0.5064	0.5152
vol of liquid	2.0 ml	2.0	2.0	2.0	2.0	2.0
pH (start)	4.0	4.0	4.0	5.6	5.6	5.6
pH (end)	5.8	5.8	4.8	5.4	5.4	5.1
K_d	111	114	77	93	135	107

DISCUSSION

When the binding of U(VI) on tuff is compared with that of Pu(VI) in the same system¹ the plutonium appears to be bound somewhat more strongly than the first well-defined uranium elution peak. The uranium in the subsequent elution peaks, however, is bound substantially more strongly. This binding of the uranium as expressed by the relative migration coefficient is

$$M = \frac{\text{rate of uranium migration}}{\text{rate of water migration}}.$$

For Pu(VI) $M = 26,000 \mu \text{ meter/meter water flow.}^1$

For the well-defined elution peaks of column C at pH 5.82 the values are*

M = 31,471 μ meters/meter water travel
 10,192 μ meters/meter water travel
 8,403 μ meters/meter water travel
 7,956 μ meters/meter water travel

For column D the peaks at pH 3.87 the values are

M = 86,496 μ meters/meter water travel
 19,362 μ meters/meter water travel
 16,431 μ meters/meter water travel
 13,504 μ meters/meter water travel

The volume of water is that required for the elution of a given peak and is indicated on the graphs in Figs. 3, 4, and 5.

It is tempting to ascribe the appearance of different elution peaks as due to the presence of differing entities of uranium. These may be uranium compounds (uranates?) or uranium complexes. However, these are only conjecture. It is recognized that the later peaks are too sharp to be proper late-eluting species. In normal columns the later the elution, the broader the peak. All that is definitely known is that the uranium in the elution peaks is U(VI).

These distinct elution peaks were not observed in the case of Pu(VI). However, since the rates of flow in that experiment were much greater (by a factor of about 60) there may have been kinetic effects which could account for the differences.

The behavior of U(VI) on crushed rock in column E is ambiguous. It is not clear why no discrete elution peaks were observed or why so much more U(VI) was bound than in the case of the intact rock under comparable conditions. After approximately the same number of f.c.v. of water passed through column E as was for column D approximately four times as much U(VI) was bound to the rock. This may be due to the formation of reactive sites during the crushing process and/or the increase in the area. Mere increase in the area, however, should not change the characteristic elution curves observed with columns C and D.

*The arithmetic of calculating M is as follows: distance a given volume of water travels is

$$\frac{\text{volume of water}}{\text{area of column} \times \text{porosity}}$$

The distance the uranium travels is the length of the column since the peak is eluted.

$$\therefore M = \frac{\text{length of column (in } \mu \text{ meters)}}{\text{distance of water travel (meters)}}$$

There appeared to be no reason to calculate a formal migration rate for the uranium in column E because of the indistinct character of the curve.

Because of these variations it will be very important to extend these studies to two sets of simultaneous triple tracer experiments using carrier free $^{237}\text{U}(\text{VI})$, $^{239}\text{Np}(\text{VI})$ and $^{237}\text{Pu}(\text{VI})$ as well as employing the IV state of these elements in a parallel experiment. In experiments of this type the various kinetic, loading, and inhomogeneity effects will be common to the migration of all species.

It is not surprising that the capacity and rates of elution of $\text{U}(\text{VI})$ are a function of pH. The difference observed between the two kinds of experiments (crushed versus intact rock) suggests that inferences concerning capacities and migration rates be cautiously drawn and that care be taken in extrapolating behavior of actinide ions from the experiments with crushed rock. It is realized that it is easier to determine " K_d 's" and elution characteristics on crushed rock rather than solid samples particularly when the material is relatively impermeable. To maintain reasonable flow rates in an intact rock in order to complete an experiment in a finite time may be difficult but any other course may be unrealistic and misleading.

It is possible to extract crude " K_d 's" from these experiments merely by observing the number of f.c.v. necessary to elute a given peak. Thus for column C the peaks elute at 33, 91, 110 and 116 f.c.v. and the " K_D " can be calculated by

$$K_D = \frac{k_v \times \text{free column volume}}{\text{wt of rock}} \quad (2)$$

where

k_v = capacity constant

= number of f.c.v. to elute peak.

In turn " K_d 's" may be calculated for each peak of columns C and D. The values can be taken from the curves by inspection.

The migration of $\text{U}(\text{VI})$ under conditions of unsaturated flow is not particularly clear. Figure 9 illustrates the penetration of $\text{U}(\text{VI})$ into tuff as a function of the quantity of water applied. It is clear that the application of three times as much water did not drive substantial quantities of uranium three times as deep. In fact 90% of the uranium remained in the first centimeter of rock regardless. Very much smaller amounts of uranium of the order of about 5% or less seem to have migrated further in response to larger quantities of rain.

Since the U(VI) does not appear to advance through the rock in the unsaturated case in the same regular manner as the saturated case previously described it seems that differing mechanisms for migration are operating. It would appear that allowing the uranium to dry on the rock permits it to form a much more tenacious bond than in the case of saturated flow and that once the uranium is relatively "fixed" it is very difficult to remobilize.

The determination of the batch " K_D 's" led to ambiguous results. Since the pH changes during the measurement it would appear that something is being leached from the rock or that some reaction is taking place. Since the rock is inhomogeneous it is difficult to make sure on this small scale that the duplicates are valid. To compare this static equilibrium experiment with the results of the flow measurements on columns C and D it is necessary to consider that in the static experiment K_D 's will tend to attain the values corresponding to the most tightly bound peaks.

In a flow experiment the rate of equilibrium among the various peaks may be so slow that it is possible to observe the separation of peaks during a run because the flow rate is faster than the rate of attainment of equilibrium. If this assumption is correct, then the K_D should be calculated for the most tightly bound peak using Eq. 2 and compared with that obtained from the batch experiments. The " K_D " calculated this way is of the order of 27.8 for the last peak of column C. This does not agree with the batch K_D within a wide margin. However, in view of the fact that the calculation is for a column at full capacity being compared with a static tracer experiment the agreement is perhaps as good as can be expected.

The employment of crushed tuff in the batch experiments introduces unknown quantities such as the formation of new active sites for binding. To this extent it should be expected that the " K_D " for the crushed material be higher.

It also may be that the calculation of " K_D " from a column which had been saturated with the uranium is not valid even though the calculations are based on conditions in which only a small amount of uranium remains on the column (of the order of a few tenths of a percent).

It may be necessary to determine a batch K_D on an intact piece of tuff through which tracer $^{237}\text{U(VI)}$ is continually recirculated until equilibrium is reached between solution and rock. This " K_D " is perhaps much more germane to the conditions existing during migration from a repository through a rock stratum.

REFERENCES

1. S. Fried, A. M. Friedman, J. Hines, and R. Atcher, *Science* 196, 1087-9 (1977).
2. S. Fried and A. M. Friedman, in CONF-701020, Proceedings of the Symposium on Waste Management, Tucson, Arizona, Oct 3-6, 1976. National Technical Information Service, U. S. Dept. of Commerce, Springfield, VA 22161.
3. S. Fried, A. M. Friedman, J. Hines, G. Schmitz, and M. Wheeler, *Transuranics in Natural Environments*, NVO-178, June 1977, p. 115. National Technical Information Service, U. S. Dept. of Commerce, Springfield, VA 22161.
4. K. A. Kraus and F. Nelson, P/837, Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955, 2, 113 (1956).