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Laboratory-Simulated Basalt HLW Repository*

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ANALYTICAL MEASUREMENTS OF ACTINIDE MIGRATION IN A LABORATORY-SIMULATED
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ABSTRACT
    Described are the analytical methods and results used to determine the
migration of actinides in a flowing-groundwater laboratory-simulation of a
basalt repository for high-level nuclear waste. The radiochemical methods
developed and employed to measure actinide activities in groundwater samples
and component surfaces include the use of gamma, X-ray, and alpha spectroscopy,
with associated preparation and calibration. These methods include double
isotope spiking with Np-235 and Pu-236 for determination of Np-237 and Pu-239
in groundwater, gamma-spectroscopic measurements of rock surfaces for spatially
profiling neptunium activity, and a leaching procedure for quantitating the
actinide activities on those rock surfaces.

INTRODUCTION
    Dispersal of actinides by flowing groundwater is the major concern related
to the isolation of high-level nuclear waste (HLW) in a basalt repository.
The analytical methods described in this paper are ones developed for an
experimental study at Argonne National Laboratory (ANL) on the effect on
radionuclide migration of interactions between flowing, simulated groundwater
and basalt repository components in laboratory analog experiments. The term
"analog" is used because the repository components are placed in the water
stream analogously to the configuration that would occur from a hydraulic
breach of the repository. Radionuclide migration from a breached nuclear-
waste repository by groundwater flow depends on the leaching of radionuclides
from solid waste and on the chemical reactions that occur as a radionuclide
moves away from the repository. Therefore, migration involves the inter-
actions of leached species and the groundwater components with (1) the waste
form and canister, (2) the engineered barrier, and (3) the geologic materials
surrounding the repository. Some of these interactions would occur in the
radiation and thermal fields centered on the solidified waste. Rather than

trying to predict what the important interactions are and then studying them individually, we consider a combination of potential interactions, using these analog experiments.

A schematic of the apparatus for an analog experiment is shown in Fig. 1. In an experiment, groundwater is pumped through the first vessel, which contains basalt chips, bentonite, and the glass waste form; then through the second vessel, which contains more bentonite and basalt chips; and then through a narrow basalt fissure in the third vessel.

Six analog experiments, with a duration of approximately 120 days each, have been run to test effects on radionuclide migration of materials of apparatus construction, gamma radiation, and hydrothermal aging of repository components. Samples of groundwater exiting the experiment at the outlets of the rock core vessel and vessels one and two were taken periodically during each experiment and at the end of each experiment. After the apparatus was disassembled, the rock core and bentonite samples from various places along the flow path were analyzed for radionuclide content.

The following sections describe three analyses that were employed in this study. These analyses are (1) $[^{237}Np]$-$[^{239}Pu]$ measurements in solution,
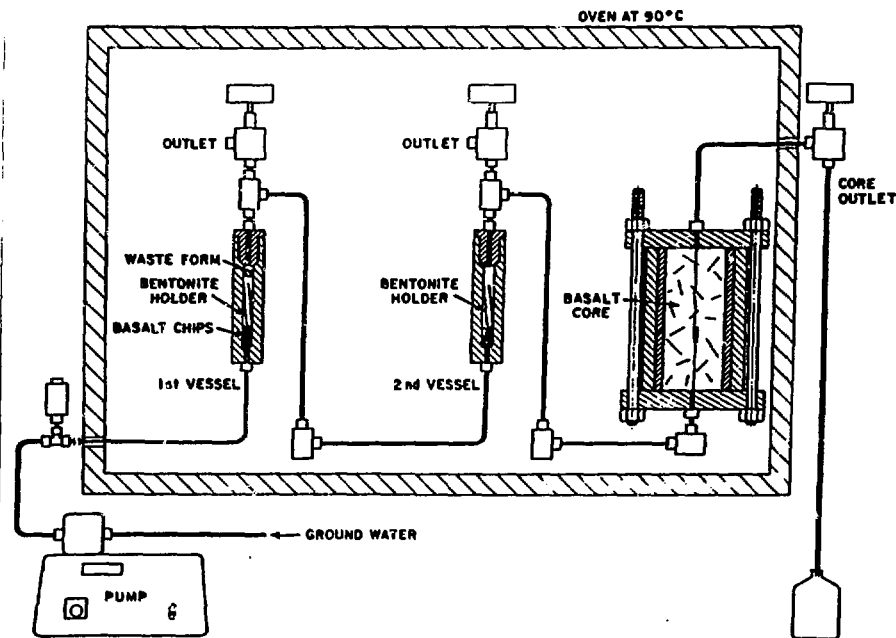

Fig. 1. Apparatus for analog experiments

(2) gamma-spectroscopic measurements of rock surfaces for spatially profiling neptunium-237 activity, and (3) a leaching procedure for quantitating the actinide activities on those rock surfaces. Comprehensive discussions of these experiments and the results of this program can be found elsewhere (refs.1-3).

METHODS AND RESULTS

Determination of [^{237}Np] and [^{239}Pu] in Groundwater

To determine the concentrations of ^{237}Np and ^{239}Pu in the groundwater, it is necessary to separate these elements from other dissolved solids in solution because, upon evaporation, these solids ($\sim$730 mg/L) interfere with determining the alpha disintegration rate using a silicon barrier alpha pulse height detector. The separation procedure is a traditional solvent extraction technique (ref.4) using methyl isobutyl ketone (hexone) as the organic solvent. Because, as with many chemical separations, 100% recovery cannot be assumed, it is necessary to spike the solution with a different isotope of the same element to monitor the recovery of a radionuclide. The spikes chosen for these analyses were ^{235}Np and ^{236}Pu. The ^{235}Np has a relatively long half-life (396 days) and can be easily detected by its 13.6 keV X-ray. The ^{236}Pu ($t_{1/2}$ = 2.8 year) has a high energy alpha decay of 5.7 MeV which is easily resolved from the ^{239}Pu (5.1 MeV) and ^{237}Np (4.8 MeV).

The choice of ^{235}Np over the more conventional ^{239}Np as a yield monitor was made because of its availability and relative ease of detection (ref.5). Neptunium-239 has to be milked from its parent ^{243}Am and its short half-life ($t_{1/2}$ = 2 days) necessitates the procedure to be completed quickly. (The characteristic gamma-ray decay of the ^{239}Np spike is counted to measure the chemical yield of neptunium.)

Although ^{235}Np spiking eliminates most of the problems associated w th that of ^{239}Np, there is still one precaution that must be addressed, its use. A sufficient amount of the ^{235}Np must be used for good counting statistics and to overshadow the contribution to the ^{235}Np signal by X-rays emitted from the other actinides that may be present, *i.e.*, the 13.3 keV X-ray emitting ^{237}Np with a branching ratio of 59%, ^{236}Pu with a 13.6 keV X-ray and branching ratio of 13%, and ^{234}Pu with a 13.6 keV X-ray and branching ratio of 4.4%. Consequently, care must be taken to limit the amount of these interfering isotopes in the analysis. Fortunately, with the high sensitivity and low backgrounds of alpha pulse counting, it is possible to measure low activities of these isotopes with high accuracy.

The procedure is as follows: An aliquot (varied from 0.1 to 50 mL, depending on the expected activities of ^{237}Np and ^{239}Pu) was spiked with a known amount of ^{235}Np and ^{236}Pu. Three drops of concentrated HF, three drops of concentrated $HClO^4$ and 2-3 mL of $8M$ HNO_3 were added. The $HF-HClO_4$ were added to ensure isotopic exchange of the actinides. The sample was evaporated to dryness in a Teflon beaker; $8M$ HNO_3 was used to redissolve the sample and it was again taken to dryness. The solids were again dissolved in 0.5-0.7 mL $8M$ HNO_3 and added to ~6 mL $2.8M$ $Al(NO_3)_3$ salting solution containing 0.1 mL $0.25M$ $KMnO_4$ (the $KMnO_4$ was added to ensure that neptunium and plutonium were both in the (VI) oxidation state necessary for extraction). The resultant solution was mixed on a Vortex mixer with a milliliter of hexone for a minimum of three minutes and then centrifuged. The hexone phase was separated from the aqueous phase and dried on a planchet, taking care that none of the aqueous salting solution was on the counting plate. The planchet was then measured for ^{235}Np content (using a high-purity, high-efficiency germanium detector with a beryllium window) and placed on an silicon barrier alpha-pulse detector for determination of ^{237}Np, ^{239}Pu, and ^{236}Pu.

A variation of this procedure was used for some of the samples analyzed in the analog program. In this variation, the sample and spikes were first reduced with HBr, taken to dryness, and oxidized with the $HF-HNO_3-HClO_4$ before extraction with hexone. Also, the extraction step used $NH_4NO_3/KBrO_3$ instead of the $Al(NO_3)_3-KMnO_4$. The data produced from this method were in general agreement with the standard method. Table 1 compares a few results of these two methods; there is no trend evident between the measured actinide activities and (1) the method employed to measure them or (2) the chemical yield.

The data in Table 1 are representative of the analyses performed, where the range of activities varied from background (0.001 d/m/mL) to 90 d/m/mL. The yields varied between 20 and 85%, with a mean value of ~50%.

Basalt Core Profile of ^{237}Np

The final component in the analog flow system is a basalt rock core which has been split axially to provide a fissure through which fluid flows. The simulated groundwater flowing into the rock core contains low concentrations of radioactive materials leached from the glass waste form; most of this activity was deposited on the rock surface. The distribution of radioactive materials retained on the rock surface was measured by counting the gamma activity using a Ge(Li) detector through a 8-mm by 58-mm opening in a 4-mm

TABLE 1

Examples of ^{237}Np-^{239}Pu groundwater analyses.

Example	Method	^{237}Np d/m/mL	% Yield	^{239}Pu d/m/mL	% Yield
A	1	0.076	38	0.05	35
	2	0.087	45	>0.001	47
B	1	1.5	42	6.8	48
	1	1.7	32	7.1	38
	1	2.6	47	9.3	52
	2	0.8	82	9.3	75
C	1	77	44	62	62
	1	89	39	64	52
	1	81	42	64	49

thick lead plate. The lead plate shielded the detector against radiation from other than the exposed part of the rock's surface. The 86.5 KeV gamma of ^{237}Np was the only signal detectable from the rock surface; ^{152}Eu, ^{133}Ba, and ^{241}Am were looked for but their activities were below detectability. The highly irregular surface geometry of the rock faces precludes quantitative data being obtained by this method; however, the qualitative data do allow comparison of the ^{237}Np distribution on the rock core face from various analog experiments.

Figure 2 shows the profile of ^{237}Np distribution obtained from gamma measurements on one rock core. The relative values of the measured activities may be in error by as much as 20% due to the irregular surfaces of the rock fissures. Even with this high uncertainty, it is clear that the adsorption of the ^{237}Np is essentially complete in the first one third of the rock core.

Core Leaching and Mass Balance of ^{237}Np

Although gamma counting of the rock core surface can give a relative profile of ^{237}Np activity, it cannot be used as a quantitative measurement. To quantitate the amount of neptunium and plutonium sorbed on the rock core, it was necessary to leach these elements from the rock core. The leach solution that was utilized was one developed for removing plutonium from sediments using sodium citrate/sodium dithionate solution (ref.6), followed by leaching with strong acid solution. The results of this analysis were coupled with results of ^{237}Np groundwater analyses to check the mass balance of the first analog experiment.
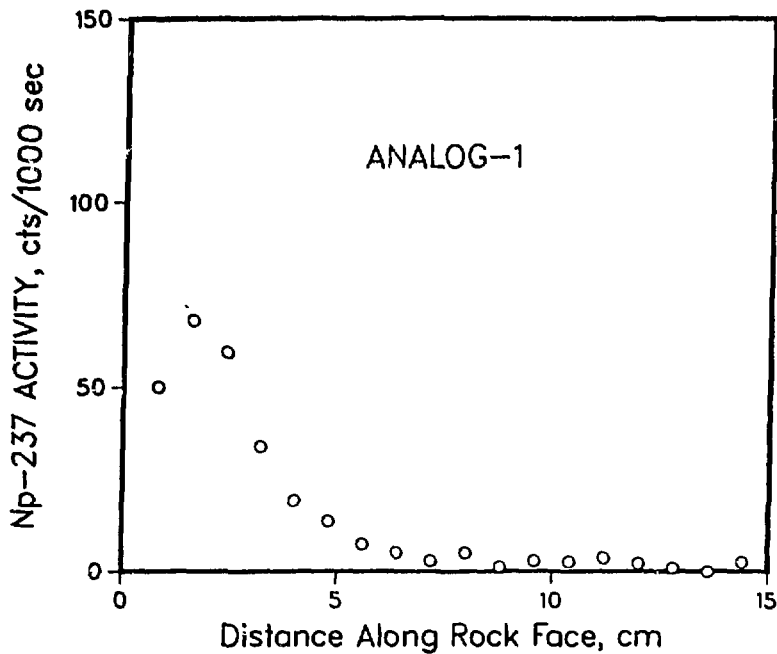
Fig. 2. Distribution of neptunium along the face of the basalt fissure from an analog experiment.

A solution consisting of 0.3M sodium citrate-0.1M sodium dithionate was used to leach the fissured face of the half core. The split core was placed fissured-face down in a trough-like Pyrex vessel, leach solution added to $\sim$0.5 cm above the face, and heated at $\sim$70 C for two hours. The leachate was transferred to a 200-mL volumetric flask and an aliquot was analyzed for ^{237}Np and ^{239}Pu using the same procedure as described previously.

To determine complete leaching of these isotopes, a portion of the core was counted on a Ge(Li) detector for the characteristic 86 keV gamma decay of ^{237}Np and compared to the activity level of the unleached core. A second leach was performed using 1M HCl-0.5M HNO$_3$ under the same conditions as the first leach. The core was recounted on the Ge(Li) detector and the results indicated that 82.2% of the ^{237}Np was removed. The leach data for this experiment are presented in Table 2. The measured content of ^{239}Pu of the second leach was at background levels, which implies that all the plutonium on the rock core was removed in the first leach. The calculated amounts of the ^{237}Np on the rock core, determined independently from the two leaching steps, compared well. The calculations were made by comparing ^{237}Np in the respective leachate solutions to the fractional loss of ^{237}Np activity measured on the rock core face.

TABLE 2

Leaching data for ^{237}Np and ^{239}Pu from a basalt core used in an analog experiment.

Leach number	Volume of leachate, mL	$[^{237}Np]$ in leachate, dpm/mL	$[^{239}Pu]$ in leachate, dpm/mL	% ^{237}Np activity remaining on core after leaching	Total actinide deposited on core, dpm	
					^{237}Np	^{239}Pu
1	200	7.16	0.70	57.1	6670	
2	100	13.34	<0.007[a]	17.8	6730	680

[a]No ^{239}Pu activity was detectable above background levels.

The concentration of ^{237}Np entering the rock core was ~5.7 dpm/mL and was ~0.03 dpm/mL at the rock core's exit. The total volume of groundwater passing through the rock core was 1675 mL. These data would predict 9500 dpm of ^{237}Np was retained in the core vessel (on either the rock surface or on the bentonite at the face of the core inlet). Previous results of gamma spectroscopic analyses of bentonite samples in the experiment showed there was ~1600 dpm ^{237}Np in bentonite deposited at the core inlet. When this amount is subtracted from the total ^{237}Np activity that entered the core holder, the predicted ^{237}Np activity on the rock fissure is 7900 dpm. This compares well to the measured value of 6700 dpm.

No mass balance of ^{239}Pu was attempted. The comparison of ^{239}Pu sorption is difficult because of its association with bentonite. Since bentonite was found throughout the apparatus and especially near the inlet core face, to find a relevant mass balance for ^{239}Pu would entail a destructive analysis of all bentonite samples to measure its alpha activity.

CONCLUSIONS

We have developed an effective and efficient method for $^{237}Np-^{239}Pu$ content in groundwater or other waters with high dissolved solids, and demonstrated that it is possible to spatially profile and quantitate sorbed radioisotope activity on rock surfaces. In laboratory analog experiments, these analyses have shown the correlation between radionuclide retardation with changes in groundwater composition and hydrothermal alteration of basalt repository components. These methods are applicable to the study of other potential repository sites.

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