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THE MEASUREMENT OF SORPTION RATIOS FOR SELECTED RADIONUCLIDES
ON VARIOUS GEOLOGIC MEDIA

S. C. MacLean, D. C. Coles, and H. C. Weed

September, 1978

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INTRODUCTION

Experiments have been conducted to determine the sorptive characteristics of a variety of rocks and minerals with respect to several radionuclides of interest. This information will be used in the determination of the rates of radionuclide migration from nuclear waste repositories.

The sorption distribution coefficient, K_d , of a nuclide is defined as the concentration of a nuclide on a solid phase divided by its concentration in the liquid phase subsequent to equilibrium being attained. In the case of "batch K_d " measurements done in the laboratory, it is difficult to ascertain the extent of equilibration and experiments may not reflect true K_d values. Kurt Wolfsberg of Los Alamos Scientific Laboratory has referred to laboratory K_d measurements as distribution ratios or R_d 's.¹ An R_d is obtained in the same manner as a K_d but does not imply equilibrium. The term " R_d " will be used in this study.

This paper gives the results of batch R_d experiments done in the LLL Nuclear Chemistry Division in support of the Waste Isolation Safety Assessment Program during FY 1978. The details of the laboratory procedure are described in the text and summarized in Fig. 1.

GEOLOGIC MATERIALS

The Water and Waste Management Section of Battelle Pacific Northwest Laboratories provided six rock samples for K_d measurement. Two samples, an oölitic limestone and Sentinel Gap basalt, were used for an interlaboratory

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comparison study in which the laboratories used standard solutions and identical methodologies to determine K_d values. The results of the standardized tests will be compared for consistency. (See Appendix I.) Other samples from BPNL were (1) Climax Stock quartz monzonite porphyry from the site of the LLL heater test at the Nevada Test Site, (2) Westerly granite from New England, (3) Conasauga shale from the OWI-DR8 drill hole in Valley and Ridge Province of Tennessee, and (4) green argillaceous shale from New York. The rock samples had been crushed in a jaw crusher and the 20 to 50 mesh size (840 to 297 μm) taken for analysis by our laboratory. The dry sieved material was manually mixed.

Several LLL rock samples were also used for the batch R_d work: (1) dolomite of the Bonanza King Formation was taken from the USGS Amargosa Tracer Site at a depth of 628 feet in hole #1, (2) biotite from Ontario, Canada, and (3) Thirsty Canyon tuff from the Nevada Test Site. The 100 to 325 mesh size (147 to 43 μm) was used for all three samples. In addition, rock samples were taken from three shear zones in the Climax Stock. The shear zone samples were sieved into three fractions: 50 to 100 mesh (297 to 147 μm), 100 to 325 mesh (147 to 43 μm), and <325 mesh (<43 μm). Only the middle fraction (100-325 mesh) was used from Shear Zone 1 but all three fractions from Shear Zones 2 and 3 were studied. Climax Shear Zone 3 appeared to be serpentinized and all three zones exhibited some hydrothermal alteration. Table I presents the x-ray diffraction analysis of the shear zone samples.

Table II gives particle size and surface area information for all the rock and mineral samples.

GROUNDWATER

The groundwater compositions were determined on the basis of their compatibility with the rock samples. The solution-rock combinations used in this study are shown in Table III. Three groundwater compositions were prescribed

by BPNL for use in the interlaboratory comparison experiments. The compositions of these groundwaters are shown in Tables IV A, IV B, IV C, and IV D. M. A. Molecke of Sandia Laboratories, Albuquerque, New Mexico, originally suggested WIPP Brine B as being representative of water which might result from the intrusion of groundwater into the Waste Isolation Pilot Plant in New Mexico.² The composition of groundwater for use with granitic rocks was suggested by Bruce Erdahl of Los Alamos Scientific Laboratory on the basis of information from Feth et al.³

The groundwater used for the Amargosa Bonanza King Formation dolomite experiment was collected at the USGS Amargosa Test Site in February, 1978. It had a pH of 7.69 at our laboratory three days after it was sampled.

The analytical reagents used in making each simulated groundwater sample were weighed individually on weighing paper before being washed through a funnel with distilled water into a one-liter volumetric flask. (The "granite" groundwater was made in a two-liter volumetric flask.) The solutions were brought to volume and thoroughly mixed. The "limestone" groundwater was sparged with CO_2 gas to dissolve all of the $\text{Ca}(\text{OH})_2$ and the "granite" groundwater required sparging with CO_2 to dissolve the SiO_2 . The solutions were then remixed.

The pH of the groundwater was measured with an Orion Research digital ionalyzer. N_2 and CO_2 gases were used to reach the desired pH for each groundwater. The volumetric flasks were left loosely covered overnight to allow excess N_2 and CO_2 to diffuse out of the groundwaters.

The synthetic groundwaters were filtered through 102 mm diameter 0.40 μm Nuclepore filters under N_2 pressure, and were then stored in polyethylene bottles. The pH was measured following filtering and adjusted, if necessary, prior to the cold wash of the rock samples. The Amargosa groundwater was not filtered before the cold contact.

The tracers used for the batch R_d experiments were ^{85}Sr , $^{95\text{m}}\text{Tc}$, ^{137}Cs , and ^{237}Pu . All were received in acidic solutions. ^{85}Sr and ^{137}Cs solutions were made up by washing each shipping vial into a separate volumetric flask with 1 N HCl (~2 ml). Each vial was then rinsed into the corresponding flask with distilled water. The $^{95\text{m}}\text{Tc}$ was transferred and brought to 100 ml with 6 N HNO_3 . The shipping vial for the ^{237}Pu -nitrate compound was washed with 1 N HNO_3 (~2 ml), washed well with distilled water, and brought to 25 ml.

The amount of spiked groundwater needed was calculated and an allowance for some loss during filtering was made. The cold groundwater was measured with volumetric pipettes and transferred to polyethylene bottles. The tracer solutions were then added to the groundwaters. In order to avoid analytical interferences, the ^{237}Pu was run separately. The amount of tracer added to the groundwater resulted in solutions containing approximately 50 μCi ^{85}Sr , 50 μCi ^{137}Cs , 10 μCi $^{95\text{m}}\text{Tc}$, and 1 μCi ^{237}Pu per sample vial. After the addition of the tracer, the solutions were mixed and left loosely covered overnight.

The initial pH of the spiked groundwaters was always well below the desired level. Adjustment was made by bubbling N_2 gas through the solution while measuring the pH. The spiked groundwaters with a pH below 3.5 required minimal amounts of 1N or 0.1N NaOH to be added along with the N_2 sparging to obtain the required pH. The spiked groundwater was allowed to equilibrate for at least three days with daily adjustment of pH if necessary.

For our most recent batch R_d experiments, we followed part of the procedure for preparing tracer solutions as described by K. Wolfsberg.¹ A mixture of ^{85}Sr , $^{95\text{m}}\text{Tc}$, and ^{137}Cs was evaporated to dryness in a polyethylene bottle. We did not add concentrated HCl and redry the mixture. The groundwater was added to the polyethylene bottle by volumetric pipettes, mixed, and the pH measured. No adjustment of the pH was necessary. After three days

the pH still remained within the correct range. The pH of the spiked groundwaters for the different geologic samples is given in Table VI.

The equilibrated spiked groundwater was filtered prior to contact with the sample material. A 25 mm Nuclepore swin-lok membrane holder (without the rubber gasket) containing a 0.40 μ m Nuclepore filter was attached to a 100 cc glass syringe with a metal adapter (large female luer to standard male luer). The spiked solution was poured into the top of the syringe and pushed through the filter into a clean polyethylene bottle. The filter was removed from the holder, pulled across a Kimwipe to dry the back, put in a press-fit counting container, and submitted for gamma-ray counting. Filtering the spiked groundwater did not cause any significant loss of tracer activity except for ^{237}Pu . Table V shows that from 11 to 63% of the ^{237}Pu remained on the filter.

PROCEDURE

A flow sheet for the procedure is given in Fig. 1. Sample vials were prepared in triplicate for each sample matrix and for the blanks. We found that the best sample containers were the Oak Ridge-type 30 ml polycarbonate centrifuge tubes with polypropylene screw caps. The lids and bottles were labeled with water resistant ink before they were weighed.

Approximately one gram of sample material (weight known to 0.01 mg) was added to each vial except the blanks. The first of two cold washes started with the addition of 15 ml of the appropriate groundwater (measured in a 25 ml polypropylene graduated cylinder) to each vial including the blanks. The samples were then placed horizontally in a shaker-table water-bath at 25°C and ~130 oscillations per minute for about 48 hours.

The first cold wash terminated with the centrifuging of the samples at 3000 rpm for 20 to 60 minutes followed by decanting the groundwater wash and discarding it. The second cold wash was carried out exactly as the first. After decanting the second cold wash, the vials were tightly capped and

weighed to determine the residual liquid remaining with each sample (including blanks).

Using a volumetric pipette, 15 ml of spiked groundwater was added to each vial and then the vial was returned to the water bath (25°C, 130 oscillations/min) for ~7 days. The samples were centrifuged in an identical manner as following the cold washes.

The spiked wash solution was decanted into a 30 ml disposable polyethylene beaker. A 10 cc (20 cc if available) disposable plastic syringe with a luer-lok tip was used to aspirate the decanted fluid. The syringe was then attached to a Nuclepore swin-lok membrane holder containing a 25 mm diameter 0.10 μ m Nuclepore filter. The solution was forced through the filter into a second 30 ml polyethylene beaker. With a volumetric pipette, 10 ml were transferred to a counting vial for gamma spectroscopy. The remaining solution was returned to the sample vial for disposal. In some cases the filter was removed from the holder and blotted dry on the back by pulling it across a Kimwipe. The dried filter was put in a press-fit container and submitted for gamma counting.

Table VII shows that minimal activity was lost to the filter from the blanks. However, filters from the samples had significant activity that was due to the "fines" of the geologic material being decanted with the solution.

CALCULATION OF BATCH R_d VALUES

To calculate our batch R_d values, we took the equation used by Serne et al.² and adjusted it to take into account the residual cold wash remaining in the blank vials before the addition of the spiked groundwater. Let

C_b = concentration of trace constituent in the blank solution (dpm/ml)

C_s = concentration of trace constituent in the sample solution (dpm/ml)

A = total volume of solution in last treatment (15 ml + x ml residual cold wash)

and B = total grams of geologic material; then

$$R_d(\text{ml/g}) = \frac{\frac{A_b}{A_s} C_b - C_s}{C_s} \frac{A_s}{B}$$

We counted (in triplicate) 500 λ of the spiked groundwater evaporated on three filter papers in a press-fit counting container. Because of geometry differences between the two types of containers, we could not accurately compare counting results between the sample solutions and the original spiked groundwater. Therefore, we used the concentration of a tracer in the blank because we counted 10 ml of the blank solution, as had been done with the sample solutions.

The triplicate R_d values calculated for a geologic material were averaged and given as the mean $\pm$ one standard deviation expressed as percent ($X \pm 1\sigma$). Some of the variation within the triplicates was very large. Fischer and Peters⁴ give statistical criteria for discarding an extreme value at a 95% probability level. Only four of our Cs R_d triplicates met the test for rejecting the third extreme value.

RESULTS AND SUMMARY

The results from the batch R_d studies done at LLL during 1978 are listed in Table VIII. The standard deviation of the counting data for each R_d is in parentheses. The R_d values can be arranged according to the following inequalities:

- Pu > Cs, except for biotite
- Cs > Sr, except for limestone
- Sr > Tc.

The exceptions are considered significant for Pu vs. Cs on biotite, but not for Cs vs. Sr on limestone. The low R_d values for Tc indicate that within the limits of measurement it is not sorbed under the experimental conditions

in this study. One possible cause for the negative values is preferential sorption of the sample on the walls of the sample container, so that the sample container sorbs less Tc than the blank container does.

ACKNOWLEDGMENTS

We would like to thank the following LLL people:

W. J. Beiriger for x-ray analysis,

A. H. Biermann and C. A. Slettevold for particle analysis and BET surface area,

R. N. Anderson for gamma spectroscopy,

J. D. Tewhey for reviewing the paper, and

J. A. Plis for typing the manuscript.

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Figure I. Batch R_d Procedure.

Table 1. X-Ray Analysis of Fracture Zone Material from Climax Stock.

	<u>Muscovite- Illite</u>	<u>Montmorillonite</u>	<u>Quartz</u>	<u>Calcite</u>	<u>K and Na Feldspar</u>
Shear Zone 1	W	10%	M	10%	M
Shear Zone 2	T	>40%	MW	15-20%	W
Shear Zone 3	MW	30%	MW	5%	MW

T = Trace
VW = Very Weak
W = Weak
MW = Moderately Weak
M = Moderate

Table II. Characterization of Geologic Materials Used in Batch R_d Studies at LLL During 1978.

Geologic Material	Sieve Size (Mesh)	Particle Size Analysis			Surface Area Analysis (BET) $\pm$ S.D. m^2/gm
		10% μm	50 % μm	90 % μm	
Oolitic limestone	20-50				
Sentinel Gap basalt	20-50				
Bonanza King dolomite		28	72	118	0.679 ± 0.006
Biotite	100-325	40	71	122	2.818 ± 0.001
Climax Stock quartz monozon- ite porphyry	20-50				
Thirsty Canyon tuff	100-325	in progress			in progress
Conasauga shale	20-50				
Green argillace- ous shale	20-50				
Climax Shear Zone 1, middle	100-325	68	122	165	4.370 ± 0.002
Climax Shear Zone 2, fine	<325				
Climax Shear Zone 2, middle	100-325	63	108	162	13.577 ± 0.001
Climax Shear Zone 2, coarse	50-100				
Climax Shear Zone 3, fine	<325				
Climax Shear Zone 3, middle	100-325	46	80	133	7.081 ± 0.001
Climax Shear Zone 3, coarse	50-100				
Westerly granite	20-50				

Table III. Solution-Rock Combinations Used in This Study.

Rock Type	Solution or Groundwater				
	"Limestone"	WIPP Brine	"Basalt"	"Granite"	Amargosa
Oolitic limestone	X	X			
Basalt		X	X		
Dolomite					X
Biotite				X	
Climax Stock quartz monzonite porphyry				X	
Westerly granite				X	
Tuff			X		
Conasauga shale	X				
Green argillaceous shale	X				
Climax Shear Zone 1, medium				X	
Climax Shear Zone 2, fine				X	
Climax Shear Zone 2, medium				X	
Climax Shear Zone 2, coarse				X	
Climax Shear Zone 3, fine				X	
Climax Shear Zone 3, medium				X	
Climax Shear Zone 3, coarse				X	

Table IV A. Simulated "Limestone" Groundwater Composition.

	<u>mg/l</u>	<u>Analytical Reagents</u>	<u>mg/l</u>
Ca ⁺²	50.	Ca(OH) ₂	92.5
Mg ⁺²	3.6	*MgSO ₄ anhyd.	18.
Na ⁺	2.3	NaCl	5.8
K ⁺	0.4	KCl	0.8
HCO ₃ ⁻	153.		
SO ₄ ⁻²	14.4	pH 8.2 ± 0.2	
Cl ⁻	3.5		

*When the groundwater for the shale samples was made, MgSO₄·7 H₂O was used (36.5 mg/l).

Table IV B. WIPP Brine B (slightly altered) Composition

	<u>mg/l</u>	<u>Analytical Reagents</u>	
Na ⁺	115,000.	NaCl	287. g/l
K ⁺	15.	Na ₂ SO ₄	6.2 g/l
Mg ⁺²	10.	Na ₂ B ₄ O ₇ ·10 H ₂ O	16. mg/l
Ca ⁺²	900.	NaHCO ₃	14. mg/l
Sr ⁺²	1.5	NaBr	520. mg/l
Cs ⁺	1.	KCl	29. mg/l
Cl ⁻	175,000.	MgCl ₂ ·6 H ₂ O	85.4 mg/l
SO ₄ ⁻²	3,500.	CaCl ₂ anhyd.	2.49 g/l
BO ₃ ⁻³	10.	SrCl ₂ ·6 H ₂ O	4.52 mg/l
HCO ₃ ⁻	10.	CsCl	1.3 mg/l
Br ⁻	400.		

pH 6.5 ± 0.5

Sentinel Gap basalt and Thirsty Canyon tuff were the sample materials used with "basalt" groundwater.

Table IV C. Simulated "Granite" Groundwater Composition.

	<u>mg/l</u>	<u>Analytical Reagents</u>	<u>mg/l</u>
SiO ₂	26.2	*MgSO ₄ ·7 H ₂ O	6.88
Ca ⁺²	8.3	KCl	2.83
Mg ⁺²	1.5	*MgCl ₂ ·6 H ₂ O	3.85
Na ⁺	6.7	MgO	0.60
K ⁺	1.5	Ca(OH) ₂	15.5
HCO ₃ ⁻	47.7	Na ₂ SiO ₃ ·9 H ₂ O	125.
SO ₄ ⁻²	2.7		
Cl ⁻	2.1		

pH 7.8 ± 0.3

*When the "granite" groundwater was made for the Westerly granite and Climax Stock, the water molecules were inadvertently neglected; 3.36 mg/l of MgSO₄·7 H₂O and 1.80 mg/l of MgCl₂·6 H₂O were used.

Table IV D. Simulated "Basalt" Groundwater Composition.

	<u>mg/l</u>	<u>Analytical Reagents</u>	<u>mg/l</u>
Na ⁺	30.	NaHCO ₃	79.8
K ⁺	9.	Na ₂ SO ₄	24.85
Ca ⁺²	6.5	*MgSO ₄ ·7 H ₂ O	9.84
Mg ⁺²	1.0	CaSO ₄	4.76
HCO ₃ ⁻	58.	CaCl ₂	14.42
SO ₄ ⁻²	23.	KCl	14.91
Cl ⁻	16.	*KF·2 H ₂ O	3.76
F ⁻	0.7		

pH 7.7 - 8.2

*When the "basalt" groundwater was made for the tuff, the water molecules were inadvertently overlooked; 4.81 mg of MgSO₄·7 H₂O and 2.32 mg of KF·2 H₂O were used to make one liter of groundwater.

Table V. Percent of Tracer Activity on 0.40 μ m Filter.

Percent of original solution activity found on 0.40 μ m filter					
<u>Groundwater</u>	<u>Date</u>	<u>⁸⁵Sr</u>	<u>^{95m}Tc</u>	<u>¹³⁷Cs</u>	<u>²³⁷Pu</u>
Limestone	2/78	0.03	—	1.0	14.
WIPP Brine B	2/78	0.006	—	0.0012	60.
Basalt	2/78	0.073	—	0.22	11.
Amargosa	3/78	0.070	—	0.14	39.
Basalt	7/78	0.038	0	0.038	16.
Granite	7/78	0.009	0.003	0.014	63.
Limestone	8/78	0.021	0.017	0.24	—
Granite	8/78	0.13	0.025	0.34	—

Table VI. pH of Groundwater Washes.

Geologic Material	"Limestone"			WIPP Brine B			"Basalt"			"Granite"			Amargosa		
	Cold	Spiked Fission products		Cold	Spiked Fission products		Cold	Spiked Fission products		Cold	Spiked Fission products		Cold	Spiked Fission products	
		Pu			Pu			Pu			Pu			Pu	
Oolitic Limestone	8.3	8.3	8.3	6.5	7.0	6.7									
Sentinel Gap basalt				6.5	7.0	6.7	8.2	7.9	7.8						
Bonanza King formation dolomite													7.7	7.8	8.1
Biotite										7.8	7.9	7.5			
Climax Stock quartz monzonite porphyry										7.8	7.9	7.5			
Westerly granite										7.8	7.9	7.5			
Thirsty Canyon tuff							8.1	8.2	7.7						
Conasauga shale	8.1		8.2												
Green argillaceous shale	8.1		8.2												
Climax Shear Zones										8.0		7.9			

Table VII. 0.10 μ m Filtration of R_d Solutions -- Activity on Filter.

	material visible on filter	Activity on Filter Expressed as % of Activity in Solution			
		<u>^{85}Sr</u>	<u>^{95m}Tc</u>	<u>^{137}Cs</u>	<u>^{237}Pu</u>
"Granite" blank	—	0.2	0.3	0.2	4.5
Biotite	Yes	2.4-2.7	0-0.2	29.-59.	193.-228.
Climax Stock	Yes	3.2-7.2	0	53.-203.	167.-352.
Westerly	Yes	4.2-9.5	0	159.-387.	736.-2000.
"Basalt" blank	—	0.1	0	0.1	0.2
Tuff	No	0.5-0.6	0	1.3-1.7	1.9-10.3

Table VIII. Batch R_d Results[†]

Geologic Material	Groundwater	R_{Sr} (ml/g)	R_{Tc} (ml/g)	R_{Cs} (ml/g)	R_{Pu} (ml/g)
Limestone	"Limestone"	2.7 ± 18.% (2.5%)*	ND	60. ± 50.% (42.%)*	770. ± 4.7% (5.4%)
Limestone	WIPP Brine B	0.88 ± 49.% (2.6%)*	ND	0.57 ± 94.% (3.3%)*	450. ± 20.% (22%)
Basalt	"Basalt"	45. ± 3.0% (1.9%)*	ND	290. ± 24.% (23.%)*	580. ± 2.1% (2.0%)
Basalt	WIPP Brine B	0.0 (0.19%)*	ND	1.6 ± 4.0% (0.43%)*	1260. ± 40.% (52.%)
Dolomite	Amargosa	1.01 ± 5.9% (5.8%)*	ND	33. ± 12.% (8.4%)*	618. ± 0.7% (0.7%)*
Biotite	"Granite"	59. ± 2.8% (2.1%)*	-1.07 ± 3.2% (0.3%)*	**663. ± 0.2% (0.3%)* 680. ± 5.0% (4.9%)*	570. ± 2.6% (2.1%)
Climax Stock	"Granite"	17. ± 7.3% (3.7%)*	-0.8 ± 26.% (2.1%)*	**306. ± 0.8% (0.7%)* 380. ± 35.% (28.%)*	560. ± 27.% (29.%)
Westerly granite	"Granite"	6.5 ± 30.% (9.3%)*	-0.91 ± 9.1% (0.8%)*	210. ± 41.% (47.%)*	520. ± 16.% (17.%)
Tuff	"Basalt"	39.7 ± 0.5% (0.4%)*	-0.21 ± 43.% (0.8%)*	122. ± 3.4% (3.8%)*	420. ± 4.8% (4.2%)
Conasauga shale	"Limestone"	29.3 ± 1.8% (1.1%)	0.1 ± 191% (1.8%)	**4430. ± 0.7% (0.6%) 3900. ± 22.2% (25.%)	ND
Green arg. shale	"Limestone"	60. ± 2.6% (1.9%)	-0.33 ± 27.% (0.5%)	8000. ± 25.% (29.%)	ND
C-Shear Zone 1-Med.	"Granite"	175. ± 2.0% (1.8%)	-0.49 ± 14.% (0.4%)	460. ± 4.6% (4.5%)	ND
C-Shear Zone 2-Fine	"Granite"	600. ± 1.2% (1.1%)	-0.6 ± 23.% (1.2%)	1010. ± 0.5% (0.5%)	ND
C-Shear Zone 2-Med.	"Granite"	608. ± 1.6% (1.6%)	-0.7 ± 22.% (1.1%)	1027. ± 1.5% (1.5%)	ND
C-Shear Zone 2-Coarse	"Granite"	601. ± 3.8% (3.7%)	-0.5 ± 21.% (1.7%)	*1061. ± 0.6% (0.7%) 1500. ± 47.% (37.%)	ND
C-Shear Zone 3-Fine	"Granite"	440. ± 2.7% (2.7%)	-0.2 ± 60.% (0.8%)	1400. ± 1.2% (1.2%)	ND
C-Shear Zone 3-Med.	"Granite"	311. ± 2.9% (2.7%)	-0.2 ± 137.% (2.4%)	940. ± 2.8% (2.7%)	ND
C-Shear Zone 3-Coarse	"Granite"	318. ± 2.2% (2.2%)	-0.4 ± 30.% (1.1%)	1100. ± 5.7% (6.0%)	ND

[†]Contact time 7 days unless indicated by * to be 8 days

*Contact time 8 days

**Using two samples⁴

ND = not determined

APPENDIX I

CONTROLLED SAMPLE PROGRAM

PURPOSE:

Large quantities of rocks were obtained to provide all WISAP subcontractors with selected common samples. Through the use of common samples it should be possible to compare K_d , sorption-desorption data or nuclide migration potentials between the various labs and between different experimental techniques. The main objectives are: 1) to ascertain whether different experimenters obtain the "same" results using common rocks, standard solutions and a dictated experimental design and 2) to ascertain the comparability of results obtained by individual laboratories using different experimental methodologies. In Objective Two Studies we will be investigating K_d or nuclide migration dependencies on experimental methodologies in hopes of formulating a standard " K_d " method or deriving calibration numbers to convert K_d numbers derived from one method to K_d values applicable to another method.

Peripheral objectives include generation of a K_d data bank on common rock-groundwater systems.

Rock materials acquired were crushed in a jaw crusher and the 20 to 50 mesh size (840 to 297 μ m) selected. The dry sieved material was well mixed manually and 1 gallon containers filled. PNL realizes that during crushing metallic impurities may have been added and that the resultant crushed rock might have acquired some "unnatural" sorption qualities compared to the virgin rock. Neither of these potential problems will effect the main objectives of the controlled sample program.

Each laboratory will receive approximately 1 gallon each of the crushed rocks. In addition those who request can obtain large chunks (5-25 lbs) of the rocks to fabricate intact cores etc.

The rock samples will be characterized by PNL as follows:

Bulk Chemical Analysis

Mineralogy by X-ray Diffraction and Microprobe

Cation-Exchange Capacity

Surface Area: Ethylene Glycol
BET

Results will be supplied to all participants.

OBJECTIVE 1: INTERLABORATORY COMPARISON

All laboratories are directed to perform the following Batch Kd Experiments:

EXP #1

Geologic Material:	LIMESTONE
Groundwater:	Ca ⁺² <u>mg/l</u>
	50.
	Mg ⁺² 3.6
	Na ⁺ 2.3
	K ⁺ .4
	HCO ₃ ⁻ 153
	SO ₄ ⁻² 14.4
pH 8.2 ± .2	Cl ⁻ 3.5

Eh: Atmospheric O₂ equilibrated

Solid to Solution: 1g/15 ml

Nuclides: Sr

Cs

Pu

²³⁷Pu will be available to all Jan 78
concentrations < 10⁻⁶ M (must be measured)

Replicates: minimum of 3 replicates

PNL Recipe	<u>mg/l</u>
Ca(OH) ₂	92.5
MgSO ₄	18
NaCl	5.8
KCl	.8

SPARGE with CO₂ gas until all lime dissolves and pH is 8.2-8.3. If pH is below pH 8.2 when all lime is dissolved sparge with N₂ gas to get back to pH 8.2. Allow pH to equilibrate overnight so excess CO₂ and N₂ can diffuse out. Measure HCO₃ alkalinity and report.

EXP #2

Geologic Material: Limestone

Groundwater: NIPP Brine #B (slightly altered)

	<u>mg/l</u>
Na ⁺	115,000
K ⁺	15
Mg ⁺²	10
Ca ⁺²	900
Sr ⁺²	1.5
Cs ⁺	1
Cl ⁻	175,000
SO ₄ ⁻²	3,500
BO ₃ ⁻³	10
HCO ₃ ⁻	10
Br ⁻	400

PNL Recipe	
NaCl	287. g/l
Na ₂ SO ₄	6.2 g/l
Na ₂ B ₄ O ₇ ·10 H ₂ O	16 mg/l
NaHCO ₃	14 mg/l
NaBr	520 mg/l
KCl	29 mg/l
MgCl ₂	40 mg/l
CaCl ₂ ·2H ₂ O	3.3 g/l
SrCl ₂ ·2H ₂ O	3.3 mg/l
CsCl	1.3 mg/l

pH: 6.5 ± .5

Eh: atmospheric O₂ equilibrated (same as EXP #1)

Solid/solution: 1g/15 mls (same as EXP #1)

Nuclides: Sr

Cs

Pu

(Same as EXP #1)

Replicates: minimum of 3 (Same as EXP #1)

EXP #3

Geologic Material: Basalt

Groundwater:

	mg/l
Na ⁺	30
K ⁺	9
Ca ⁺²	6.5
Mg ⁺²	1.0
HCO ₃ ⁻	58
SO ₄ ⁻²	23
Cl ⁻	16
F ⁻	0.7

PNL Recipe

NaHCO ₃	.95 meq/l	79.8 mg/l
Na ₂ SO ₄	.35 meq/l	24.85 mg/l
MgSO ₄	.08 meq/l	4.81 mg/l
CaSO ₄	.07 meq/l	4.76 mg/l
CaCl ₂	.26 meq/l	14.42 mg/l
KCl	.20 meq/l	14.91 mg/l
KF	.04 meq/l	2.32 mg/l

pH: 7.7-8.2

Eh: Same as EXP #1

Solid/Solution: Same as EXP #1

Nuclides: Same as EXP #1

Replicates: Same as EXP #1

EXP #4

Geologic Material: Basalt

Groundwater: Same as EXP #2

pH: Same as EXP #2

Eh: Same as EXP #1

Solid/solution: Same as EXP #1

Nuclides: Same as EXP #1

Replicates: Same as EXP #1

Subcontractors are encouraged to use other controlled samples and pertinent nuclides also. WIPP Brine B represents one groundwater which could be used with all controlled samples. If you decide to perform batch Kd work on the other controlled samples I will concoct an appropriate groundwater.

PROCEDURE:

Make up aliquots of spike solutions (gw + nuclides) adjust pH to desired value. Equilibrate for at least 3 days. Check pH daily and adjust. Filter solutions through 0.45 μ m before contacting with "cold wash equilibrated" rocks.

Place material in container (suggest 1-2g in 50 ml Oak Ridge Polycarbonate Centrifuge tube. Wash material twice with cold solution (gw without spikes for periods of ~48 hours. Separate rock from cold solution by centrifugation. Discard cold washes.

Add known amount of spiked groundwater to rocks, contact for 7 days. Separate solution, count and calculate Kd. Blank containers (with no rocks) should be used to account for any container sorption. Nuclides may be mixed together or run separately.

PNL method of calculating Kd is shown in enclosure.

OBJECTIVE 2

METHODOLOGY EVALUATION

Using the control rocks, groundwaters and nuclides specified run your own style batch, flow through column, soil chromatography, axial filtration, etc., type of Kd experiments to compare with results obtained for Objective 1.

You are also encouraged to use the other rock samples and pertinent nuclides in your program.

As more large rock samples are obtained other samples will be available.

GENERAL COMMENTS

Detailed notes and write ups should be prepared on laboratory procedures utilized for this program including step by step "cookbooks", materials utilized (containers, chemicals, nuclides) etc. such that anyone could duplicate your work.

The work for Objective 1 (Controlled Batch Kd's) should be completed by May 1, 1978. Work for Objective 2 should be completed by August 15, 1978. If you have questions please call. (These deadlines are firm.)

BATCH Kd CALCULATIONS

Tare weights are determined on 250 ml polycarbonate screw cap centrifuge bottles. From 5-10 g of well mixed soils are weighed into the centrifuge bottles. Fifty mls of the simulated waste solution without the trace constituent are added to the centrifuge bottle. A piece of PARAFILM sealing material is placed over the mouth of the bottle before screwing down the cap to prevent solution leakage through the threads of the cap during the mixing stage. The capped bottle is placed in a variable speed shaker and moderately agitated for 30 minutes. The bottles are then centrifuged for 15-20 minutes at 4000 rpm and the supernatant is carefully decanted. Loss of soil should be avoided. Three prewashes of the matrix solution (solution without the trace constituent) are performed. After the third decanting the centrifuge bottle is reweighed and the amount of residual solution is calculated by difference. This value is needed because of the residual solution's dilution effect. Fifty mls of the simulated waste solution containing the trace constituent are then pipeted into the centrifuge bottle and the capped bottle is agitated for a designated period. For tracer work in which pH is not important shaking times of 18-24 hours are utilized. For pH dependent reactions shaking times vary with the rate of change of solution pH; solutions are centrifuged and extracted when the mixed solution attains the desired pH. The sample is centrifuged as before and an effluent sample is extracted for analysis of the trace constituent.

Samples of the effluent and influent are then analyzed for the trace constituent. The Kd is calculated from equation

$$K_d = \frac{rC_o - C_e}{C_e} \frac{A}{B}$$

where

A = total mls of solution in last treatment
(50 ml + X residual mls)

B = total g of soil present

r = ratio of tracer solution to total solution (50/50 + X)

C_o = concentration of trace constituent in influent solution m/l,
cpm/ml, etc.

C_e = concentration of trace constituent in effluent solution.