Waste Isolation Safety Assessment Program

**Controlled Sample Program
Publication Number 2:
Interlaboratory Comparison
of Batch Kd Values**

J. F. Relyea
R. J. Serne

June 1979

Prepared for the
Office of Nuclear Waste Isolation
U.S. Department of Energy
under Contract EY-76-C-06-1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

The views, opinions and conclusions contained in this report are those of the contractor and do not necessarily represent those of the United States Government or the United States Department of Energy.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$ ____*; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.00
026-050	\$4.50
051-075	\$5.25
076-100	\$6.00
101-125	\$6.50
126-150	\$7.25
151-175	\$8.00
176-200	\$9.00
201-225	\$9.25
226-250	\$9.50
251-275	\$10.75
276-300	\$11.00

3 3679 00053 2269

Waste Isolation Safety Assessment Program

CONTROLLED SAMPLE PROGRAM

PUBLICATION NUMBER 2:

INTERLABORATORY COMPARISON OF BATCH KD VALUES

J. F. Relyea

R. J. Serne

June 1979

Prepared for the
Office of Nuclear Waste Isolation
U.S. Department of Energy
under Contract EY-76-C-06-1830

Pacific Northwest Laboratory
Richland, Washington 99352

ACKNOWLEDGMENT

This research was supported by the Waste Isolation Safety Assessment Program being conducted by Pacific Northwest Laboratory. This program is sponsored by the Office of Nuclear Waste Isolation, which is managed by Battelle Memorial Institute under its contract with the Department of Energy.

SUMMARY

The objectives of the controlled sample program interlaboratory comparison were to: 1) ascertain whether different experimenters obtain the same results for the adsorption of Cs, Sr and Pu using common rocks, standard solutions and a prescribed method; and 2) compare the results obtained by individual laboratories using different experimental methodologies and resolve any differences found or determine what conversions can be made to compare results from one method with another.

Results from Objective 1 indicate that several parameters that were uncontrolled may have affected results. The uncontrolled parameters were: 1) method of tracer addition to solution, 2) solution to rock ratio, 3) initial tracer concentration in influent solution, 4) particle size distribution, 5) solid-solution separation method, 6) sample containers, and 7) temperature.

Observed Kds for Cs and Sr in brine showed agreement among laboratories for both limestone and basalt rock samples. Comparable results were also found for Sr and Cs in the basalt groundwater. Results for $K_d(\text{Cs})$ in the limestone groundwater varied over three orders of magnitude, and $K_d(\text{Sr})$ varied by one order of magnitude in the limestone system. Observed K_d values for Pu typically varied by two to three orders of magnitude in all systems studied.

Adsorption of Pu by container walls and by colloidal particles caused much of the variation in $K_d(\text{Pu})$. Direct measurement of Pu adsorbed by the rock (rather than measured by the difference between influent and effluent activities) also failed to reduce the $K_d(\text{Pu})$ variability.

CONTENTS

ACKNOWLEDGMENT	iii
SUMMARY	v
INTRODUCTION	1
METHODS AND MATERIALS	2
RESULTS	5
CONCLUSIONS	13
REFERENCES	15
LIST OF CONTRIBUTORS	15
APPENDIX A - CONTROLLED SAMPLE PROGRAM	A-1

INTRODUCTION

Disposal of radioactive waste in deep geologic media has been proposed as a method that would isolate waste from the biosphere for long periods of time. This method is intended to allow radioactive decay to reduce the waste's radiotoxicity and to preclude contact between the biosphere and radioactive waste in amounts which could adversely affect humans or their environment. To analyze the effectiveness of deep geologic disposal, defensible safety assessments of geologic repository systems must be made that cover extended periods of geologic time. The Waste Isolation Safety Assessment Program (WISAP) has been established to develop capability for making these analyses. These analyses require data on the sorption-desorption behavior of radionuclides in geologic media. Reproducible, defensible data based on scientifically accepted methodologies must be obtained for input to the safety assessment models.

Presently, investigators determine sorption-desorption Kds, retardation factors, or radionuclide migration rates using a variety of experimental methods. Data currently being obtained are dependent on the methodology used, and the type of solution and geologic media studied. A controlled sample program was established under WISAP to resolve the differences found among methodologies and to determine which method or methods are most appropriate for providing accurate data on the migration of radionuclides in geologic media.

The objectives of the controlled sample program interlaboratory comparison were to: 1) ascertain whether different experimenters obtain the same results for the adsorption of Cs, Sr and Pu using common rocks, standard solutions and a prescribed method; and 2) compare the results obtained by individual laboratories using different experimental methodologies and resolve any differences found or determine what conversions can be made to compare results from one method with another.

METHODS AND MATERIALS

Large quantities of rocks were provided to all WISAP subcontractors involved in sorption-desorption data development and to the Atomic Energy of Canada Ltd. (AECL). The rock samples were analyzed at Pacific Northwest Laboratory (PNL)^(a) to characterize the mineralogy, the cation exchange capacity (CEC) and surface area. Mineralogy was determined by X-ray diffraction and microprobe analysis in conjunction with bulk chemical analysis. The characterizations of the two rock types used in this program, oolitic limestone and sentinel gap basalt, are given in Table 1.

TABLE 1. Characterization of Rocks Used in Controlled Sample Program

	<u>Oolitic Limestone</u>	<u>Sentinel Gap Basalt</u>
Cation Exchange Capacity (meq/100g $\pm$ s.d.)	42 $\pm$ 16	4.7 $\pm$ 0.2
Surface Area (m ² /g)		
BET	0.75	2.5
Ethylene Glycol	5.6 $\pm$ 1.7	10.3 $\pm$ 1.0
Mineralogy	Calcite 99%	Plagioclase
	Clays 1%	Ab ₅₅ -Ab ₄₀ 44%
		Pyroxenes 32%
		Groundmass 13%
		Metallic Oxides 6%
		Clays 5%

Recipes for solutions and instructions used in Objective 1 were prescribed for all participants (see Appendix A). A representative limestone solution and a representative basalt solution were used with the respective

(a) Operated by Battelle Memorial Institute

rocks. A brine recipe (WIPP Brine #B, slightly altered) was also used with both rock types. These synthetic groundwater compositions are given in Table 2. Four experiments were carried out by each participant:

- #1 - limestone with the limestone groundwater
- #2 - limestone with the brine solution
- #3 - basalt with the basalt groundwater
- #4 - basalt with the brine solution.

The Kds for Pu, Sr and Cs were to be determined in each of the four experiments by each of the laboratories.

TABLE 2. Controlled Sample Program Synthetic Groundwater Compositions

Groundwater Type	Cation	Concentration		Anion	Concentration	
		(mg/l)	(meq/l)		(mg/l)	(meq/l)
Limestone water pH 8.0 to 8.4	Ca ²⁺	50	2.50	HCO ₃ ⁻	153	2.51
	Mg ²⁺	3.6	0.30	SO ₄ ²⁻	14.4	0.30
	Na ⁺	2.3	0.10	Cl ⁻	3.5	0.10
	K ⁺	0.4	0.01			
Basalt water pH 7.7 to 8.2	Ca ²⁺	6.5	0.33	HCO ₃ ⁻	58	0.95
	Mg ²⁺	1.0	0.08	SO ₄ ²⁻	23	0.48
	Na ⁺	30.0	1.30	Cl ⁻	16	0.46
	K ⁺	9.0	0.23	F ⁻	0.7	0.04
WIPP Brine #B slightly altered pH 6.0 to 7.0	Ca ²⁺	900	45.00	HCO ₃ ⁻	10	0.16
	Mg ²⁺	10	0.82	SO ₄ ²⁻	4190	87.3
	Sr ²⁺	1.5	0.03	Cl ⁻	175,000	4936
	Na ⁺	115,000	5000	BO ₃ ³⁻	10	0.51
	K ⁺	15	0.38	Br ⁻	400	5.00
	Cs ⁺	1.0	0.01			

Before contact with the prepared rock, spiked groundwater (groundwater containing radionuclides) was equilibrated for at least three days with pH adjustment as needed and filtered through a 0.45 μm filter (or smaller). Blank containers (spiked groundwater without rocks) were required to correct nuclide activity caused by container wall adsorption of the tracers. The rocks were equilibrated with a cold (nonradioactive) wash of the appropriate groundwater solution for 48 hours and then separated by centrifugation. The cold wash was repeated and the spiked groundwater was contacted with the rock. After contact for seven days, the rocks and solutions were separated for determination of the tracer distribution between the solid and solution phases. The Kds were calculated using the following formula:

$$K_d = \frac{rA_i - A_e}{A_e} \frac{V}{W}$$

where

r = ratio of tracer solution to total solution

A_i = radionuclide activity in solution from the blank container (spiked influent groundwater without rocks)

A_e = radionuclide activity left in solution after contact with the geomedial for seven days (effluent)

V = total solution volume

W = mass of the geomedial used.

The K_d has dimensions of ml/g.

RESULTS

Results of Objective 1 (interlaboratory comparison) have been received from nine laboratories: Argonne National Laboratory (ANL), Atomic Energy of Canada Ltd. (AECL), Los Alamos Scientific Laboratory (LASL), Lawrence Berkeley Laboratory (LBL), Lawrence Livermore Laboratory (LLL), Oak Ridge National Laboratory (two groups, ORNL-I and ORNL-II), Pacific Northwest Laboratory (PNL), and Rockwell Hanford Operations (RHO).

After receiving the data, we discovered that several parameters had varied among laboratories, including: 1) the method for adding tracer radionuclides to groundwater solutions, 2) the solution to rock ratio, 3) the final tracer concentration in the influent solutions, 4) the final distribution of particle sizes used, 5) the solid-solution separation method, 6) sample containers used, and 7) temperature. Initially, parameters were thought to have had little influence on Kd values.

The addition of tracer to the groundwater solutions was accomplished by either evaporating an aliquot of radionuclide and adding synthetic groundwater solution or by adding the spike (from an acid stock solution) to the synthetic groundwater and adjusting the pH back to the initial value. The necessity for pH adjustment is essentially eliminated by adding the tracer in the evaporated form; this may prevent inadvertent precipitation of the tracer resulting from overcorrection of the pH to high values. On the other hand, effects on valence states, especially of Pu, caused by evaporation to dryness may complicate the interpretation of the data.

Possibly the solution to solid ratio affects the composition of the solution that results from weathering of the solid or the solid surface. The reported solution to solid ratios were 15:1 in all cases except the ratio of 20:1 for ^{137}Cs and ^{85}Sr adsorption experiments conducted at PNL.

The tracer concentrations that were reported by the different laboratories are shown in Table 3. Molar concentrations varied over several orders of magnitude for each nuclide used. The variations in observed Kds, however, do not correlate with influent radionuclide concentrations.

TABLE 3. Tracer Concentrations (Molar)

	Cs*	Sr*	Pu*
ANL (a)	$<6 \times 10^{-12}$	$<3 \times 10^{-13}$	$<3 \times 10^{-12}$
AECL (b)	$<2 \times 10^{-7}$	$<5 \times 10^{-6}$	$<1 \times 10^{-6}$
LASL	$<2 \times 10^{-7}$	$<2 \times 10^{-12}$	$<2 \times 10^{-13}$
LBL	$<5 \times 10^{-9}$	$<5 \times 10^{-8}$	$<2 \times 10^{-12}$
LLL	$<1 \times 10^{-7}$	$<1 \times 10^{-9}$	$<1 \times 10^{-11}$
ORNL-I	$<1 \times 10^{-6}$	$<1 \times 10^{-6}$	$<1 \times 10^{-6}$
PNL	$<3 \times 10^{-9}$	$<3 \times 10^{-13}$	$<3 \times 10^{-13}$

* ^{137}Cs , ^{85}Sr and ^{237}Pu used unless stated otherwise

(a) ^{134}Cs used instead of ^{137}Cs

(b) ^{90}Sr and ^{239}Pu used instead of ^{85}Sr and ^{237}Pu

The approximate particle size range of the rocks was determined at PNL by crushing and dry sieving before distribution to the participants. Fine particles, especially rock dust below the 20 to 50 mesh range, were probably present or produced during transport to the the other laboratories. ANL reported wet sieving the samples to eliminate rock dust prior to use for the adsorption experiments. No other laboratory reported pre-experimental cleanup of the rock samples. This uncertainty in particle size distribution may be another cause for Kd variations.

Three main methods were used to separate of solid and solution phases:

- 1) centrifugation to produce supernatant solution for direct counting;
- 2) centrifugation and filtration of supernatant before counting; and
- 3) centrifugation, direct counting of the activity adsorbed on the solid, and direct counting of the supernatant. These differences in separation techniques could affect resulting Kd values.

Variations in the final pH of the rock-groundwater systems ranged from 0.8 pH units for experiment #1 to 1.3 pH units in experiment #3 (shown in Table 4).

TABLE 4. Effluent pH Values

Lab	Isotope Used	Experiment			
		1	2	3	4
ANL	(Pu)	7.6	6.6	7.5	6.5
	(Pu,Cs)	7.9	6.5	7.8	6.7
	(Sr)	8.0	6.5	8.1	6.7
AECL	(Sr)	7.6	7.4	7.4	7.3
	(Cs)	7.8	7.4	7.4	7.3
	(Pu)	7.5	7.5	7.5	7.3
LASL	(Sr,Cs)	8.5	6.8	8.4	6.8
	(Pu)	8.1	6.6	8.0	6.7
ORNL-I	(Sr)	8.3	7.2	8.4	7.2
	(Cs)	8.2	7.2	8.3	7.2
	(Pu)	8.2	7.2	8.2	7.2
PNL	(Sr,Cs)	7.9	7.1	8.7	6.9
	(Pu)	7.9	7.2	8.6	7.2
Target pH*		8.0-8.4	6.0-7.0	7.7-8.2	6.0-7.0

1 = Limestone with limestone groundwater

2 = Limestone with brine

3 = Basalt with basalt groundwater

4 = Basalt with brine

* = pH range at the start of an experiment

The observed K_d values for cesium, strontium and plutonium are given in Tables 5, 6 and 7, respectively. Absorption of cesium (Table 5) by limestone in the presence of synthetic limestone groundwater (experiment #1) was surprisingly varied with K_d values ranging over nearly three orders of magnitude. The distribution of K_d appeared to be lognormal, which may indicate that the K_d is a logarithmic function of some variable not recorded in this study. From the reported data, changes in pH and tracer concentration do not appear to correlate with the K_d variation.

TABLE 5. Kd Values for Cs (ml/g $\pm$ s.d.)

Lab	Experiment			
	1	2	3	4
ANL ^(a)	65 $\pm$ 2	.14 $\pm$.01	401 $\pm$ 21	1.48 $\pm$.05
AECL ^(e)	1.3 $\pm$.4	.2 $\pm$.4 ^(f)	31 $\pm$ 2	1.4 $\pm$.4
LASL ^(b)	88 $\pm$ 1	-.12 $\pm$.12 ^(f)	265 $\pm$ 4	.6 $\pm$.2
LBL ^(e)	49 $\pm$ 5	.16 $\pm$.9	296 $\pm$ 10	1.52 $\pm$.04
LLL ^(a)	60 $\pm$ 30	.5 $\pm$.5 ^(f)	290 $\pm$ 70	1.6 $\pm$.1
ORNL-I ^(e)	227 $\pm$ 14	.6 $\pm$.3	380 $\pm$ 5	2.2 $\pm$.2
ORNL-II ^(c)	663 $\pm$ 61	.1 $\pm$.3 ^(f)	453 $\pm$ 12	1.79 $\pm$.01
PNL ^(d)	880 $\pm$ 160	3.3 $\pm$.1	380 $\pm$ 70	4.6 $\pm$.3
RHO ^(e)	6.8 $\pm$.6	.04 $\pm$.03 ^(f)	255 $\pm$ 7	.95 $\pm$.13

(a) effluent was filtered

(b) effluent centrifuged at 16,000 rpm for 1 hr, decanted and repeated 3 times

(c) time of solution-rock contact was 700 hr

(d) effluent centrifuged for 20 min. at 7000 rpm

(e) effluent was obtained by centrifugation and the blank correction used

(f) not significantly different from zero

The Kd values for Cs, or Kd(Cs), in the remaining experiments, (#2, 3 and 4), appeared more normally distributed about the mean Kd values. Tracer concentrations and measured final pH values had no apparent influence on Kd(Cs) in any of the controlled sample experiments.

Strontium adsorption was generally found to increase with an increase in pH. Observed Kds in the limestone-limestone groundwater system (experiment #1) were not normally distributed. Instead, the Kds were apparently distributed exponentially with four less than 3 ml/g, two between 3 and 6 ml/g and the remaining three greater than 9 ml/g. Experiment #1 was the only system in which Kd(Sr) did not appear to increase with an increase in pH.

TABLE 6. Kd Values for Sr (ml/g $\pm$ s.d.)

Lab	Experiment			
	1	2	3	4
ANL (a)	5.4 $\pm$ 0.3	0.18 $\pm$ 0.01	68 $\pm$ 17	.05 $\pm$ 0.005
AECL	1.8 $\pm$ 0.5	4.2 $\pm$ 1.6	41 $\pm$ 6	2.9 $\pm$ 0.4
LASL (b)	1.4 $\pm$ 0.2	0.1 $\pm$ 0.2	81 $\pm$ 1	0.2 $\pm$ 0.2
LBL	2.4 $\pm$ 0.1	0.1 $\pm$ 0.1	55 $\pm$ 2	0.1 $\pm$ 0.1
LLL (a)	2.7 $\pm$ 0.5	0.9 $\pm$ 0.4	45 $\pm$ 1	0.0
ORNL-I	5.9 $\pm$ 0.2	1.0 $\pm$ 0.1	89 $\pm$ 5	0.7 $\pm$ 0.3
ORNL-II (c)	9.3 $\pm$ 2.4	0.9 $\pm$ 0.1	93 $\pm$ 6	0.4 $\pm$ 0.1
PNL	14.9 $\pm$ 4.6	3.4 $\pm$ 0.3	92 $\pm$ 3	3.6 $\pm$ 0.8
RHO	13.4 $\pm$ 0.6	8.0 $\pm$ 1.2	73 $\pm$ 4	0.23 $\pm$ 0.02

(a) effluents were filtered

(b) effluent centrifuged for 1 hr at 16,000 rpm, decanted and repeated 3 times

(c) time of solution-rock contact was 7,000 hr

Results for Kd(Cs) and Kd(Sr) varied much more in the limestone-limestone groundwater system than in any of the other experiments. In general, Kd(Cs) and Kd(Sr) varied only by a factor of two in the basalt-basalt groundwater system. In the presence of the WIPP Brine, both Kd(Cs) and Kd(Sr) were reduced to low values. Tracer concentrations for Sr and Cs were not found to affect observed Kds in the controlled sample program.

Consistently high Sr and Cs Kds were observed by PNL. The only difference in procedure reported by PNL was the 20:1 solution to solid ratio used instead of 15:1 as reported by all other laboratories. The temperature at PNL ($27 \pm 2^\circ\text{C}$) may have been higher than at the other laboratories, but no other temperatures were reported. The Kd values obtained at PNL, however, are consistent with other Cs and Sr adsorption data obtained under the WISAP program at PNL⁽²⁾.

Effects of solid to solution ratios on strontium Kds are discussed by Routson and Serne.⁽³⁾ Limited amounts of Ca^{2+} were available for dissolution in the soils used in their work. Increasing the solution to solid ratio resulted in a more dilute solution with a lower Ca^{2+} concentration, which increased $\text{Kd}(\text{Sr})$. It is not likely that Ca^{2+} availability was limited in the limestone, however.

Co-precipitation or occlusion of nuclides (Cs and Sr) with monolayers of CaCO_3 , which may have formed on crushed limestone surfaces might account for some of the variability in $\text{Kd}(\text{Cs})$ for the controlled sample program. As temperature was not controlled, the solutions may have been near saturation with respect to CaCO_3 and slight changes in the temperature could have caused a monolayer of precipitate to form or dissolve, scavenging or releasing nuclides. This process could lead to large variability in Kd determinations and could explain the larger than expected variations.

Very little adsorption by container walls was found for Cs and Sr as expected. Filtering Cs and Sr effluent by ANL and LLL and supercentrifuging by LASL in conjunction with direct determination of adsorbed activity did not increase the observed Kds compared to the more slowly centrifuged, unfiltered, blank corrected Kd values observed.

Controlled sample adsorption Kds for plutonium are given in Table 7. Line plots of the reported Kds are shown in Figure 1. Filtered effluent blank corrected Kd values are generally larger than the corresponding values obtained with unfiltered effluent. Kds determined by direct measurement of adsorbed activity were either larger than or no different statistically from the blank corrected Kd value obtained by the same experimental group doing both determinations. Direct measurements did not solve all problems, since at least one of the three Kd determinations by direct measurement of adsorbed activity was always an order of magnitude different from the other two values found. Reported plutonium tracer concentration and solution pH had no apparent affect on observed Kds, but the high variability in Kd might have masked this or any other functional dependency.

TABLE 7. Kd Values for Pu (ml/g $\pm$ s.d.)

Lab	Experiment			
	1	2	3	4
AECL (a)	547 $\pm$ 356	69 $\pm$ 14	1000 $\pm$ 590	221 $\pm$ 140
LASL (b)*	4745 $\pm$ 4931	96 $\pm$ 63	1078 $\pm$ 716	294 $\pm$ 80
LASL (c)	32000 $\pm$ 11000	3709 $\pm$ 2114	13000 $\pm$ 8000	12000 $\pm$ 3000
LBL (a)*	242 $\pm$ 41	2.6 $\pm$ 2.4	30 $\pm$ 26	271 $\pm$ 156
LBL (c)	1009 $\pm$ 162	130 $\pm$ 16	221 $\pm$ 147	2473 $\pm$ 1506
PNL (a)	690 $\pm$ 320	150 $\pm$ 20	15 $\pm$ 2	220 $\pm$ 30
RHO (a)	2616 $\pm$ 1135	235 $\pm$ 25	89 $\pm$ 17	73 $\pm$ 20

ANL (d)*	1027 $\pm$ 41	1283 $\pm$ 89	8.8 $\pm$ 3.4	1304 $\pm$ 222
LLL (d)	770 $\pm$ 36	450 $\pm$ 90	580 $\pm$ 12	1260 $\pm$ 504
ORNL-I (d)	198 $\pm$ 50	280 $\pm$ 21	592 $\pm$ 134	2056 $\pm$ 1405
ORNL-II (d,e)	63000 $\pm$ 19000	1146 $\pm$ 137	312 $\pm$ 66	37000 $\pm$ 41000
PNL (d)	1090 $\pm$ 120	260 $\pm$ 20	200 $\pm$ 170	430 $\pm$ 60

ANL (f)	2134 $\pm$ 77	1457 $\pm$ 75	67 $\pm$ 14	1280 $\pm$ 188
ANL (f) (Pu with Cs)	285 $\pm$ 75	160 $\pm$ 10	32 $\pm$ 4	234 $\pm$ 93
LASL (b,f)	3198 $\pm$ 512	139 $\pm$ 31	843 $\pm$ 658	256 $\pm$ 19

* some values recalculated by PNL using data supplied by subcontractors

(a) unfiltered effluent, Kd calculated with blank correction

(b) unfiltered effluent centrifuged at 16,000 rpm for 1 hr, decanted, repeated 3 times blank corrected

(c) unfiltered effluent, Kd calculated with original influent

(d) filtered effluent, Kd calculated with blank correction

(e) contact time 700 hr

(f) activity sorbed by rock measured directly

FIGURE 1. Measured K_d (Pu) Values Observed in the Controlled Sample Program.

Two problems are readily apparent: 1) adsorption of Pu on colloidal particles (or formation of Pu colloids) in solution and 2) adsorption of Pu by container walls. Small particles may be essentially eliminated from the effluent by filtration, but Pu adsorption on the filter may then become a problem. Several labs reported that a sizable fraction of the Pu in the influent solution (up to 95%) was removed by filtration before it came into contact with rocks. Adsorption of up to 90% of the added Pu by container walls was also reported for prefiltered influent solutions. Greater adsorption of Pu by container walls was reported by ANL and LBL in blank containers than in containers with crushed rock material. The ANL data from experiments 1 and 3 show this effect. Adsorption of Pu by container walls in a blank corrected experiment lowers the apparent influent tracer concentration, giving a lower K_d than that obtained by direct measurement of the activity adsorbed on the solid and in the effluent. There was no difference (at a 95% confidence level) detected at ANL between blank corrected and directly measured K_d s for Pu in either of the brine experiments. No significant differences were observed at LASL between direct measurement of the K_d and blank corrected K_d for the same system. (The blank corrected value shown for LASL was calculated at PNL using additional data supplied by Dr. Bruce Erdal.)

There were insufficient data to determine whether or not the method with which a tracer was added to synthetic groundwater solutions had any affect on the resulting K_d s.

CONCLUSIONS

The controlled sample program to date has identified differences of two to three orders-of-magnitude in certain experimental K_d values. It was anticipated that close agreement could be found for Cs and Sr adsorption results and that Pu would possibly behave erratically.

There was some agreement of $K_d(\text{Cs})$ and $K_d(\text{Sr})$ on both rocks in the brine. Adsorption results for both Cs and Sr in the dilute basalt and limestone groundwaters were more widely scattered than anticipated. $K_d(\text{Sr})$ values generally appeared to depend on the final solution pH but not on the tracer

concentration. $K_d(\text{Cs})$ values did not appear to be dependent on either final pH or tracer concentration. The reported data are insufficient to determine why $K_d(\text{Cs})$ had a range of three orders of magnitude in the limestone-limestone groundwater system.

Batch adsorption determinations of $K_d(\text{Pu})$ were not satisfactory because of adsorption of Pu on container walls, formation of, or adsorption on, filterable particles, as well as other variables (e.g., pH, Pu concentration, spiking method) whose effects were masked by adsorption effects. Direct determination of Pu adsorbed by the rock and Pu in effluent solution also failed to reduce the variability in $K_d(\text{Pu})$ in a prescribed rock-solution system.

The controlled sample program points out the need for a more in-depth study of the factors controlling sorption-desorption reactions of radionuclides in geologic media. The distribution of a radionuclide between solid and solution phase has little meaning without detailed information that characterizes the radionuclide, the solution, and the geologic media of the system investigated. More specifically, information concerning the radionuclide chemistry in groundwater type solutions, mineral and precipitate formation and dissolution, adsorption and desorption mechanisms, and the equilibrium between groundwaters and geologic media is needed to predict concentrations of radionuclides in solution that are involved in transport processes.

Continuing studies, to explain and hopefully remove the larger than expected K_d variability, will be formulated. At present, safety assessments should consider the fact that confidence intervals for K_d values reported for rocks may be as large as two or three orders of magnitude for selected nuclide-groundwater-rock systems.

REFERENCES

1. Ames, L. L., Controlled Sample Program Publication No. 1, Characterization of Rock Samples, PNL-2797, 1978.
2. Relyea, J. F., L. L. Ames, R. J. Serne, R. W. Fulton and C. D. Washburne, Batch Kd Experiments with Common Minerals and Representative Groundwaters; in, Waste Isolation Safety Assessment Program, Task 4 Contractor Information Meeting Proceedings, PNL-SA-7352, 1979.
3. Routson, R. C. and R. J. Serne, Experimental Studies for the Percol and Transport Models, BNWL-1719, 1972.

LIST OF CONTRIBUTORS

<u>AECL</u>	T. T. Vandergraaf
<u>ANL</u>	P. Rickert, M. G. Seitz, S. Fried, A. M. Friedman and M. Steindler
<u>LASL</u>	B. R. Erdal, P. Q. Oliver, R. D. Aquilar and Francine Lawrence
<u>LBL</u>	R. J. Silva and Larry Benson
<u>LLL</u>	D. G. Coles, J. Tewhey, and D. Isherwood
<u>ORNL-I</u>	Phyllis Rafferty and R. E. Meyer
<u>ORNL-II</u>	C. W. Francis and E. A. Bondietti
<u>RHO</u>	G. S. Barney
<u>PNL</u>	R. W. Fulton, C. D. Washburne and J. F. Relyea

APPENDIX A

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 among the various labs and among different experimental techniques. The main objectives are: 1) to ascertain whether different experimenters obtain comparable results using common rocks, standard solutions and a specified experimental design and 2) to ascertain the comparability of results obtained by individual laboratories using different experimental methodologies. In Objective 2 studies, we will investigate K_d value or nuclide migration dependencies on experimental methodologies, intending to formulate a standard K_d method or to derive calibration numbers to convert K_d numbers from one method to K_d values from another method.

Ancillary 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 μm) was selected. The dry sieved material was well mixed manually, and 1 gallon containers were filled. We realize that during crushing metallic impurities may have been added and that the resultant crushed rock may have acquired some artificial sorption qualities compared to the virgin rock. Neither of these potential problems will affect the main objectives of the controlled sample program.

Each laboratory received 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.

The rock samples were characterized by PNL as follows:

- Bulk Chemical Analysis
- Mineralogy by X-ray Diffraction and Microprobe
- Cation Exchange Capacity
- Surface Area: Ethylene Glycol
BET

Results were supplied to all participants.

OBJECTIVE 1: INTERLABORATORY COMPARISON

All laboratories were directed to perform the following batch Kd experiments:

EXP #1

Geologic Material: Limestone

Groundwater:

	mg/l	PNL Recipe
Ca ⁺²	50.	Ca(OH) ₂ 92.5
Mg ⁺²	3.6	MgSO ₄ 18
Na ⁺	2.3	NaCl 5.8
K ⁺	.4	KCl .8
HCO ₃ ⁻	153	SPARGE with CO ₂ 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 N ₂ gas to get back to pH 8.2. Allow pH to equilibrate overnight so excess CO ₂ and N ₂ can diffuse out. Measure HCO ₃ alkalinity and report.
SO ₄ ⁻²	14.4	
Cl ⁻	3.5	
pH 8.2 ± .2		

Eh: Atmospheric O₂ equilibrated

Solid/solution: 1 g/15 mls

Nuclides: Sr

Cs

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

Replicates: minimum of 3 replicates

EXP #2

Geologic Material: Limestone

Groundwater: WIPP Brine #B (slightly altered)

	<u>mg/l</u>	<u>PNL Recipe</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	40 mg/l
SO ₄ ⁻²	3,500	CaCl ₂ •2H ₂ O	3.3 g/l
BO ₃ ⁻³	10	SrCl ₂ •2H ₂ O	3.3 mg/l
HCO ₃ ⁻	10	CsCl	1.3 mg/l
Br ⁻	400		

pH: 6.5 ± .5

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

Solid/solution: 1 g/15 mls

Nuclides: Sr

Cs

Pu

(same as EXP #1)

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

EXP #3

Geologic Material: Basalt

Groundwater:	<u>mg/l</u>		PNL Recipe
Na ⁺	30	NaHCO ₃	.95 meq/l 79.8 mg/l
K ⁺	9	Na ₂ SO ₄	.35 meq/l 24.85 mg/l
Ca ⁺²	6.5	MgSO ₄	.08 meq/l 4.81 mg/l
Mg ⁺²	1.0	CaSO ₄	.07 meq/l 4.76 mg/l
HCO ₃ ⁻	58	CaCl ₂	.26 meq/l 14.42 mg/l
SO ₄ ⁻²	23	KCl	.20 meq/l 14.91 mg/l
Cl ⁻	16	KF	.04 meq/l 2.32 mg/l
F ⁻	0.7		

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, PNL will concoct an appropriate groundwater.

PROCEDURE

Make up aliquots of spike solutions (groundwater + nuclides), adjust pH to desired value. Equilibrate for at least 3 days. Check pH daily and adjust. Filter solutions through 0.45 μm 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 (groundwater 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 TWO

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 the 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.

BATCH Kd CALCULATIONS

Tare weights are determined on 250 ml polycarbonate screw cap centrifuge bottles. Well-mixed soils (5 to 10 g) 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:

$$K_d = \frac{rA_i - A_e}{A_e} \frac{V}{W}$$

where

V = total volume of solution in last treatment (50 ml + X residual
mls)
W = total mass of soil present (g)
r = ratio of tracer solution to total solution (50/50 + X)
A_i = activity of trace constituent in influent solution
A_e = activity of trace constituent in effluent solution

DISTRIBUTION LIST

No. of
Copies

No. of
Copies

OFFSITE

A. A. Churm
DOE Patent Division
9800 South Cass Avenue
Argonne, IL 60439

27 DOE Technical Information
Center

2 Argonne National Laboratory
Reference Library
9800 South Cass Avenue
Argonne, IL 60439

Battelle Memorial Institute
Office of Nuclear Waste
Isolation
Attn: Beverly Rawles
505 King Avenue
Columbus, OH 43201

2 Brookhaven National Laboratory
Reference Section
Information Division
Upton, Long Island, NY 11973

20 Wayne A. Carbiener
Office of Nuclear Waste
Isolation
Battelle Memorial Institute
505 King Avenue
Columbus, OH 43201

Carl R. Cooley
DOE Office of Waste Management
Washington, DC 20545

Jared Davis
27 Nuclear Regulatory
Commission
Washington, DC 20555

Environmental Protection Agency
Office of Radiation Programs
Technical Assessment Division
AW559
Washington, DC 20460

Colin A. Heath
DOE Division of Waste Management
Washington, DC 20545

William M. Hewitt
Office of Nuclear Waste
Isolation
Battelle Memorial Institute
505 King Avenue
Columbus, OH 43201

Muzaffer Kehnemuyi
Office of Nuclear Waste
Isolation
Battelle Memorial Institute
505 King Avenue
Columbus, OH 43201

John F. Kircher
Office of Nuclear Waste
Isolation
Battelle Memorial Institute
505 King Avenue
Columbus, OH 43201

2 Lawrence Berkeley Laboratory
Reference Library
University of California
Berkeley, CA 94720

No. of
Copies

- 2 Lawrence Livermore Laboratory
Reference Library
P.O. Box 808
Livermore, CA 94550
- 2 Los Alamos Scientific Laboratory
Reference Library
P.O. Box 1663
Los Alamos, NM 87544
- John T. McGinnis
Office of Nuclear Waste
Isolation
Battelle Memorial Institute
505 King Avenue
Columbus, OH 43201
- 2 Savannah River Laboratory
Reference Library
Aiken, SC 29801
- Sheldon Meyers
DOE Office of Nuclear Waste
Management
Washington, DC 20545
- 2 Barry Naft
NUS Corporation
4 Research Place
Rockville, MD 20805
- J. O. Neff
Department of Energy
Columbus Program Office
505 King Avenue
Columbus, OH 43201
- 2 Neil A. Norman
Environmental Sciences
Department
Bechtel National Inc.
P.O. Box 3965
San Francisco, CA 94105

No. of
Copies

- 2 Oak Ridge National Laboratory
Central Research Library
Document Reference Section
Oak Ridge, TN 37830
- Howard P. Stephens
Sandia Laboratories
P.O. Box 5800
Albuquerque, NM 87115
- David B. Stewart
U.S. Geological Survey
National Center 959
Reston, VA 22092
- B. Allard
Transuranium Research Laboratory
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37830
- Gary W. Beall
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37830
- Larry Benson
Lawrence Berkeley Laboratory
1 Cyclotron Road
Bldg 70A/1160
Berkeley, CA 94720
- Ernest Bondietti
Oak Ridge National Laboratory
Bldg 3504
P.O. Box X
Oak Ridge, TN 37830
- H. Clyde Clairborne
Oak Ridge National Laboratory
Bldg 3017
P.O. Box X
Oak Ridge, TN 37830

No. of
Copies

Edward Norris
Los Alamos Scientific Laboratory
P.O. Box 1663
Los Alamos, NM 87545

Paul Rickert
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Barry E. Scheetz
Penn State University
Materials Research Laboratory
Room 223
University Park, PA 16802

Martin Seitz
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439

John Shade
University of Toledo
Toledo, OH 43606

Victor Swan
Washington State University
Geology Department
Pullman, WA 99163

John Tewhey
Lawrence Berkeley Laboratory
L-205
P.O. Box 808
Livermore, CA 94550

Rosemary Vidale
Los Alamos Scientific Laboratory
P.O. Box 1663
Los Alamos, NM 87545

Barry G. Wahlig
School of Nuclear Engineering
Georgia Institute of Technology
Atlanta, GA 30332

No. of
Copies

Robert L. Watters
DOE Division of Biomedical and
Environmental Research
Washington, DC 20545

Allen Weiss
Brookhaven National Laboratory
Bldg 830
Upton, L.I., NY 11973

FOREIGN

Bundesministerium fur Forschung
und Technologie
Stressemannstrasse 2
D-5300 Bonn
F.R. of GERMANY

Ferruccio Gera
Radiation Protection and
Waste Management Division
Nuclear Energy Agency/OECD
38 boulevard Suchet
75016 Paris
FRANCE

2 INIS Clearinghouse
International Atomic Energy
Agency
P.O. Box 590
A-1011, Vienna
AUSTRIA

Library
Studsvik Energiteknik AB
S-611 01 Nykoping
SWEDEN

F. P. Sargent
Atomic Energy of Canada Limited
Whiteshell Nuclear Research
Establishment
Pinawa, Manitoba
Canada ROE 1LQ

No. of
Copies

Jess M. Cleveland
Chief, Transuranium Research
Project
USGS
Water Resources Division
Box 25046
Denver Federal Center
Lakewood, CO 80225

David G. Coles
Lawrence Livermore Laboratory
University of California
P.O. Box 808
Livermore, CA 94550

George A. Cowan
Los Alamos Scientific Laboratory
P.O. Box 1163
Los Alamos, NM 87545

Robert G. Dosch
Sandia Laboratories
P.O. Box 5800
Albuquerque, NM 87115

Geoffrey Eichholz
Regent's Professor of Nuclear
Engineering
School of Nuclear Engineering
Georgia Institute of Technology
Atlanta, GA 30332

Bruce R. Erdal
Los Alamos Scientific Laboratory
CNC-11, MS-514
Los Alamos, NM 87545

Chet W. Francis
Oak Ridge National Laboratory
Bldg 2001
P.O. Box X
Oak Ridge, TN 37830

Sherman Fried
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439

No. of
Copies

Dana Isherwood
Lawrence Livermore Laboratory
MS L-224
P.O. Box 808
Livermore, CA 94550

George Al. Kolstad
DOE Division of Energy Research
Washington, DC 20545

Kurt Draus
110 Ogontz Lane
Oak Ridge, TN 37830

Harry Landon
NRC, Research Division
Washington, DC 20555

Paul W. Levy
Brookhaven National Laboratory
Physics Department
Upton, L.I., NY 11973

Stan E. Logan
Nuclear Waste Management Program
Los Alamos Technical Associates,
Inc.
P.O. Box 410
Los Alamos, NM 87554

I. Wendell Marine
E. I. du Pont de Nemours Co.
Savannah river Laboratory
Aiken, SC 29081

Robert E. Meyer
Oak Ridge National Laboratory
P.O. Box X
Oak ridge, TN 37830

Anthony Mucciardi
Adaptronics, Inc.
Westgate Research Park
7700 Old Springhouse Road
McLean, VA 22101

No. of
Copies

Egbert Schapermeier
Battelle-Institute e.V.
Am Romerhof 35
D-6000 Frankfurt am Main 90
F.R. of GERMANY

Dr. Les Dole
c/o Dr. Klaus Kuhn
Institut fur Tiefiagerung
Wissenschaftliche Abteilung
Berliner Strasse 2
D-3392 Clausthal - Zellerfeld
West Germany (FRG)

Robert Gillham
Department of Earth Sciences
University of Waterloo
Waterloo, Ontario
CANADA

David Grey
Institute of Geologic Sciences
Exhibition Road
S. Kensington
London, SW7-2DE
UNITED KINGDOM

Alex T. Jakubick
Nuclear Research Center
7500 Karlsruhe
P.O. 3640
FEDERAL REPUBLIC OF GERMANY

Tjalle Vandergraff
Atomic Energy of Canada Limited
Whiteshell Nuclear Research
Establishment
Pinawa, Manitoba
CANADA ROE 1LO

ONSITE

6 DOE Richland Operations Office

O. J. Elgert
R. B. Goranson
H. E. Ransom
J. J. Schreiber
D. J. Squires
F. R. Standerfer

No. of
Copies

8 Rockwell Hanford Operations

R. C. Arnett
G. S. Barney
R. A. Deju
M. R. Fox
G. S. Hunt
M. J. Smith
W. W. Schulz
Rockwell Document Control

60 Pacific Northwest Laboratory

L. L. Ames
G. L. Benson
A. Brandstetter (10)
D. B. Cearlock
D. J. Bradley
M. A. Harwell
B. W. Howes
M. R. Kreiter
A. M. Platt
D. Rai
J. R. Raymond
J. F. Relyea (5)
R. J. Serne
R. G. Strickert
R. P. Turcotte
Technical Information Library
(5)
Publishing Coordination (2)
Water and Land Resources
Department Library (25)
RO