**Batch Kd Measurements of
Nuclides to Estimate Migration
Potential at the Proposed
Waste Isolation Pilot Plant
in New Mexico**

October 7, 1977

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BATCH Kd MEASUREMENTS OF NUCLIDES TO ESTIMATE
MIGRATION POTENTIAL AT THE PROPOSED WASTE
ISOLATION PILOT PLANT IN NEW MEXICO

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ABSTRACT

Laboratory measurements to determine the sorption distribution coefficients, K_d , of radionuclides present in, and potentially leached from radioactive wastes, in contact with representative geologic media have been conducted. The nuclides studied include Cs, Sr, Tc, Ru, Sb, Ce, Eu, Pu, Np, Cm, Am, U, and Pa. The crushed rock materials used were from the vicinity of the Waste Isolation Pilot Plant, a project to isolate radioactive wastes in a bedded salt facility, near Carlsbad, New Mexico. Solutions used consist of salt brine and groundwater, specific to the WIPP site, plus distilled water, for laboratory intercomparisons. The batch K_d data reported herein, plus data from sorption and migration measurements being conducted or planned elsewhere, will be used to evaluate the potential for radionuclide migration from the bedded salt WIPP facility. The data can be used for transport modeling and for safety assessment determinations.

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BATCH Kd MEASUREMENTS OF NUCLIDES TO ESTIMATE
MIGRATION POTENTIAL AT THE PROPOSED WASTE
ISOLATION PILOT PLANT IN NEW MEXICO

INTRODUCTION

In order to evaluate the potential for radionuclide migration from a radioactive waste isolation facility, and the consequences of such migration, many parameters must be evaluated. Important parameters include chemical and physical waste form, amount of nuclear waste present, solubility or leachability of the waste matrix, geologic stability and hydrologic regimes in the repository and adjacent horizons, potential for geochemical interactions (sorption-desorption) and transport time to the biosphere. The purpose of this study is to measure the geochemical interactions (sorption-desorption) of water borne nuclides in contact with various geologic materials. From knowledge of this waste-geologic media interaction and other mentioned parameters, preliminary evaluations of the potential for nuclide migration to the biosphere can be made.

A common parameter used to quantify the nuclide-geologic media sorption-desorption reactions is the distribution coefficient, Kd. The Kd for a nuclide is defined as the ratio of activity sorbed onto the solid (geologic) matrix divided by the activity remaining in the fluid phase:

$$K_d = \frac{\text{Activity on Solid}}{\text{Activity in Solution}}$$

The Kd value has units of ml/g or ml/m² depending upon whether one is assuming chemical interactions throughout a porous geologic structure or flow through cracks or fissures with chemical interactions occurring only on the exposed surfaces. The conversion between a Kd for porous and fracture flow cases is theoretically possible with knowledge of the surface area to volume ratio of fissures present of the geologic material.

Waste-rock interactions almost exclusively retard the movement of nuclides relative to the movement of the carrier water. In the specific case that the K_d is not a function of nuclide concentration (i.e., the sorption isotherms of the trace nuclide are linear) or time (equilibrium prevails at all points and all times), the retardation factor, R , is related to the K_d by the following equations (1, 2):

Porous Flow Case

$$R = \frac{V_{\text{Fluid}}}{V_{\text{Nuclide}}} = 1 + \frac{\rho_b}{\theta} K_d$$

where R = retardation factor

V_{Nuclide} = velocity of nuclide

V_{Fluid} = velocity of carrier solution

ρ_b = bulk density of porous media (g/cm^3)

θ = fractional porosity of porous media

K_d = distribution coefficient ($\text{ml/g} - \text{cm}^3/\text{g}$)

Fracture Flow Case

$$R = \frac{V_{\text{Water}}}{V_{\text{Nuclide}}} = 1 + \frac{SA}{L_v} K_d$$

where SA = surface area of fracture (m^2)

L_v = volume of liquid in fracture (ml)

K_d = distribution coefficient (ml/m^2)

The mathematical treatment of the coupled water transport-nuclide sorption has taken two paths. The simpler approach assumes that the porosity remains constant, the K_d remains a constant and the water velocity remains constant. With these further restrictions an exact or analytical solution is possible^(1, 2). The other approach uses numerical techniques to approximate the solution of the coupled water-sorption equations without requiring the additional assumptions^(3, 4).

Therefore, if one can evaluate the hydrologic regimes of interest, the migration of nuclides can be estimated from measurement of K_d 's and calculation of the appropriate retardation factor.

The staff at Battelle Pacific Northwest Lab was presented a subcontract from Sandia Laboratories to make preliminary Kd measurements on long lived actinide and fission product nuclides in ground waters contacting representative rock types from a potential radioactive waste disposal facility located near Carlsbad, New Mexico. Sandia Laboratories is managing this program for ERDA. It is entitled the Waste Isolation Pilot Plant (WIPP). The objective of this program is to evaluate the scientific and engineering feasibility of operating a facility for the long-term isolation of radioactive wastes in a deep geologic salt bed. Assuming a favorable thorough evaluation, this "pilot plant" facility will be converted to a terminal repository, primarily for ERDA defense related wastes. The batch Kd results reported herein will be used in part to evaluate the potential for radionuclide migration from the WIPP facility, for transport modeling, and for safety assessment determinations.

MATERIALS AND METHODS

GEOLOGIC MEDIA CHARACTERIZATION

Seven core samples of salt and rocks, including samples from geologic horizons above and below the proposed repository were obtained. The major crystalline constituents were determined by x-ray diffraction techniques. Results are given in Table 1.

Table 1. Mineral Identification

<u>Sample</u>	<u>Major Minerals</u>
Culebra-853'	Dolomite (Ca, Mg carbonate); very minor quartz (SiO_2) and calcite (CaCO_3)
Magenta-734'	Dolomite (Ca, Mg carbonate); minor quartz and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
#1 Cherry Canyon	Limestone (CaCO_3)
#2 Cherry Canyon	Arkosic sandstone (feldspar bearing) with calcic cement
#3 Cherry Canyon	Arkosic sandstone (feldspar bearing) with siliceous cement
Salt Core-2726'	NaCl (~99%), less than 1% by weight of the clays montmorillonite, illite, chlorite, possibly some magnesite and gypsum
Salt Core-2150'	NaCl (~90+%), montmorillonite, chlorite kaolinite, illite, magnesite

The five nonsalt samples were also studied using optical microscopy techniques from which pore sizes and configurations can be determined. A rough estimate of porosity can also be performed by simple area calculations. The porosity and average pore sizes were determined by measurement of black regions of the optical photographs which represent the void spaces. Optical photographs of the cores are shown in Figures A-1 to A-24 in Appendix A.

The Culebra and Magenta samples are part of the Salado formation, a now dry but potential aquifer region overlying (by many hundreds of feet) the salt bed where wastes are to be deposited. Samples #1, #2, and #3 Cherry Canyon represent a potential aquifer region over a thousand feet below the waste storage horizon. These samples were obtained from outcroppings, not from actual corings at the WIPP site. The salt core at 2726' down (from the surface) is from the WIPP horizon where intermediate-level wastes and high-level waste experiments will be placed. The salt core at 2150' down is from the WIPP horizon where low-level transuranic waste will be stored.

Portions of the core samples of the five nonsalt rocks were crushed in a ball mill to provide material for batch Kd determinations. The size fraction 44-149 μ m was separated and used for subsequent experimentation.

Surface areas of the crushed rocks, within the particle range 44-149 μ m, were determined by the ethylene glycol method.⁽⁵⁾

Carrier Solution Compositions

Per initial Sandia suggestions, August 11, 1976 (see Appendix B), two salt brines were prepared. These brines were to simulate realistic geologic solutions which could potentially intrude into the waste repository, leach the wastes contained therein, and then serve as a transport medium for radionuclides to escape from the repository. Brine "XA" is representative of concentrated brines originating in the overlying Salado region, and which may intrude into the repository from above. Brine "XB" is a hypothetical Castile region brine which might intrude upon the repository from below. The chemical compositions for brines "XA" and "XB" are in Appendix B. These compositions had been based on commercial laboratory analyses of similar brines found near the WIPP site. It was later found, however, that these analyses, obtained from a commercial laboratory, were in error, particularly for the sodium ion.

The Brine "XA" recipe appeared to be supersaturated and would not totally dissolve. Several days of heating and stirring did not help. The supernatant solution was filtered through .45 μ m filters and adjusted to

pH 6.5. (Major cations were determined so that the actual concentrations could be determined.) The Brine "XB" recipe would not support a 50 ppm Fe^{+3} and also necessitated filtration through .45 μm filters before final pH adjustment.

For the first series of experiments, distilled water was used as a carrier solution, primarily for laboratory expediency and for interlaboratory comparisons of results. Upon contact with the rocks a finite amount of material was expected to dissolve into the distilled water. As the Kd for each nuclide is dependent on the solution composition after contact with the rock, the total amount of rock material which could dissolve in the distilled water was determined by contacting 1 gram dry weight of crushed rock with 30 mls of distilled water. This solid to solution ratio was used in all batch Kd experiments. The equilibration process was performed for 47 days. The concentration of major cations found in the effluents and percentage weight loss in the rocks were calculated from atomic absorption and weighing procedures, respectively.

The brine solutions "XA" and "XB" were modified midway through this experimental study by mutual agreement. This eliminated the error in the initial analyses that these solutions were based on, and simplified preparation of the carrier solutions. The new solutions, brine "A", brine "B", and groundwater "C" are described (ionic composition and formulations for preparation) in the October 8, 1976 Sandia letter found in Appendix B. New brine "B" is the resultant solution occurring when water dissolves rock salt originating in the ILW-HLW horizon of the WIPP facility. It was originally prepared (at Sandia Laboratories) by preparing a saturated mixture of salt core (~99% pure NaCl) and water, heating, stirring, then filtering the solution and analyzing. Brine "B" prepared this way is not 100% theoretically saturated. The new brine "A" is again a Salado region brine. Solution "C" is representative of the groundwater that livestock drink in the vicinity of the WIPP site. After lab makeup of solutions "A", "B", and "C", they were allowed to equilibrate for several days after pH adjustment and filtered through 0.45 μm filters.

Carrier Solution Radioisotope Doping

Subsamples of the Brines "XA" and "XB" and distilled water were spiked with ^{152}Eu , ^{144}Ce , ^{125}Sb , ^{85}Sr , ^{137}Cs , and ^{106}Ru . These represent the most common fission products found in radioactive wastes. The europium and cerium can also be used to estimate the behavior of other rare earths isotopes and some actinides present in the wastes.

Subsamples of Brines "A" and "B" and groundwater "C" were spiked with ^{85}Sr , ^{137}Cs , $^{95\text{m}}\text{Tc}$, ^{237}Np , ^{241}Am , ^{237}Pu , ^{233}Pa , ^{243}Cm , and ^{235}U . These isotopes represent the most important actinide and long lived fission products found in nuclear wastes.

After readjustment of pH and several days mixing the solutions were filtered through $0.45\mu\text{m}$ membranes to remove any precipitates.

Batch Kd Experimental Design⁽⁶⁾

One gram samples of the crushed rocks, $44\text{--}149\mu\text{m}$ were placed in 50 ml polycarbonate centrifuge tubes. The samples were contacted with two-30 ml cold washes of either brine, groundwater or distilled water. Each wash step was 24 hours in duration. The samples were centrifuged at 5000 rpm for 20 minutes and the washes decanted. Effluent pH's were recorded and the next influent adjusted in the direction to cause the equilibrium effluent pH to approach the appropriate pH (6.5 for brines, 7.5 for groundwater "C"). This procedure for pH adjustment after rock contact is representative of the situation where large quantities of carrier solution, leachant, or transport fluid are present compared to the available rock material. (Data obtained without pH adjustment after rock-solution contact will be reported by R. G. Dosch, Sandia Laboratories, at a later date.) It was not possible to force the pH of the distilled water effluents to pH 6.5 as the rocks contained carbonates.

A third solution-rock contact utilizing radionuclide spiked carrier solution was used. At periodic intervals the spiked solutions were removed from the shaker and centrifuged. Supernatant solutions were counted utilizing gamma ray spectroscopy (Li drifted Ge detector) or x-ray-gamma ray

spectroscopy (intrinsic Ge detector). Influent solutions were placed in identical polyethylene test tubes without crushed rock as blank tests to account for any container sorption. Effluent pH's were also monitored at each counting period. After counting the solution was placed back in contact with the crushed rocks and agitation continued.

Kd values for the isotopes were calculated with units of ml/g and ml/m² surface area. The average value of triplicates and standard deviation are reported after several equilibration periods to evaluate the time dependence of Kd.

The Kd was calculated by observing the difference in count rates between a blank tube (without geologic media) and the effluents from each slurry tube upon centrifugation and supernatant solution removal. The following equations were used:

Porous Flow Case

$$K_d \text{ (ml/g)} = \frac{r(\text{Blank Count Rate}) - (\text{Effluent Count Rate})}{(\text{Effluent Count Rate})} \times \frac{\text{Total mls of Liquid}}{\text{g of rock}}$$

$$r = \frac{\text{Spike Solution Volume}}{\text{Total mls of Liquid}}$$

Total mls of Liquid = Spike Solution Volume + Excess Cold Solution not Removed Upon Centrifugation

Fracture Flow Case

$$K_d \text{ (ml/m}^2\text{)} = \frac{r(\text{Blank Count Rate}) - (\text{Effluent Count Rate})}{\text{Effluent Count Rate}} \times \frac{\text{Total mls of Liquid}}{\text{Surface Area of Rock in m}^2}$$

Counting Information

The following isotopes were mixed together and corrections made for the compton scattering contributions to the energy levels of each isotope. The mixtures and counting method utilized are shown in Table 2.

Table 2. Counting Information

Mixtures of Isotopes	Method
$^{152}\text{Eu} - ^{125}\text{Sb} - ^{106}\text{Ru}$	Ge(Li) Detector Gamma Spectroscopy
$^{144}\text{Ce} - ^{85}\text{Sr} - ^{137}\text{Cs}$	Ge(Li) Detector Gamma Spectroscopy
$^{95\text{m}}\text{Tc} - ^{85}\text{Sr} - ^{137}\text{Cs}$	Ge(Li) Detector Gamma Spectroscopy
$^{235}\text{U} - ^{243}\text{Cm}$	Ge(Li) Detector Gamma Spectroscopy
^{237}Pu	Ge(Li) Detector Gamma Spectroscopy
$^{237}\text{Np} - ^{241}\text{Am} - ^{233}\text{Pa}$	Ge Intrinsic Diode X and Gamma

	Energy Level Windows (kev)
^{152}Eu	119. - 125.
^{125}Sb	425. - 431.
^{106}Ru	509. - 515. (^{106}Rh)
^{144}Ce	131. - 137.
^{85}Sr	511. - 517.
^{137}Cs	659. - 665.
^{235}U	183. - 189.
^{243}Cm	275. - 281.
^{237}Pu	94. - 104.
^{237}Np	28.8 - 30.0
^{241}Am	58.9 - 60.1
^{233}Pa	97.8 - 99.0

RESULTS AND DISCUSSIONS

The porosity and average pore size of the core materials available were determined by visual measurement of the black regions of the optical photographs which represent the void spaces in the rocks. The results are shown in Table 3.

The Magneta and Culebra samples showed respectively two and three homogeneous circular pore sizes. The Magenta pore sizes were 13-16 μ m and 74-91 μ m. The Culebra pore sizes were 4-7 μ m, 25-48 μ m, and 266-319 μ m. There appears to be a slightly larger transverse (perpendicular to core) porosity compared to longitudinal (parallel to core) porosity. The pore shapes in Cherry Canyon #2 and #3 are highly irregular with estimated radii of up to 40-70 μ m. Cherry Canyon #1 is very closely packed with little optically determinable porosity. The rock materials, excepting Cherry Canyon #1, show a bulk porosity of 10-20% by this optical methodology and would thus be expected to yield some porous water flow even if the horizons are devoid of cracks and fractures.

Optical photographs of the cores are shown in Figures 1-24 in Appendix A.

Surface areas of the crushed rocks, 44-149 μ m, were determined by the ethylene glycol method so the batch Kd measurements can be calculated on weight and surface area bases. The surface areas and size range of particles used in the batch Kd experiments are shown in Table 4.

Table 4. Surface Areas of Crushed Rock Samples

	<u>(μm)</u>	<u>m²/g</u>
Magenta	44-149	8.1
Culebra	44-149	7.1
Cherry Canyon #1	88-149	1.3
Cherry Canyon #2	88-149	5.2
Cherry Canyon #3	44-149	11.0
Reference Bentonite		736 $\pm$ 16

Table 3. Estimated Porosity and Pore Sizes in Rock Materials

<u>Rock</u>	<u>Photo Magnification</u>	<u>Negative File No.</u>	<u>Determined Porosity % Volume</u>	<u>Pore Size (radius in μm)</u>
Magenta-L	8x	4L585 A	5.5	79
-T	8x	4L586 A	10.	77
-L	50x	4L585 B	6.0	74
			7.0	16
-T	50x	4L586 B	9.6	91
			4.8	13
Culebra-L	8x	4L587 A	4.0	266
			2.0	31
-T	8x	4L588 A	3.7	319
			4.5	45
-L	50x	4L587 B	4.0	27
			12.0	4
-T	50x	4L588 B	1.0	48
			2.0	25
			4.0	7
Cherry Canyon #1-L	250x	4L1164 A to D	Very Low	Very Small
Cherry Canyon #1-T		4L1165 A to D	Very Low	Very Small
Cherry Canyon #2-L	200x	4L1166 E	18	Irregular Up to 75 μm
Cherry Canyon #2-T		4L1167 F	20	Irregular Up to 40 μm
Cherry Canyon #3-L	200x	4L1168 G	16	Irregular Up to 40 μm
Cherry Canyon #3-T		4L1169 G	17	Irregular Up to 35 μm

Compared to clay material such as bentonite, the five rocks from neighboring horizons adjacent to the WIPP facility have low surface areas per mass of material. If sorption is proportional to surface area, the rocks under study would offer less capacity for sorption. Specutatively, this fact may not be important since the mass of nuclides which might be mobilized would be small compared to available exchange sites. Selectivity for sorption rather than capacity is probably a much more important parameter in predicting nuclide migration. It might also be possible to engineer a barrier of high sorptive capacity material such as clay to surround the repository and aid in nuclide retention in the event of solution contact. This possibility, termed "gettering", is being investigated at Sandia Laboratories with E. J. Nowak as a principle investigator.

Table 5 shows the major cation concentrations measured in the synthetic brines "XA" and "XB" versus the expected concentrations determined from their specified formulation. All analyses were performed with flame atomic adsorption.

Table 5. Major Cation Concentrations of Synthetic Brines

Salt Brine "XA"				
	<u>Ca</u> <u>%</u>	<u>Mg</u> <u>%</u>	<u>Na</u> <u>%</u>	<u>K</u> <u>%</u>
Measured	0.11	3.71	4.07	5.02
Calculated	0.13	3.80	5.70	5.20

Salt Brine "XB"				
	<u>Ca</u> <u>mg/l</u>	<u>Mg</u> <u>mg/l</u>	<u>Na</u> <u>%</u>	<u>K</u> <u>mg/l</u>
Measured	912	945	8.3	4870
Calculated	800	1000	11.5	5000

Comparison of measured values versus calculated values (based on the specified formulations) for the influents show acceptable agreement for Mg and K and fair agreement for Ca. In both instances the measured sodium concentrations are about 30% low. As Brine "XB" had an insignificant

insoluble portion after makeup, it is doubtful that the low sodium observed in Brine "XA" or "XB" was due to incomplete dissolution. It is most likely due to the error in the original commercial brine analyses mentioned earlier or the salt brine matrix may be causing a negative interference on the sodium analysis. The amount of salt left undissolved in the salt brine "XA" makeup was not quantified but was estimated to be <10%.

The amount of rock material which dissolved on contact with distilled water is shown in Tables 6 and 7.

Table 6. Distilled Water Effluents (mg/l)

<u>Media</u>	<u>Ca</u>	<u>Mg</u>	<u>Na</u>	<u>K</u>
Magenta	12.0	7.2	2.2	0.9
Culebra	5.8	4.0	2.2	0.4
Cherry Canyon #1	16.5	0.9	2.1	0.1
Cherry Canyon #2	9.2	1.3	2.4	0.3
Cherry Canyon #3	9.4	1.2	2.3	0.3

Table 7. Wt% Media Dissolved in Distilled Water
(1g media/30 mls)

<u>Media</u>	<u>%</u>
Magenta	4
Culebra	3
Cherry Canyon #1	1
Cherry Canyon #2	1
Cherry Canyon #3	2

The distilled water samples dissolved only small portions of the rock materials. The Cherry Canyon #1 sample (limestone) released about .495 mg Ca/g of crushed rock (16.5 ppm Ca in 30 mls of solution). The Magenta sample (dolomite) released .360 mg Ca/g whereas the Culebra sample (also a dolomite) released the least Ca. The two dolomites, Magenta and Culebra released substantially more magnesium than the other rock types as might be expected. Small portions of alkali metals, Na and K, were released by all the rocks. The equilibrium solutions formed by distilled water in contact with the rocks under study are similar to a low ionic strength groundwater

but are still over 25 times more dilute than the groundwater (solution "C") pumped from an aquifer in the Rustler formation. Thus if cationic competition is an important mechanism in the exchange or sorption of trace nuclides, the Kd results using distilled water may be biased high compared to expected results in typical non-salt brine groundwaters in the region. The utilization of distilled water as a carrier water for any Kd determinations is probably a poor choice as the results cannot be easily compared with a naturally occurring environment. As mentioned earlier, distilled water was used for experimental expediency and to facilitate interlaboratory comparisons of results.

In order to truly reflect the interactions of trace nuclides with geologic media after repository disruption and water contact, realistic concentrations of tracer must be used in spiked experiments. Concentrations much higher than probable may have a significant biasing effect and should be avoided. The activity and concentration of radiotracers added to the influents are reported in Table 8. As several of the tracer solutions were not free of carrier element, the total concentration of each element added to the solutions is estimated in the third column.

Table 8. Initial Activity of Batch Influent

	<u>μci/l</u>	<u>μg/l (Assuming Carrier Free)</u>	<u>μg/l (Estimated)</u>
⁸⁵ Sr	0.65	2.73×10^{-5}	$2.73 \times 10^{-2*}$
¹⁰⁶ Ru	8.12	2.43×10^{-3}	2.43×10^{-3}
¹⁴⁴ Ce	4.49	1.41×10^{-3}	1.41×10^{-3}
¹⁵² Eu	10.90	5.92×10^{-2}	1.2
¹²⁵ Sb	5.27	5.09×10^{-3}	5.09×10^{-3}
¹³⁷ Cs	2.03	2.33×10^{-2}	$2.33 \times 10^{-2**}$
²³⁷ Np	0.03 - 0.26	40-370	40-370
²⁴¹ Am	0.06 - 0.78	$0.2-2.4 \times 10^{-1}$	$0.2-2.4 \times 10^{-1}$
²³⁵ U	0.002 - 0.008	$3.9-8.7 \times 10^3$	$3.9-8.7 \times 10^3$
²³⁷ Pu	0.003 - 0.023	$0.3-1.9 \times 10^{-6}$	$0.3-1.9 \times 10^{-6}$
²³³ Pa	0.0006 - 0.005	$0.3-2.4 \times 10^{-7}$	$0.3-2.4 \times 10^{-7}$
²⁴³ Cm	0.02 - 0.07	$0.4-1.5 \times 10^{-3}$	$0.4-1.5 \times 10^{-3}$

*Brines have 5,000 to 20,000 μg/l stable element

**Brines have 1,000 to 10,000 μg/l stable element

For comparison the range of maximum concentrations of fission products and actinides found upon leaching several pieces of ~10 grams of Battelle high level zinc borosilicate glass (19 cm² geometric surface area) in 500 ml of distilled water are shown in Table 9 (D. J. Bradley, Battelle Northwest data to be published).

Table 9. Concentration of Radioelements in Batch Solutions vs. Actual Leachate

	Batch Solutions μg/l	Glass Leachate μg/l
Sr	2.73×10^{-2}	39*
Ru	2.43×10^{-3}	5×10^{-5} to 5×10^{-4}
Ce	1.41×10^{-3}	8×10^{-5} to 8×10^{-3}
Eu	1.2	9×10^{-4} to 9.7×10^{-2}
Sb	5.09×10^{-3}	2×10^{-4} to 4×10^{-2}
Cs	2.33×10^{-2}	40-120
Np	40-70	26.2*
Am	$0.2-2.4 \times 10^{-1}$	4×10^{-3} to 1×10^{-1}
U	$3.9-8.7 \times 10^3$	Not Determined
Pa	$0.3-2.4 \times 10^{-7}$	Not Determined
Pu	$0.3-1.9 \times 10^{-6}$	4×10^{-2} to 1×10^1
Cm	$0.4-1.5 \times 10^{-3}$	6×10^{-4} to 1×10^{-1}

*Only one data point to date.

The concentrations of radioelements found in the actual leachate are for a 30 day static leach in distilled water. The actual leached concentrations which will be found in a waste repository are probably less. The actual concentration of stable fission product elements found in groundwaters will, in most cases, be controlled by the concentration of leached stable, naturally occurring isotopes. Thus, the amount of tracer to add to batch Kd experiments for fission products to approximate the concentration in groundwaters should consider data available for average groundwaters which, for rare earth elements, runs in the parts per trillion-parts per billion range and for alkaline earths and alkali metals are in the low parts per million range.

In all cases (with the exception of U and Eu) the absolute concentrations of tracer used in these batch Kd experiments are of the correct order of magnitude, or lower, than observed leach concentrations. Thus, the Kd results presented herein are realistic from a tracer concentration view point.

One complicating factor not addressed in this preliminary study which could affect the actinide Kd's significantly is the possibility of anionic complex formation (for example, chloro complexes in a NaCl rich system) and variable valence states. Pu, Np, and U especially may be present in the repository environment in numerous valence states or complexes which could lead to a wide variation in Kd. Several studies on the migration behavior of actinides of various oxidation states on various rock samples, of the oxidation state of actinides leached from waste, and of actinide chemistry in neutral solutions have been conducted or are planned at Argonne National Laboratory^(7, 8) and Battelle Pacific Northwest Labs.⁽⁹⁾ In this study, the isotopes are assumed to be predominately in their most stable valence states for neutral groundwaters in equilibrium with the atmosphere, i.e., Pu⁺⁴, Am⁺³, Np⁺⁵ (NpO₂⁺), Cm⁺³, U⁺⁶ (UO₂⁺²). Rai and Serne,⁽¹⁰⁾ and Ames, Rai and Serne⁽¹¹⁾ discuss the thermodynamic data on aqueous actinide chemistry.

The pH of the slurries of rock and solutions after each cold wash are shown in Table 10.

The pH of Brine "B" and distilled water after cold washes were one pH unit greater than initial values reflecting the alkaline buffering capacity of the rocks. After two cold washes of Brine "XA" and Brine "XB", and groundwater "C", the pH reached the desired value. The pH values of the effluents as a function of transporting solution, equilibration times, and nuclide mixture are shown in Table 11a through 11c.

Resultant Kd values for each nuclide versus rock type, solution type and equilibration time are shown in Tables 12a-d, 13a-b, 14a-d, and 15a-b. Tables 12a-d and 13a-b portray the Kd data for fission products and actinides respectively in units of ml/g (porous flow). Tables 14a-d and 15a-b portray the Kd data for fission products and actinides respectively in

Table 10. pH of Cold Washes

<u>Rock</u>	<u>Distilled H₂O</u>		<u>Brine "XA"</u>		<u>Brine "XB"</u>		<u>Brine "B"</u>		<u>Groundwater "C"</u>	
	<u>1st</u>	<u>2nd</u>	<u>1st</u>	<u>2nd</u>	<u>1st</u>	<u>2nd</u>	<u>1st</u>	<u>2nd</u>	<u>1st</u>	<u>2nd</u>
Magenta	8.2	8.9	6.5	-	6.7	6.6	-	-	-	-
Culebra	8.6	8.9	6.6	-	6.7	6.7	7.5	7.5	7.7	7.6
Cherry Canyon #1	7.8	8.9	6.6	6.6	6.8	6.8	7.2	7.2	7.8	7.8
Cherry Canyon #2	8.1	8.7	6.6	-	6.7	6.7	-	-	-	-
Cherry Canyon #3	8.4	8.8	6.5	-	6.7	6.7	-	-	-	-

- Not available

Table 11a. Effluent pH

	<u>Distilled Water Equilibration</u>	<u>Brine "XA" Equilibration</u>	<u>Brine "XB" Equilibration</u>
	Eu, Sb, Ru		
	<u>7 Days</u>	<u>4 Days</u>	<u>5 Days</u>
Magenta	8.30 ± .00	6.05 ± .00	6.68 ± .00
Culebra	8.40 ± .00	6.05 ± .00	6.70 ± .00
Cherry Canyon #1	8.33 ± .03	6.10 ± .00	6.80 ± .00
Cherry Canyon #2	8.25 ± .00	6.03 ± .03	6.70 ± .00
Cherry Canyon #3	8.23 ± .06	6.05 ± .00	6.70 ± .00
	<u>13 Days</u>	<u>14 Days</u>	<u>13 Days</u>
Magenta	8.18 ± .03	6.40 ± .00	6.70 ± .01
Culebra	8.33 ± .03	6.40 ± .00	6.75 ± .00
Cherry Canyon #1	8.27 ± .08	6.47 ± .02	6.85 ± .00
Cherry Canyon #2	8.22 ± .03	6.40 ± .00	6.75 ± .00
Cherry Canyon #3	8.15 ± .05	6.41 ± .01	6.75 ± .00
	<u>47 Days</u>	<u>47 Days</u>	<u>40 Days</u>
Magenta	8.08 ± .03	6.58 ± .00	7.15 ± .00
Culebra	8.28 ± .03	6.55 ± .00	7.20 ± .00
Cherry Canyon #1	8.05 ± .13	6.79 ± .00	7.35 ± .00
Cherry Canyon #2	8.00 ± .13	6.60 ± .00	7.20 ± .00
Cherry Canyon #3	7.95 ± .05	6.60 ± .00	7.20 ± .00

Table 11b. Effluent pH

	Distilled Water Equilibration	Brine "XA" Equilibration	Brine "XB" Equilibration
		Ce, Sr, Cs	
	7 Days	4 Days	5 Days
Magenta	8.51 ± .07	6.40 ± .00	6.60 ± .00
Culebra	8.68 ± .03	6.40 ± .00	6.60 ± .00
Cherry Canyon #1	8.58 ± .03	6.42 ± .00	6.80 ± .00
Cherry Canyon #2	8.43 ± .06	6.40 ± .00	6.70 ± .00
Cherry Canyon #3	8.47 ± .08	6.41 ± .01	6.70 ± .00
	13 Days	14 Days	13 Days
Magenta	8.30 ± .05	6.60 ± .00	6.65 ± .00
Culebra	8.50 ± .05	6.63 ± .01	6.65 ± .00
Cherry Canyon #1	8.49 ± .04	6.60 ± .00	6.90 ± .00
Cherry Canyon #2	8.30 ± .09	6.58 ± .02	6.75 ± .00
Cherry Canyon #3	8.30 ± .10	6.60 ± .00	6.75 ± .00
	47 Days	47 Days	40 Days
Magenta	8.12 ± .03	6.75 ± .00	7.00 ± .00
Culebra	8.32 ± .06	6.75 ± .00	7.08 ± .00
Cherry Canyon #1	8.37 ± .06	6.88 ± .00	7.35 ± .00
Cherry Canyon #2	8.10 ± .10	6.75 ± .00	7.20 ± .00
Cherry Canyon #3	8.13 ± .08	6.75 ± .00	7.20 ± .00

Table 11c. Effluent pH

	<u>Brine "B"</u> <u>Equilibration</u>	<u>Groundwater "C"</u> <u>Equilibration</u>
	Cm-U	
	<u>5 Days</u>	<u>5 Days</u>
Culebra	7.67 ± .15	8.09 ± .01
Cherry Canyon #1	7.67 ± .10	8.23 ± .03
	<u>8 Days</u>	<u>8 Days</u>
Culebra	6.53 ± .06	7.50 ± .00
Cherry Canyon #1	6.68 ± .03	7.55 ± .01
	Am, Np, Pa	
	<u>5 Days</u>	<u>5 Days</u>
Culebra	6.93 ± .49	8.03 ± .03
Cherry Canyon #1	7.40 ± .06	8.21 ± .01
	<u>8 Days</u>	<u>8 Days</u>
Culebra	6.55 ± .17	7.39 ± .01
Cherry Canyon #1	6.66 ± .04	7.52 ± .07
	Pu	
	<u>8 Days</u>	<u>8 Days</u>
Culebra	6.83 ± .06	7.42 ± .10
Cherry Canyon #1	6.78 ± .03	7.52 ± .03
	Cs, Sr, Tc	
	<u>16 Days</u>	<u>16 Days</u>
Culebra	6.52 ± .03	7.51 ± .01
Cherry Canyon #1	6.58 ± .03	7.48 ± .06

Table 12a. Fission Product Kd's (ml/g)

	Distilled Water Equilibration 7 Days			Brine "XA" Equilibration 4 Days			Brine "XB" Equilibration 5 Days		
	Kd_{Eu}								
Magenta	451	±	102	48.3	±	14.9	54.6	±	4.7
Culebra	359	±	87	87.2	±	5.2	54.2	±	8.4
Cherry Canyon #1	272	±	105	69.4	±	6.5	61.6	±	15.1
Cherry Canyon #2	113	±	10	24.6	±	8.0	35.3	±	11.2
Cherry Canyon #3	91	±	14	35.8	±	6.1	35.4	±	4.5
	Kd_{Sb}								
Magenta	3.7	±	1.2	-0.1	±	0.8	1.2	±	0.8
Culebra	2.4	±	0.2	-0.4	±	0.4	0.9	±	0.7
Cherry Canyon #1	1.6	±	0.6	-0.5	±	0.8	-0.1	±	0.1
Cherry Canyon #2	3.2	±	0.2	-2.1	±	2.5	3.1	±	0.1
Cherry Canyon #3	2.8	±	1.8	0.2	±	1.3	1.1	±	0.4
	Kd_{Ru}								
Magenta	99.8	±	12.2	1.9	±	1.2	3.0	±	0.5
Culebra	81.4	±	6.3	3.6	±	0.2	4.1	±	0.4
Cherry Canyon #1	63.2	±	7.7	2.7	±	0.4	3.5	±	0.9
Cherry Canyon #2	68.3	±	4.0	1.9	±	0.2	3.7	±	0.1
Cherry Canyon #3	62.8	±	10.3	2.0	±	1.0	3.9	±	0.4
	Kd_{Ce}								
Magenta	466	±	446	22.7	±	2.1	408	±	180
Culebra	1360	±	2015	39.3	±	7.8	706	±	374
Cherry Canyon #1	210	±	169	58.6	±	27.5	5060	±	5906
Cherry Canyon #2	496	±	344	28.1	±	11.0	147	±	18
Cherry Canyon #3	99.8	±	6.4	20.5	±	4.0	115	±	20
	Kd_{Sr}								
Magenta	5.6	±	0.2	-0.3	±	0.5	-0.1	±	0.3
Culebra	12.4	±	1.2	-0.8	±	0.3	-0.3	±	0.3
Cherry Canyon #1	9.6	±	1.0	-0.4	±	0.1	0.4	±	0.4
Cherry Canyon #2	37.5	±	1.2	-0.2	±	0.4	-0.3	±	0.2
Cherry Canyon #3	19.2	±	1.5	-0.5	±	0.3	-0.5	±	0.4
	Kd_{Cs}								
Magenta	2656	±	88	-0.3	±	0.5	0.1	±	0.3
Culebra	1739	±	59	-0.6	±	0.3	0.2	±	0.1
Cherry Canyon #1	7518	±	686	-0.5	±	0.3	0.2	±	0.2
Cherry Canyon #2	18567	±	5798	0.2	±	0.3	0.5	±	0.1
Cherry Canyon #3	6751	±	865	-0.3	±	0.1	0.8	±	0.3

Table 12b. Fission Product Kd's (ml/g)

	Distilled Water Equilibration 13 Days			Brine "XA" Equilibration 14 Days		Brine "XB" Equilibration 13 Days	
	Kd_{Eu}						
Magenta	640	±	302	56.2	± 4.8	46.2	± 10.8
Culebra	639	±	342	96.7	± 1.3	61.2	± 16.8
Cherry Canyon #1	459	±	54	84.8	± 5.4	56.4	± 19.1
Cherry Canyon #2	203	±	57	27.1	± 0.4	22.0	± 6.9
Cherry Canyon #3	171	±	39	42.7	± 0.9	30.1	± 13.0
	Kd_{Sb}						
Magenta	5.3	±	0.3	0.4	± 0.9	1.2	± 0.7
Culebra	3.2	±	0.7	-0.3	± 0.7	1.5	± 0.7
Cherry Canyon #1	2.1	±	0.5	0.2	± 0.6	0.9	± 0.3
Cherry Canyon #2	4.6	±	0.5	0.4	± 0.2	5.2	± 0.5
Cherry Canyon #3	3.1	±	0.2	-0.0	± 0.4	1.6	± 0.4
	Kd_{Ru}						
Magenta	153.6	±	9.0	3.0	± 0.8	3.7	± 0.3
Culebra	134.3	±	9.7	5.1	± 1.0	5.3	± 0.1
Cherry Canyon #1	94.4	±	6.0	4.8	± 0.4	5.6	± 2.0
Cherry Canyon #2	119.2	±	3.6	3.6	± 0.3	6.4	± 0.3
Cherry Canyon #3	94.5	±	6.1	3.4	± 0.2	5.4	± 0.3
	Kd_{Ce}						
Magenta	797	±	944	22.5	± 7.7	626	± 113
Culebra	1364	±	2040	54.8	± 17.8	791	± 245
Cherry Canyon #1	170	±	130	57.9	± 3.9	5264	± 3750
Cherry Canyon #2	930	±	1392	28.5	± 13.0	174	± 43
Cherry Canyon #3	2540	±	2040	26.0	± 13.2	148	± 23
	Kd_{Sr}						
Magenta	5.3	±	0.1	1.0	± 0.3	0.6	± 0.1
Culebra	10.3	±	0.7	0.7	± 0.6	0.6	± 0.7
Cherry Canyon #1	9.0	±	1.2	0.9	± 0.7	0.1	± 0.4
Cherry Canyon #2	33.7	±	2.9	1.1	± 0.5	-0.1	± 0.3
Cherry Canyon #3	16.4	±	1.8	0.7	± 0.4	0.4	± 0.4
	Kd_{Cs}						
Magenta	2345	±	111	0.3	± 0.3	-0.2	± 0.3
Culebra	1809	±	320	-0.1	± 0.4	-0.1	± 0.5
Cherry Canyon #1	6995	±	494	0.4	± 0.5	-0.1	± 0.1
Cherry Canyon #2	18560	±	8200	1.0	± 0.5	-0.1	± 0.1
Cherry Canyon #3	6855	±	1462	0.4	± 0.4	0.0	± 0.2

Table 12c. Fission Product Kd's (ml/g)

	Distilled Water Equilibration 47 Days			Brine "XA" Equilibration 47 Days			Brine "XB" Equilibration 40 Days		
				Kd_{Eu}					
Magenta	9873	±	4	34	±	5	31	±	9
Culebra	45584	±	49655	50	±	2	31	±	8
Cherry Canyon #1	1287	±	963	39	±	4	38	±	15
Cherry Canyon #2	>1307	±	698	8.3	±	1.5	21	±	4
Cherry Canyon #3	1163	±	95	19	±	1	25	±	10

				Kd_{Sb}					
Magenta	6.39	±	0.64	0.73	±	0.45	1.7	±	0.2
Culebra	3.30	±	1.40	1.07	±	0.45	1.9	±	0.5
Cherry Canyon #1	1.57	±	0.11	0.22	±	0.40	0.8	±	0.2
Cherry Canyon #2	5.99	±	0.98	1.66	±	0.46	6.6	±	0.4
Cherry Canyon #3	2.80	±	1.20	0.92	±	0.36	1.9	±	0.5

				Kd_{Ru}					
Magenta	389	±	54	3.6	±	0.3	5.6	±	0.4
Culebra	291	±	41	7.5	±	0.2	10.2	±	0.2
Cherry Canyon #1	274	±	33	6.3	±	0.3	8.5	±	4.0
Cherry Canyon #2	554	±	123	6.1	±	0.5	9.9	±	0.0
Cherry Canyon #3	351	±	59	5.8	±	0.5	8.9	±	0.7

				Kd_{Ce}					
Magenta	71	±	61	19	±	20	179	±	63
Culebra	108	±	100	8	±	2	227	±	32
Cherry Canyon #1	>310	±		13	±	8	>608	±	
Cherry Canyon #2	293	±	189	22	±	20	106	±	13
Cherry Canyon #3	538	±	826	13	±	18	62	±	4

				Kd_{Sr}					
Magenta	8	±	4	0.4	±	0.3	-0.4	±	0.4
Culebra	8	±	0.3	0.6	±	0.5	0.3	±	0.4
Cherry Canyon #1	13	±	10	0.4	±	0.3	0.7	±	0.2
Cherry Canyon #2	22	±	2	0.7	±	0.7	0.1	±	0.2
Cherry Canyon #3	12	±	3	1.0	±	0.6	0.1	±	0.2

				Kd_{Cs}					
Magenta	2237	±	216	-0.5	±	0.2	-0.2	±	0.3
Culebra	110	±	19	-0.2	±	0.5	-0.1	±	0.3
Cherry Canyon #1	6540	±	1800	-0.8	±	0.1	-0.1	±	0.7
Cherry Canyon #2	12191	±	699	0.3	±	0.5	0.6	±	0.8
Cherry Canyon #3	5248	±	1693	-0.0	±	0.3	-0.1	±	0.1

Table 12d. Fission Product Kd's (ml/g)

	Brine "B" Equilibration 16 Days	Groundwater "C" Equilibration 16 Days
	$K_{d_{Tc}}$	
Culebra	0.24 $\pm$ 0.97	0.47 $\pm$ 0.84
Cherry Canyon #1	1.88 $\pm$ 1.56	6.70 $\pm$ 4.80
	$K_{d_{Sr}}$	
Culebra	0.85 $\pm$ 0.86	1.02 $\pm$ 1.41
Cherry Canyon #1	0.62 $\pm$ 0.84	1.67 $\pm$ 2.11
	$K_{d_{Cs}}$	
Culebra	1.30 $\pm$ 1.09	13.60 $\pm$ 2.40
Cherry Canyon #1	1.14 $\pm$ 1.10	4.15 $\pm$ 3.75

Table 13a. Actinide Kd's (ml/g)

	Brine "B" Equilibration 5 Days		Groundwater "C" Equilibration 5 Days	
	Kd _{Cm}			
Culebra Cherry Canyon #1	>11697 6468	±5010	>42930 25551	±16942
	Kd _U			
Culebra Cherry Canyon #1	4.5± 2.9±	2.7 1.0	4.3± -3.8±	4.2 5.3
	Kd _{Am}			
Culebra Cherry Canyon #1	653 >900	± 118	>900 >900	
	Kd _{Np}			
Culebra Cherry Canyon #1	22.4± 27.0±	5.4 4.7	8.8± 23.5±	1.3 1.3
	Kd _{Pa}			
Culebra Cherry Canyon #1	44.0± 94	18.4 ± 86	31.2± 55.1±	3.4 25.7
	Kd _{Pu}			
Culebra Cherry Canyon #1	Not Determined Not Determined		Not Determined Not Determined	

Table 13b. Actinide Kd's (ml/g)

	Brine "B" Equilibration 8 Days		Groundwater "C" Equilibration 8 Days	
	$K_{d_{Cm}}$			
Culebra	6213	± 6224	1902	± 255
Cherry Canyon #1	1119	± 789	6585	± 735
	K_{d_U}			
Culebra	-0.9 ±	1.5	5.8±	7.2
Cherry Canyon #1	-2.4 ±	2.4	6.7±	14.3
	$K_{d_{Am}}$			
Culebra	752	± 410	2716	± 159
Cherry Canyon #1	1132	± 252	4681	± 184
	$K_{d_{Np}}$			
Culebra	11.3 ±	1.3	8.1±	2.4
Cherry Canyon #1	22.8 ±	4.8	20.5±	8.6
	$K_{d_{Pa}}$			
Culebra	54	± 74	24.7±	2.5
Cherry Canyon #1	>7	±	59.3±	20.1
	$K_{d_{Pu}}$			
Culebra	125	± 71	1124	± 1082
Cherry Canyon #1	80	± 20	90.8±	14.0

Table 14a. Fission Product Kd's (ml/m²)

	Distilled Water Equilibration 7 Days			Brine "XA" Equilibration 4 Days		Brine "XB" Equilibration 5 Days	
	Kd _{Eu}						
Magenta	56	±	13	5.96	± 1.84	6.74	± 0.58
Culebra	51	±	12	12.28	± 0.73	7.63	± 1.18
Cherry Canyon #1	209	±	81	53.38	± 5.00	47.38	± 11.62
Cherry Canyon #2	22	±	2	4.73	± 1.54	6.79	± 2.15
Cherry Canyon #3	8	±	1	3.25	± 0.55	3.22	± 0.41
	Kd _{Sb}						
Magenta	0.5	±	0.2	-0.01	± 0.10	0.15	± 0.10
Culebra	0.3	±	0.0	-0.05	± 0.05	0.13	± 0.11
Cherry Canyon #1	1.2	±	0.5	-0.40	± 0.58	-0.06	± 0.04
Cherry Canyon #2	0.6	±	0.0	-0.40	± 0.48	0.60	± 0.02
Cherry Canyon #3	0.3	±	0.2	0.02	± 1.18	0.10	± 0.04
	Kd _{Ru}						
Magenta	12.3	±	1.5	0.23	± 0.15	0.37	± 0.06
Culebra	11.5	±	0.9	0.51	± 0.03	0.58	± 0.06
Cherry Canyon #1	48.6	±	5.9	2.08	± 0.31	2.68	± 0.66
Cherry Canyon #2	13.1	±	0.8	0.37	± 0.15	2.88	± 0.02
Cherry Canyon #3	5.7	±	0.9	0.18	± 0.09	0.35	± 0.04
	Kd _{Ce}						
Magenta	57.5	±	55.1	2.80	± 0.26	50.37	± 22.22
Culebra	191.6	±	283.8	5.54	± 1.10	99.44	± 52.68
Cherry Canyon #1	161.6	±	130.0	45.08	± 21.15	3892.31	± 4543.08
Cherry Canyon #2	95.4	±	66.2	5.40	± 2.12	28.27	± 3.46
Cherry Canyon #3	9.1	±	0.6	1.86	± 0.36	10.45	± 1.82
	Kd _{Sr}						
Magenta	0.7	±	0.0	-0.04	± 0.06	-0.02	± 0.04
Culebra	1.8	±	0.2	-0.11	± 0.04	-0.04	± 0.04
Cherry Canyon #1	7.4	±	0.8	-0.31	± 0.77	0.06	± 0.06
Cherry Canyon #2	7.2	±	0.2	-0.04	± 0.05	-0.05	± 0.04
Cherry Canyon #3	1.8	±	0.2	-0.04	± 0.03	-0.04	± 0.04
	Kd _{Cs}						
Magenta	328	±	11	-0.04	± 0.06	0.02	± 0.04
Culebra	245	±	8	-0.08	± 0.04	0.02	± 0.01
Cherry Canyon #1	5783	±	528	-0.04	± 0.22	0.17	± 0.14
Cherry Canyon #2	3571	±	1115	0.03	± 0.07	0.10	± 0.01
Cherry Canyon #3	614	±	79	-0.03	± 0.01	0.04	± 0.02

Table 14b. Fission Product Kd's (ml/m²)

	Distilled Water Equilibration 13 Days			Brine "XA" Equilibration 14 Days		Brine "XB" Equilibration 13 Days	
	K_{dEu}						
Magenta	79	±	37	11.7 ± 0.6		5.7	± 1.3
Culebra	90	±	42	48.2 ± 0.2		8.6	± 2.4
Cherry Canyon #1	353	±	41	65.2 ± 4.1		43.4	± 14.7
Cherry Canyon #2	39	±	11	5.2 ± 0.1		4.2	± 1.3
Cherry Canyon #3	15	±	3	3.9 ± 0.1		2.7	± 1.2
	K_{dSb}						
Magenta	0.7	±	0.1	0.05± 0.11		0.15	± 0.09
Culebra	0.5	±	0.1	-0.04± 0.10		0.21	± 0.10
Cherry Canyon #1	1.6	±	0.4	0.15± 0.46		0.69	± 0.23
Cherry Canyon #2	0.9	±	0.1	0.08± 0.04		1.0	± 0.10
Cherry Canyon #3	0.3	±	0.0	0.00± 0.04		0.15	± 0.04
	K_{dRu}						
Magenta	19	±	1	0.37± 0.10		0.46	± 0.04
Culebra	19	±	1	0.72± 0.14		0.75	± 0.01
Cherry Canyon #1	73	±	5	3.69± 0.31		4.31	± 1.54
Cherry Canyon #2	23	±	1	0.69± 0.06		1.23	± 0.06
Cherry Canyon #3	9	±	1	0.31± 0.02		0.49	± 0.03
	K_{dCe}						
Magenta	98	±	117	2.78± 0.95		77.28	± 13.95
Culebra	192	±	287	7.72± 2.51		111.41	± 34.51
Cherry Canyon #1	131	±	100	44.54± 3.00		4049.23	± 2884.62
Cherry Canyon #2	179	±	268	5.48± 2.50		33.46	± 8.27
Cherry Canyon #3	231	±	185	2.36± 1.20		13.45	± 2.09
	K_{dSr}						
Magenta	1	±	0.0	0.12± 0.04		0.07	± 0.01
Culebra	1	±	0.1	0.10± 0.08		0.08	± 0.10
Cherry Canyon #1	7	±	0.9	0.69± 0.54		0.08	± 0.31
Cherry Canyon #2	6	±	0.6	0.21± 0.10		-0.02	± 0.06
Cherry Canyon #3	1	±	0.2	0.06± 0.04		0.04	± 0.04
	K_{dCs}						
Magenta	290	±	14	0.04± 0.04		-0.02	± 0.04
Culebra	260	±	45	-0.01± 0.06		-0.01	± 0.07
Cherry Canyon #1	5381	±	380	0.31± 0.38		-0.08	± 0.08
Cherry Canyon #2	3569	±	1577	0.19± 0.10		-0.02	± 0.02
Cherry Canyon #3	623	±	133	0.04± 0.04		0.00	± 0.02

Table 14c. Fission Product Kd's (ml/m²)

	Distilled Water Equilibrium 47 Days			Brine "XA" Equilibration 47 Days	Brine "XB" Equilibration 40 Days
	$K_{d_{Eu}}$				
Magenta	1219	±	1	4.20 ± 0.62	3.83 ± 1.11
Culebra	6420	±	6994	7.04 ± 0.28	4.37 ± 1.13
Cherry Canyon #1	990	±	741	30.00 ± 3.08	29.23 ± 11.54
Cherry Canyon #2	>251	±	134	1.60 ± 0.29	4.04 ± 3.08
Cherry Canyon #3	106	±	9	1.73 ± 0.09	2.27 ± 0.91
	$K_{d_{Sb}}$				
Magenta	0.8	±	0.1	0.09 ± 0.06	0.23 ± 0.02
Culebra	0.5	±	0.2	0.15 ± 0.06	0.27 ± 0.07
Cherry Canyon #1	1.2	±	0.1	0.17 ± 0.31	0.62 ± 0.38
Cherry Canyon #2	1.2	±	0.2	0.32 ± 0.09	1.27 ± 0.08
Cherry Canyon #3	0.3	±	0.1	0.08 ± 0.03	0.17 ± 0.05
	$K_{d_{Ru}}$				
Magenta	48	±	7	0.44 ± 0.04	0.69 ± 0.05
Culebra	41	±	6	1.06 ± 0.03	1.44 ± 0.03
Cherry Canyon #1	211	±	25	4.85 ± 0.23	6.54 ± 3.08
Cherry Canyon #2	107	±	24	1.17 ± 0.10	1.90 ± 0.00
Cherry Canyon #3	32	±	5	0.53 ± 0.05	0.81 ± 0.06
	$K_{d_{Ce}}$				
Magenta	9	±	8	2.35 ± 2.47	22.10 ± 7.78
Culebra	15	±	14	1.13 ± 0.28	31.97 ± 4.51
Cherry Canyon #1	>239	±		10.00 ± 6.15	467.69
Cherry Canyon #2	56	±	36	4.23 ± 3.85	20.38 ± 2.50
Cherry Canyon #3	49	±	75	1.18 ± 1.64	5.64 ± 0.36
	$K_{d_{Sr}}$				
Magenta	1	±	0.5	0.05 ± 0.04	-0.05 ± 0.05
Culebra	1	±	0.0	0.08 ± 0.07	0.04 ± 0.06
Cherry Canyon #1	10	±	7.7	0.31 ± 0.23	-0.54 ± 0.15
Cherry Canyon #2	4	±	0.4	0.13 ± 0.13	0.02 ± 0.12
Cherry Canyon #3	1	±	0.3	0.09 ± 0.05	0.01 ± 0.02
	$K_{d_{Cs}}$				
Magenta	276	±	27	-0.06 ± 0.02	-0.02 ± 0.04
Culebra	16	±	3	-0.03 ± 0.07	-0.01 ± 0.10
Cherry Canyon #1	5031	±	1385	-0.62 ± 0.08	0.08 ± 0.54
Cherry Canyon #2	2344	±	134	0.06 ± 0.10	0.12 ± 0.15
Cherry Canyon #3	477	±	154	-0.00 ± 0.03	-0.01 ± 0.01

Table 14d. Fission Product Kd's (ml/m²)

	Brine "B" Equilibration 16 Days	Groundwater "C" Equilibration 16 Days
	Kd_{Tc}	
Culebra	0.03 ± 0.14	0.07 ± .12
Cherry Canyon #1	1.45 ± 1.20	5.15 ± 3.69
	Kd_{Sr}	
Culebra	0.12 ± 0.12	0.14 ± 0.20
Cherry Canyon #1	0.48 ± 0.65	1.28 ± 1.62
	Kd_{Cs}	
Culebra	0.18 ± 0.15	1.92 ± 0.34
Cherry Canyon #1	0.88 ± 0.85	3.19 ± 2.88

Table 15a. Actinide Kd's (ml/m²)

	Brine "B" Equilibration 5 Days		Groundwater "C" Equilibration 5 Days	
	Kd_{Cm}			
Culebra Cherry Canyon #1	>1647 4975	± 3854	> 6046 19654	± 13032
	Kd_U			
Culebra Cherry Canyon #1	0.63 $\pm$ 2.23 $\pm$	0.38 0.77	0.61 $\pm$ -2.90 $\pm$	0.59 4.08
	Kd_{Am}			
Culebra Cherry Canyon #1	92.0 $\pm$ >700	16.6	127 >700	
	Kd_{Np}			
Culebra Cherry Canyon #1	3.15 $\pm$ 20.80 $\pm$	0.76 3.60	1.24 $\pm$ 18.13 $\pm$	0.18 1.08
	Kd_{Pa}			
Culebra Cherry Canyon #1	6.24 $\pm$ 72.07 $\pm$	2.68 66.61	4.39 $\pm$ 42.42 $\pm$	0.48 19.86
	Kd_{Pu}			
Culebra Cherry Canyon #1	Not Determined Not Determined		Not Determined Not Determined	

Table 15b. Actinide Kd's (ml/m²)

	Brine "B" Equilibration 8 Days		Groundwater "C" Equilibration 8 Days	
	$K_{d_{Cm}}$			
Culebra	875	± 877	268	± 36
Cherry Canyon #1	860	± 607	5065	± 565
	K_{d_U}			
Culebra	-0.13 $\pm$	0.21	0.8 $\pm$	1.0
Cherry Canyon #1	-1.8 $\pm$	1.8		
	$K_{d_{Am}}$			
Culebra	106	± 58	382	± 22
Cherry Canyon #1	871	± 194	3601	± 142
	$K_{d_{Np}}$			
Culebra	1.6 $\pm$	0.2	1.1 $\pm$	0.3
Cherry Canyon #1	17.5 $\pm$	3.7	15.6 $\pm$	6.6
	$K_{d_{Pa}}$			
Culebra	7.6 $\pm$	10.4	3.5 $\pm$	0.4
Cherry Canyon #1	>5		45.6 $\pm$	15.5
	$K_{d_{Pu}}$			
Culebra	17.6 $\pm$	10.0	158.3 $\pm$	152.4
Cherry Canyon #1	61.5 $\pm$	15.4	69.8 $\pm$	10.8

units of ml/m^2 (fracture flow). In all cases the values shown are the averages of triplicate samples and the $\pm$ values represent one standard deviation. Negative values are an artifact of the counting and blank container adsorption corrections and indicate no or very low sorption has occurred.

DISCUSSION

The pH of the effluents varied despite the pre-equilibration. The Brines "XA", "XB", and "B" and distilled water were prepared with an initial pH of 6.5 while the groundwater "C" pH was set at 7.5. After each equilibration period a drop of acid or base was added if the system had strayed from the desired pH. With this crude pH control, the pH range in Table 16 was found for each solution. Detailed pH results versus rock type and equilibration time are shown in Tables 11a-c.

Tables 11a-c show a maximum of 0.4 pH units variation for a given solution in contact with various rocks. In most instances the final effluent pH values for a given solution versus the rocks vary by less than 0.2 pH units. If there is any effect of this slight pH variation in a given solution, it would probably effect Eu, Ce, and the actinides the most. Thus observed differences in K_d 's for a given solution probably reflect differences in the rock's affinity for a nuclide rather than effects of solution pH variations.

Table 16 shows significant pH differences occurred between solutions.

Table 16. Range of pH Found in Effluents

<u>Solution</u>	<u>pH Range</u>	<u>pH Average</u>
Brine "XA"	6.03 - 6.88	6.48 ± 0.24
Brine "XB"	6.60 - 7.35	6.88 ± 0.24
Brine "B"	6.52 - 7.67	6.90 ± 0.43
Ground Water "C"	7.39 - 8.23	7.70 ± 0.33
Distilled Water	7.95 - 8.68	8.29 ± 0.17

Except for Brine "XA" the solutions in general tended towards more alkaline pH's than desired. As the rare earth and several of the actinide isotopes may be very sensitive to pH, the differences in observed Kd's for a given rock versus the various solutions may reflect some dependency on pH as well as chemical composition. Thus it will be difficult to relate the differences in Kd for a given rock entirely to solution composition (competing cation content).

The distilled water dissolved small portions of ions as reported in Table 5 but for further discussion will be designated "distilled water".

The batch Kd values for the fission products studied in general show much higher sorption will occur in distilled water than the groundwater and salt brines. In all cases except cerium there is significantly more sorption occurring in the distilled water environment. The above data could support a simple ion exchange mechanism wherein the bulk salt solution (containing single and multiply charged ions) competes for available sites and lowers the Kd.* Even though the groundwater "C" total salt concentration is only 1% of the salt brine, the Kd_{Sr} is low and the Kd_{Cs} is only 4-13 ml/g compared to distilled water values of 2000-7000 ml/g. It appears that the sandstones, dolomites, and limestone materials studied retard the movement of alkali metals moderately and alkaline earth metals only slightly if the carrier solution is similar to the groundwater present in the Rustler formation ("C").

Besides this exchange mechanism, especially for the rare earths cerium and europium, the pH differences of the distilled water and brines (pH 8.0 to 8.4 vs. 6.0 to 7.2) may also contribute to the observed higher sorption. We have observed a large pH dependence for europium sorption over the range pH 5-8 and assume cerium would behave in a similar fashion. The rare earth elements can hydrolyze and subsequently precipitate in basic and weakly acidic solutions, such as those used in this study, and have a significant effect on Kd. Mechanisms other than ion exchange which may be of significant importance regarding the distribution of radionuclides among the rock and solution phases include physical sorption and desorption, precipitation

anionic complexation, oxidation-reduction changes, mineralization or any combination of these. Such complexity makes a totally conclusive interpretation of results obtained quite difficult.

The europium results cannot totally be explained by simple ion exchange theory because Brine "XB", with a lesser salt content and lower proportion of divalent cations, should yield a larger K_d than samples in Brine "XA". Differences in pH also cannot explain why Brine "XA" results in a larger K_d than Brine "B". As one might expect, the sandstones sorb less europium than the dolomites and limestone. On a surface area basis, limestone sorbs significantly more europium than the other four rock samples.

The antimony results can presumably be explained by ion exchange theory. Antimony in natural waters is usually found as an anionic oxide complex. Since rock materials have a much lower anion exchange capacity than cation exchange capacity, the low $K_{d_{Sb}}$ are understandable. Again, the bulk anion competition of the brines lowers the K_d from values obtained in distilled water. Sorption of Sb from Brine "XB" is slightly greater than from Brine "XA" which could support the ion exchange mechanism. No rock type appears to sorb significantly more Sb than another.

The technetium results appear to follow the same trends found for antimony. In the natural environment technetium should be found as the anionic complex TcO_4^- and thus would not be expected to show much sorptive affinity for rocks. The value of 6.70 for $K_{d_{Tc}}$ on limestone (Cherry Canyon #1) for the groundwater "C" is the highest value that we have observed for Tc. Further studies would be necessary to further elucidate the sorption mechanism.

The ruthenium results also agree with simple ion exchange theory with the K_d being much larger in distilled water than the brines. The most concentrated salt ("XA") yields the lowest K_d as one would expect. The chemistry of ruthenium is also pH dependent and may be causing part of the larger K_d value in distilled water. The speciation of ruthenium in nuclear wastes has been shown to be quite complex. Certain unidentified ruthenium species have been shown to be very mobile in carbonate dominated groundwaters

on the Hanford reservation. It will be quite important to identify the chemical form of ruthenium, as well as that of other radionuclides with multiple oxidation states, released by solidified wastes before an accurate K_d may be determined. Again, the Cherry Canyon limestone sorbed the most Ru of all the rocks based on surface area calculations.

Over the first two equilibration times the cerium data follow trends predicted by ion exchange and pH dependent precipitation mechanisms. In the brines, cerium was the fission product most readily sorbed, with (Cherry Canyon #1) limestone sorbing the most cerium and the two sandstone samples (Cherry Canyon #2 and #3) sorbing the least based on surface areas.

The strontium data show a mediocre sorption in distilled water and rather poor sorption in the groundwater and brines. If simple ion exchange theory was controlling the sorption, one might expect the groundwater "C" to show a $K_{d_{Sr}}$ ranking "C" $\gg$ Brine "XB" $\sim$ Brine "B" $>$ Brine "XA" instead of the observed results which show no significant sorption in any of the four solutions. On a surface area basis the limestone appear to sorb the most Sr from distilled water and groundwater "C", but the brine data show no trends.

The batch $K_{d_{Cs}}$ in distilled water is extremely large for all of the rock materials studied and moderate in the groundwater, but K_d 's in the brine are essentially zero. It doesn't appear that a significant difference in sorption is present between brines "XA", "XB", and "B". The dolomite samples appear to show significantly lower K_d s than the limestone and sandstones in distilled water. The cesium component of brines "XA" (10 mg/l), "XB" (10 mg/l), and "B" (1 mg/l) may have resulted in saturation of selective Cs sorptive sites in the rocks, preventing the bulk of the tracer ^{137}Cs from being sorbed. In similar Cs sorption studies to be published by R. G. Dosch at Sandia Laboratories, electron microprobe studies showed that cesium was being selectively sorbed by trace amounts of clay in the Culebra and Magenta rock samples. This type of study may prove useful in interpreting other sorption and K_d results.

Five of the seven fission products investigated showed very small sorption K_d values with the high surface area crushed rock material used so far. This

tends to indicate that experimentation with thin rock wafers simulating rock fractures may not be of great benefit or of high priority at the moment. However, radionuclide sorptive behavior with solution contact of actual rock fractures, aged, weathered and possibly coated with clays, may yield significantly different results. This may not be an easy, repeatable, or reliable experiment to perform. Experiments determining the sorptive capacity of solid rocks (columns) in contact with radionuclides in solution may provide a more realistic simulation of transport behavior in an actual repository, more realistic than batch Kd experiments on crushed rocks. Such experiments may be considered as a second generation of radionuclide migration experiments, expanding upon the data presented here. Such experiments are planned or in progress at other laboratories.

The actinide Kd's show extremely high sorption (>1000 ml/g) occurring for curium and americium, good sorption (>100 ml/g) for plutonium and fair sorption for protactinium and neptunium. Uranium was only poorly sorbed by the crushed rock materials.

There appears to be a significant difference in Kd between the salt brine and groundwater solutions for only the americium and plutonium data. These results might lead one to conclude that simple ion exchange theory does not describe the observed sorption of trace actinides. The results for the fission products based on only the two solutions Brine "B" and groundwater "C" did not show much sensitivity to solution ionic strength, either therefore more experiments with several solutions at variable ionic strengths need to be run to identify whether trace actinide sorption is significantly affected by cation ion exchange. More than likely, the effects of oxidation-reduction chemical behavior in solution, hydrolysis, precipitation, and anionic complexation have a significant effect on the determined actinide Kd values.

The curium data for the 5 and 8 day equilibration periods show a wide variation which may have been caused by the decrease in pH between the two equilibration times. There is evidence that curium hydrolysis can occur which might decrease the sorption as $\text{Cm}(\text{OH})_3$ precipitate redissolves. The

extremely high K_d and apparent lack of sensitivity to solution ionic strength leads us to believe that mechanisms other than ion exchange are controlling the fate of curium.

The high Am sorption and apparent sensitivity to salt content substantiate the belief that trace Am in solution would be present as Am^{+3} free ions.

Although the Pu data are meager, it appears that Pu in trace concentrations will sorb and migrate much slower than the carrier water. The observed dependence on solution salt composition may be caused by Pu^{+4} being present and competing with other cations for available exchange sites.

The protactinium data is presented because enough ^{233}Pa daughter product of ^{237}Np was present to analyze. Very little migration behavior information is available on Pa; it is not considered a long term environmental problem.

The neptunium data show moderate sorption which lends credence to theoretical data which identifies NpO_2^+ as the predominate species present in neutral groundwaters. Although other actinides with high positive charges sorb to a greater extent, Np still shows more tendency to sorb than Sr and Cs, especially from salt brines.

Uranium was observed to sorb very poorly; however, the fact that the tracer concentration used was rather high (3-8 ppm) and the rocks have low exchange capacities could be biasing the results (similar to the results discussed for Cs). The rocks may have become saturated without needing much of the U mass in solution, thus leaving the bulk of uranium in solution. Future experiments at much lower U concentrations should be run. This will necessitate chemical separations and alpha counting or chemical analysis. The results obtained do support the trends observed in natural weathering sequences that U^{+6} as UO_2^{+2} is mobile. Therefore, the low K_d 's may be correct if U^{+6} should be the predominant species present in these experiments.

In all cases, the effects of container adsorption and simple precipitation from carrier solutions have been removed from the K_d data presented. The measured values should reflect the interaction and removal caused by the geologic media contacting the radionuclide containing leachant solution. If the container sorption and precipitation (upon ageing or solution pH change) are not removed, the K_d 's of the rare earths, Ru and the actinides would appear larger. Care must be taken not to over-estimate K_d 's for these complex nuclides.

The percentage of the initial spike remaining in solution for the blank samples are shown in Table 17. The Sr, Cs, and Sb remained in solution throughout the experiment. Very little precipitation or container adsorption occurred with these three isotopes.

The amount of Ru remaining in solution was constant with time for each solution, but the percentage varied with each solution. From past experience, container adsorption of Ru has been a recognized problem. If the loss in Ru connotes container adsorption the kinetics are rapid. The distilled water solution with the higher pH and no competing ions lost the most Ru. It is impossible to separate container adsorption effects from possible pH effects.

The Ce data show a continual decrease in the percentage of original spike remaining in solution with time for all systems. The distilled water sample showed an almost quantitative loss of Ce. Precipitation and container sorption again are the probable causes.

A significant portion of the Eu spiked into the samples was removed from the blank solutions. For salt solutions "XA" and "XB" the decrease continued with time. Unlike the Ce, the distilled water solution lost less Eu than one of the Brines ("XB"). Direct pH and container sorption trends were not recognizable. For Sb, Sr, and Cs, which remain in solution in the blanks, the K_d values versus time show no trends. The K_d values after 4 to 7 days were about the same as after 47 days equilibration.

The $K_{d_{Ru}}$ values appear to increase at each equilibration time. One hypothesis is slow "physical" sorption onto the rock material as opposed to more rapid chemical sorption.

Table 17. % of Isotope Remaining in Blank Supernate

EQUILIBRATION TIME				
<u>DISTILLED WATER</u>				
	<u>7 Days</u>	<u>13 Days</u>	<u>47 Days</u>	<u>σ</u>
Sr	100	100	100	± 2
Cs	98	99	96	± 1
Ce	6	6	2	± 4
Ru	73	75	73	± 1
Eu	13	12	17	± 3
Sb	100	100	97	± 1

<u>BRINE "XA"</u>				
	<u>4 Days</u>	<u>14 Days</u>	<u>47 Days</u>	<u>σ</u>
Sr	99	98	98	± 2
Cs	99	99	99	± 1
Ce	32	19	7	± 4
Ru	87	84	86	± 1
Eu	15	13	8	± 3
Sb	100	100	100	± 1

<u>BRINE "XB"</u>				
	<u>5 Days</u>	<u>13 Days</u>	<u>40 Days</u>	<u>σ</u>
Sr	100	96	100	± 2
Cs	97	99	100	± 1
Ce	62	53	17	± 3
Ru	94	92	91	± 1
Eu	9	6	5	± 4
Sb	99	100	100	± 1

The apparent decrease in Ce sorption at the 40-47 equilibration period reflects the loss of Ce in the blanks used for influent concentrations in the calculations. The influent count rates dropped dramatically, while the effluent count rates remained quite low because of rock sorption, and the mathematical calculations based on count rate differences decreased. Thus the apparent drop in K_d is an artifact of the experimental design rather than Ce remobilization.

The large increase in $K_{d_{Eu}}$ in distilled water at 47 days equilibration was caused presumably by the observed increase in Eu concentration in the blank at 47 days. This increase is probably spurious, caused by resuspension of fine hydroxide precipitates (colloids) after centrifugation and before sampling. The difference in count rates between effluents and the blank influent was thus made artificially high and resulted in erroneously high K_d values. Excepting the time dependence of $K_{d_{Ru}}$, the other fission product nuclides appear to yield a stable value after 4-7 days equilibration.

Preliminary experiments with the actinides showed considerable precipitation of spikes as the solution pH was adjusted to the desired value of 6.5 or 7.5. For these experiments, the amount of spike added to solutions was calculated to be less than the solubility product at a given pH. Therefore, precipitation should have been minimal. The Np, Am, Cm, and U blank samples did not show any loss of count rate between the fifth and eighth day of equilibration. As the experiments were not continued to longer times, a full assessment of container adsorption and precipitation cannot be performed. The time dependence of actinide K_d 's cannot be adequately addressed from the data presented herein. No significant changes in U, Cm, Am, and Np data at 5 and 8 days were evident.

SUMMARY

Preliminary K_d values for the isotopes of Sr, Tc, Ru, Sb, Cs, Ce, Eu, Pa, U, Np, Pu, Am, and Cm were obtained for solutions and rock types specific to the existing subsurface environment at the Waste Isolation Pilot Plant site in southeastern New Mexico. The values were obtained by the batch method on freshly crushed material in contact with solution. Data was

reported in units of both ml/g and ml/m² to allow migration rate calculations assuming either porous or fracture flow. The solutions utilized represent salt brine, groundwater and distilled water. The rocks studied included two dolomites, two feldspar sandstones, and a limestone.

In general, sorption of Sr, Tc, Ru, Sb, Cs, and U on crushed rock materials was poor (<5 ml/g) in brine solutions. The sorption of rare earths (Eu, Ce) and actinides (Pa, Np, Pu, Am, and Cm) was significantly higher even though the cation competition in the concentrated brines would be intense and the sorption capacity of the materials studied is believed to be very low.

Crushed rock materials in contact with groundwater "C" (which had an ionic salt concentration 25 times greater than the equilibrated "distilled" water) showed poor sorption of Sr and low sorption for Cs. Rock material in contact with distilled water (containing about 2 meq/l of ions at equilibrium) sorbed Sr, Ru, Cs, Ce, and Eu fairly well, with measured K_d values being in the range of 20-1000 ml/g. If Pu, Np, Am, and Pa distilled water solutions had been contacted with rock, K_d values would probably also have been of this magnitude, or higher.

More work should be performed at intermediate ionic strengths between the distilled water and salt brine concentrations to fully assess the effects of competing ions.

The data for actinides are few and must be considered provisional. More work with actinides in geologically realistic solutions contacting site specific and other appropriate rock types should be performed.

In order to assess whether the retardation afforded by the rocks studied is adequate to prevent hazards to man, water velocities, waste leach rates, time periods to reach the biosphere and specific mechanisms of radionuclide transport and retardation must be determined. The observed results should be used to identify which radionuclides may be most critical and should be emphasized in future studies.

RECOMMENDATIONS

1. The K_d data for actinides presented in this document and available in the literature are sparse. More data should be collected on the actinides before attempts are made to adequately perform safety assessment analyses.

Similar studies on actinides are being conducted and planned at Sandia Laboratories (R. G. Dosch) and in programs managed by Battelle Pacific Northwest (R. J. Serne), (Waste Isolation Safety Assessment Program) for the Office of Waste Isolation (Union Carbide, Oak Ridge, Tennessee).

2. All the experiments performed in this document investigate nuclide sorption only. As the K_d used in the safety assessment analysis is assumed to be reversible by the nature of the mathematical treatment, experiments to study desorption should be performed. Many of the nuclides may desorb at a slower rate or not at all which would increase the overall retardation substantially and would reduce potential hazards. The mathematical coupled water transport-sorption equations for nuclides which are not strictly reversible will need to be changed to include a K_d sorption and K_d^{dc} sorption.
3. Migration studies through intact porous cores and through fractured cores should be performed to verify or support migration rates based on batch experiments. A proposed waste repository geology will resemble solid and fractured rock material much more than it will resemble crushed rock. Again, such experiments are planned or in progress. Batch K_d measurements are quite valuable, however, to get initial data and trends of sorption behavior in a limited time period and via relatively simple laboratory procedures.
4. Elements of major significance in waste management which have multiple oxidation states, such as Pu, Np, and U, etc. need to be investigated in much more detail. Their potential migration/sorption behavior should be measured at the Eh expected in situ in a repository. Experiments should determine: what oxidation state does an element have when

leached from the waste matrix; what is the migration/sorption behavior of this particular ion; and can the ion change its oxidation state as it migrates.

5. All important waste radionuclides, not just those having multiple oxidation states, should be investigated to determine effects of temperature; radiolytic effects on solution chemistry and resultant effects on migration/sorption; anionic complexes formed in solution; secondary barriers or getters to retard migration; etc. There is obviously a lot of experimentation to be performed; the results reported in this study are only a small, but valuable portion of that total.
6. The extrapolation of short-term laboratory K_d data to the thousand to million year time frame under consideration should be addressed. To date all known slow reactions such as mineral and amorphous coating formation should decrease the mobility of trace constituents but more studies on time extrapolation are needed.

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APPENDIX A
OPTICAL PHOTOGRAPHS OF ROCK SAMPLES

Magenta - Longitudinal - 8X
Negative #4L585A

Magenta - Longitudinal - 50X
Negative #4L585B

Magenta - Longitudinal - 250X
Negative #4L585C

Magenta - Transverse - 8X
Negative #4L586A

Magenta - Transverse - 50X
Negative #4L586B

Magenta - Transverse - 250X
Negative #4L586C

Culebra - Longitudinal - 8X
Negative #4L587A

Culebra - Longitudinal - 50X
Negative #4L587B

Culebra - Longitudinal - 250X
Negative #4L587C

Culebra - Transverse - 8X
Negative #4L588A

Culebra - Transverse - 50X
Negative #4L588B

Culebra - Transverse - 250X
Negative #4L588C

#1-Limestone - Longitudinal - 250X
Negative #4L1164A

#1-Limestone - Longitudinal - 250X
Negative #4L1164B

#1-Limestone - Longitudinal - 250X
Negative #4L1164C

#1-Limestone - Logitudinal - 250X
Negative #4L1164D

#1-Limestone - Transverse - 250X
Negative #4L1165A

#1-Limestone - Transverse - 250X
Negative #4L1165B

#1-Limestone - Transverse - 250X
Negative #4L1165C

#1-Limestone - Transverse - 250X
Negative #4L1165D

#2-Sandstone - Longitudinal - 12X
Negative #4L1166A

#2-Sandstone - Longitudinal - 50X
Negative #4L1166B

#2-Sandstone - Longitudinal - 50X
Negative #4L1166C

#2-Sandstone - Longitudinal - 50X
Negative #4L1166D

#2-Sandstone - Longitudinal - 200X
Negative #4L1166E

#2-Sandstone - Longitudinal - 200X
Negative #4L1166F

#2-Sandstone - Longitudinal - 200X
Negative #4L1166G

#2-Sandstone - Transverse - 12X
Negative #4L1167A

#2-Sandstone - Transverse - 50X
Negative #4L1167B

#2-Sandstone - Transverse - 50X
Negative #4L1167C

#2-Sandstone - Transverse $\approx$ 50X
Negative #4L1167D

#2-Sandstone - Transverse - 200X
Negative #4L1167E

#2-Sandstone - Transverse - 200X
Negative #4L1167F

#2-Sandstone - Transverse - 200X
Negative #4L1167G

#3-Sandstone - Longitudinal - 12X
Negative #4L1168A

#3-Sandstone - Longitudinal - 50X
Negative #4L1168B

#3-Sandstone - Longitudinal - 50X
Negative #4L1168C

#3-Sandstone - Longitudinal - 50X
Negative #4L1168D

#3-Sandstone - Longitudinal - 200X
Negative #4L1168E

#3-Sandstone - Longitudinal - 200X
Negative #4L1168F

#3-Sandstone - Longitudinal - 200X
Negative #4L1168G

#3-Sandstone - Transverse - 12X
Negative #4L1169A

#3-Sandstone - Transverse - 50X
Negative #4L1169B

#3-Sandstone - Transverse - 50X
Negative #4L1169C

#3-Sandstone - Transverse - 50X
Negative #4L1169D

#3-Sandstone - Transverse - 200X
Negative #4L1169E

#3-Sandstone - Transverse - 200X
Negative #4L1169F

#3-Sandstone - Transverse - 200X
Negative #4L1169G

APPENDIX B
CARRIER SOLUTION COMPOSITIONS

APPENDIX B

Sandia Laboratories

Albuquerque, New Mexico
Livermore, California

date: August 11, 1976

to: Distribution

from: M. A. Molecke - 1141

subject: Representative Simulated Brines For WIPP Experimentation

This memo is intended to provide the ionic composition of two representative saturated brines to be utilized by the various laboratory groups supporting the WIPP project. For uniformity and intercomparison purposes, these particular brines, plus distilled water, should be utilized in all distribution coefficient, leaching, corrosion, ion mobility, etc. tests.

The composition of "Brine~~X~~A" is based on analyses of concentrated brines from the Salado region. This is a potash bearing region and is consequently quite rich in potassium ions and calcium plus magnesium. "Brine B" is a hypothetical Castile brine, relatively low in potassium and magnesium content. Both brines are essentially saturated with respect to sodium chloride. Brines ~~X~~A" and ~~X~~B" represent brines which may theoretically intrude upon the waste repository horizon from both overlaying and underlaying regions, respectively.

The pH of the two brine simulants should be adjusted to about pH = 6.5, the slight acidity of quite a few "as measured" brine samples. The pH of the prepared brine simulants can be adjusted with small additions of either HCl or NaOH, as necessary.

Future experimental work is being planned to utilize a non-saturated brine/groundwater and brines of differing pH. This will be the topic of a future memo.

REPRESENTATIVE SIMULATED BRINES FOR
WIPP EXPERIMENTATION

<u>ion</u>	<u>"BrineXA"</u> (mg/liter)	<u>"BrineXB"</u> (mg/liter)
Na ⁺	57,000	115,000
K ⁺	52,000	5,000
Mg ⁺⁺	38,000	1,000
Ca ⁺⁺	1,300	800
Fe ⁺⁺⁺	50	50
Sr ⁺⁺	20	20
Li ⁺	20	20
Rb ⁺	20	20
Cs ⁺	10	10
Cl ⁻	240,000	200,000
SO ₄ ⁻⁻	7,000	10,000
B (as BO ₃ ⁻⁻⁻)	1,200	1,200
HCO ₃ ⁻	700	700
Br ⁻	400	400
I ⁻	10	10
specific gravity	~1.2g/cc	~1.2g/cc
pH	6.5	6.5

Note: Distilled water should be utilized for WIPP experimentation in addition to brines "XA" and "XB."

Sandia Laboratories

date: October 8, 1976

Albuquerque, New Mexico
Livermore, California

to: Distribution

from: M. A. Molecke - 1141

subject: Revised Representative Brines/Solutions for WIPP
Experimentation

This memo is intended to provide specifications for the ionic content and chemical formulations for three solutions/brines for experimental purposes. These solutions are representative of waters which can potentially intrude into the Waste Isolation Pilot Plant. Brine transport of radionuclides from the radioactive waste stored in a salt mine into the geosphere and biosphere are of major concern. Experiments in progress or planned (at Sandia plus other laboratories) to quantify and evaluate such transport plus related aspects of brine intrusion include: radionuclide distribution coefficient measurements, waste matrix leaching, radionuclide mobility and interactions, and corrosion aspects. The various laboratory groups supporting the WIPP project should utilize the specified brines/solutions for both uniformity and intercomparison purposes.

The ionic compositions of the representative brines/solutions "A", "B", and "C" are given in Table I, attached, in units of mg/liter of solution. To facilitate preparation of these solutions, the required chemical compounds, also in units of mg added per liter of solution, are presented in Table II. All ions added have been balanced in terms of milliequivalents/liter for both cations and anions. If substitutions are made for various compounds in preparation, rebalancing calculations will be necessary. Following preparation, the pH of the solutions should be adjusted, as specified, with small additions of either dilute HCl or NaOH, as required. The specified pH values of solutions "A", "B", and "C" are representative of the "as measured" pH's of the naturally occurring solutions on which they are based.

Solutions "A" and "B" are near-saturated brines. Solution "A" is based on the analyses of several brines from the Salado region overlying the planned WIPP facility/horizon. This is a potash bearing region and consequently is enriched in both potassium and magnesium ions, relative to sodium chloride. Solution "A" is intended to be representative of brine which could intrude into the waste horizon via flow or percolation from above.

October 8, 1976

Solution "B" is based on the analysis of the brine obtained by dissolving a portion of rock salt core in de-ionized water. The salt core was from AEC #8 at approximately the same horizon (2725 ft.) as the intermediate-level waste and high-level waste experiment horizon of the WIPP facility. Since the AEC #8 hole is less than four miles from the center of the WIPP facility, no significant differences in the salt content are expected. This analyzed brine has an approximately 98% NaCl content and a total undissolved content (not included in analysis) of less than 1%. Solution "B" is representative of the brine resulting from a conceivable catastrophic scenario at the WIPP mine (flooding, service water line rupture, etc.) whereby water pours in, dissolves the salt, becomes saturated, then begins to attack the waste.

Solution "C" is representative of groundwater pumped from one of the aquifers in the Rustler formation. This potable water was sampled near the WIPP location. The solution "C" composition is based on two separate analyses; it consists primarily of a dilute solution of calcium and magnesium sulfates. Being representative of the WIPP hydrological and geographical locale, solution "C" was deemed more suitable for experimental tests and intercomparisons than was de-ionized water. Once tracers and geological specimens are added to de-ionized water, it no longer simulates de-ionized water. The higher ionic strength of solution "C" solves this problem.

This memo supercedes my memo entitled "Representative Simulated Brines for WIPP Experimentation," dated August 11, 1976. The brines specified there were based on commercial brine analyses which were erroneously high for several ions. This resulted in greater than saturated solutions. Brines/solutions "A", "B", and "C" have been tested in-house for solubility.

MAM:1141:blk

October 8, 1976

TABLE I
REVISED REPRESENTATIVE BRINES/SOLUTIONS
FOR
WIPP EXPERIMENTATION

<u>Ion</u>	<u>Solution "A"</u>	<u>Solution "B"</u>	<u>Solution "C"</u>
	(mg/liter) ($\pm$ 3%)	(mg/liter) ($\pm$ 3%)	(mg/liter) ($\pm$ 3%)
Na ⁺	42,000	115,000	100
K ⁺	30,000	15	5
Mg ⁺⁺	35,000	10	200
Ca ⁺⁺	600	900	600
Fe ⁺⁺⁺	2	2	1
Sr ⁺⁺	5	15	15
Li ⁺	20	-	-
Rb ⁺	20	1	1
Cs ⁺	1	1	1
Cl ⁻	190,000	175,000	200
SO ₄ ⁻⁻	3,500	3,500	1,750
B (BO ₃ ⁻⁻⁻)	1,200	10	-
HCO ₃ ⁻	700	10	100
NO ₃ ⁻	-	-	20
Br ⁻	400	400	-
I ⁻	10	10	-
pH (adjusted)	6.5	6.5	7.5
specific gravity	1.2	1.2	1.0

October 8, 1976

TABLE II
RECOMMENDED CHEMICAL COMPOUNDS FOR
PREPARING REPRESENTATIVE BRINES/SOLUTIONS
FOR
WIPP EXPERIMENTATION

<u>Compound</u>	<i>2100'</i> <u>Solution "A"</u>	<i>2700'</i> <u>Solution "B"</u>	<u>Solution "C"</u>
	(mg/liter)	(mg/liter)	(mg/liter)
NaCl	100.10g	287.00g	-
Na ₂ SO ₄	6.20g	6.20g	170
Na ₂ B ₄ O ₇ ·10H ₂ O	1.95g	16	-
NaHCO ₃	960	14	-
NaBr	520	520	-
NaNO ₃	-	-	27
KCl	57.20g	29	9.5
KI	13	13	-
MgCl ₂	137.00g	40	-
MgSO ₄	-	-	990
CaCl ₂ ·2H ₂ O	2.20g	3.30g	380
CaSO ₄ ·2H ₂ O	-	-	2.13g
FeCl ₃	6	6	3
SrCl ₂ ·2H ₂ O	11	33	33
LiCl	125	-	-
Rb ₂ SO ₄	30	1.6	1.6
CsCl	1.3	1.3	1.3
pH (adjusted)	6.5	6.5	7.5
Total Dissolved Solids	306.3g/liter	297.2g/liter	3.72g/liter

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