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INTERACTION OF RADIONUCLIDES WITH GEOMEDIA
ASSOCIATED WITH THE WASTE ISOLATION PILOT
PLANT (WIPP) SITE IN NEW MEXICO

R. G. Dosch and A. W. Lynch

Sandia Laboratories

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NOTE REGARDING SAND 78-0297

This interim report is the first of a series that will deal with nuclide transport in geomedia associated with the Waste Isolation Pilot Plant in New Mexico. The results reported in this initial survey are preliminary in nature and will be used as a basis for further investigations. Accordingly, these results do not provide sufficient information to draw any final conclusions regarding the detailed nature of nuclide transport at the WIPP site.

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ABSTRACT

A survey of the potential of geological media from the vicinity of the Waste Isolation Pilot Plant site in Southeastern New Mexico for retardation of radionuclide migration in an aqueous carrier was conducted. The survey included the measurement of sorption coefficients (K_d) for twelve radionuclides between three natural water simulants and ten samples from various geological strata.

The nuclides included ^{137}Cs , ^{85}Sr , ^{131}I , ^{99}Tc , ^{125}Sb , ^{144}Ce , ^{152}Eu , ^{153}Gd , ^{106}Ru , ^{243}Am , ^{244}Cm , and ^{238}Pu . The compositions of the simulant solutions were those expected of water in contact with potash minerals or halite deposits in the area and in a typical groundwater found in the Delaware Basin. The geological samples were obtained from potential aquifers above and below the proposed repository horizons and from bedded salt deposits in the repository horizons. In brine solutions, Tc and I were not significantly adsorbed by any of the minerals and Cs and Sr showed minimal adsorption (K_d 's < 1). The lanthanide and actinide K_d 's were typically $> 10^3$ and Ru and Sb K_d 's varied in the range of 25 to $> 10^3$. In the groundwater simulant, Tc and I showed the same behavior, but the K_d 's of the other nuclides were generally higher.

Some initial parametric studies involving pH, trace organic constituents in the simulant solutions, and radionuclide concentrations were carried out. Significant differences in the observed K_d 's can result from varying one or more of these solution parameters.

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Introduction

The first major step in the isolation of radioactive waste via deep geologic storage is site identification. The criteria used in this exercise are chosen to define a geologically stable media in an area where the probability of a radionuclide release to the biosphere is extremely low. The Los Medanos area in Southeastern New Mexico fits this description and has been selected as the site to be investigated for the proposed Department of Energy's (DOE) Waste Isolation Pilot Plant (WIPP). The site investigation is managed for DOE by Sandia Laboratories. Low level transuranic (TRU) contact handled wastes will be implanted 2100 feet below the surface in bedded salt deposits which underlie the area and remotely handled waste and high level waste experiments are proposed for the 2600 foot level in the same formation.

In any geologic storage site, there exists a finite probability of radionuclide release. For long term considerations, one scenario for such a release would be an unexpected infusion of water resulting in leaching and aqueous transport of radionuclides from the bedded salt to the surrounding media and subsequently to the biosphere. Although groundwater movement in the area--estimated to be in the lower part of a 0.01-0.5 foot per day range⁽⁹⁾--is slow, longer lived nuclides traveling unimpeded in groundwater could be expected to reach the biosphere in a time period of shorter duration than the ten half-lives generally considered to represent complete radioactive decay.

An important mechanism in retarding nuclide movement in groundwater is sorption. In the following discussion, this term will be used to encompass all mechanisms pertinent to interaction between nuclides and geomedial which include ion exchange, adsorption, and precipitation.

In the scenario described above, water would have to enter the repository, contact and leach the waste form, and eventually find its way out of the salt deposit into the surrounding rock and mineral strata. During this exit, the nuclide-bearing liquid would contact clay-containing halite in the repository horizon, polyhalite formations, anhydrite formations, and finally the sandstone and dolomite formations which are the upper bound of the repository. To a rough approximation, the concentration per unit mass of a given nuclide, C_{solid} , sorbed on a solid mineral phase can be related to the concentration per unit volume, C_{liquid} , in the liquid phase by the relation:

$$C_{\text{solid}} = KC_{\text{liquid}}$$

where K is generally known as the distribution coefficient, K_d , with units of ml/g. The use of the term K_d implies an equilibrium condition for a given reaction which is both instantaneous and reversible. In the interaction of a nuclide with a complex mineral assemblage, neither condition may apply and the nuclide sorption observed can result from one or more sorption phenomena on one or more mineral phases. To prevent confusion in nomenclature, the term K_d is used in this report, but with the understanding that what is being measured is a sorption coefficient which applies only to the system described and for the particular set of conditions used in making the measurement.

The parameter of interest in assessing the probability of radionuclide

migration is not the Kd, but rather a retardation factor (R), i.e., the average velocity of a nuclide relative to the average velocity of the aqueous carrier. Neglecting convection and dispersion effects, the Kd can be related to R as shown below:⁽¹⁾

$$\frac{V_{\text{nuclide}}}{V_{\text{fluid}}} = R = \frac{1}{1 + \frac{1-\theta}{\theta} \rho K_d}$$

where θ is the porosity and ρ is the bulk density of the geomedia. The expression addresses flow in a porous media; however, an equation of similar form using units of surface area rather than mass is applicable to fracture flow.

Ideally, retardation factors would be measured in situ in the geological formation of interest using long path lengths and available groundwater. This is not generally feasible and must be supplanted with data generated in a laboratory. This report provides the results of a series of laboratory Kd measurements for 12 radionuclides and ten samples of different geological media from the vicinity of the WIPP site, and a discussion of the conditions used in making the measurements. The nuclides chosen for study have either a high potential for leaching and/or migration, a high radiotoxicity, or a chemistry similar to that of a nuclide with these properties. They included ^{137}Cs , ^{85}Sr , ^{131}I , ^{125}Sb , ^{144}Ce , ^{152}Eu , ^{153}Gd , ^{106}Ru , ^{243}Am , ^{244}Cm and ^{238}Pu .

A given set of conditions including pH, Eh, particle size, nuclide concentrations, and brine and/or groundwater simulant composition was defined prior to starting the work and maintained throughout. The Kd values reported are considered to be a set of baseline data for use in evaluating the effects of changes in those conditions which will undoubtedly be necessary as more information about the WIPP site itself and interactions of the waste forms with bedded salt become available.

The results of some parametric studies with lanthanide elements are also given. Significant differences in K_d 's were observed as a result of varying pH and nuclide concentrations, and from the addition of trace quantities of organic contaminants to simulant solutions.

Section I. Geological Media

I-A Source and Composition

The geological samples used in this work were taken from four inch diameter core samples from AEC #8 and ERDA #9 boreholes. The locations of these boreholes in relation to the proposed WIPP site are shown in the map in Figure 1. Figures 2 and 3 represent geologic sections of the same area with arrows indicating the approximate borehole depths from which the samples used in this work were taken. These include five samples from various rock formations, four halite samples from the Salado Formation, and samples of polyhalite and Cowden anhydrite also from the Salado Formation. The specific source and composition of these samples are given below:

Magenta - Magenta is a member of the Rustler Formation which is principally dolomite, $\text{CaMg}(\text{CO}_3)_2$, containing gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and quartz, SiO_2 . Samples were taken from the 728.5' level of AEC #8 borehole.

Culebra - Culebra is also a member of the Rustler formation which is principally dolomite containing small amounts of calcite, CaCO_3 , and quartz. Samples were obtained from the 852' level of the AEC #8 borehole.

2056 Halite - Halite sample from the 2056' level in the ERDA #9 borehole. The sample contained 0.17% by weight of water insoluble material consisting of mixed-layer vermiculite-montmorillonite and glauconite.

2186 Clay - The sample was obtained from a halite core sample from the 2186.6' horizon of the AEC #8 borehole. It comprised 7.8% by weight of the

halite sample and contained montmorillonite, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$, chlorite, $(\text{Mg},\text{Fe},\text{Al})_6(\text{Al},\text{Si})_4\text{O}_{10}(\text{OH})_8$, kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, illite, $\text{KAl}_4(\text{Si},\text{Al})_2\text{O}_{20}(\text{OH})_4$, mixed layer montmorillonite - chlorite, along with some magnesite, MgCO_3 , and talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. Qualitative x-ray fluorescence analysis detected Cl, Ti and S in the material as well as the major constituents listed above.

Polyhalite - The polyhalite, $\text{Ca}_2\text{K}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, sample was from the 2304' horizon of the ERDA #9 borehole.

Cowden Anhydrite - The anhydrite, CaSO_4 , sample was from the 2562' horizon of AEC #8 borehole.

2611 Halite - Halite, NaCl , from the 2611' horizon of the ERDA #9 borehole, containing 0.38% by weight of water insoluble material.

2725 Clay - This material was obtained from a halite core from the 2725' horizon of the AEC #8 borehole. It comprised 0.96% by weight of the core and contained montmorillonite, illite, mixed layer montmorillonite - chlorite, magnesite, and possibly some gypsum and allophane. Qualitative x-ray fluorescence analysis also detected Sr, Ca, S and Ti.

Bell Canyon - A dense sandstone cemented with calcite from the 4823.4' horizon of the AEC #8 borehole. Feldspar grains and kaolinite were also identified in the material.

Cherry Canyon #4 - Sample was taken from an outcropping of the Cherry Canyon Formation in the Pine Springs area, 60 miles south of Carlsbad, New Mexico, near Highways 60 and 180. It contained quartz, dolomite, gypsum, and small amounts of two feldspars: albite, $\text{NaAlSi}_3\text{O}_8$, and microcline, KAlSi_3O_8 .

Cherry Canyon #6 - The sample was taken from the same area as Cherry Canyon #4. The sample was primarily dolomite and quartz containing a small amount of calcite.

Attempts were made to detect clay or zeolite minerals in Culebra, Magenta, and Cherry Canyon samples. Conventional separation techniques in combination with x-ray diffraction analyses failed to detect the presence of either.

The selection of the geological media for study was based on both the hydrology of the WIPP site and surrounding area and on a reasonable scenario for radionuclide transport from a bedded salt repository. The Magenta, Culebra, and Bell Canyon formations represent actual or potential aquifers. The Cherry Canyon samples were chosen because they underlie the Bell Canyon aquifer, however, subsequent data indicate a low probability of water movement through the formation and these samples have since been eliminated from the experimental matrix.

Any path to the biosphere for water which may have contacted and leached a waste form would involve migration through halite formations, and also through anhydrite and polyhalite strata interspersed in the halite. Thus these materials along with the clay contained in the halite are included in this study as they represent potential barriers to nuclide migration.

I- Preparation of Samples

Culebra, Magenta, Cherry Canyon, Bell Canyon, polyhalite, and anhydrite samples were reduced to a powder prior to use. The initial reduction was done by passing 500-1000 g samples from the cores through a jaw crusher to obtain 1/8" to 1/4" particulate. Fifty-gram portions of this were ground in a tungsten carbide ball mill until the entire amount passed through a No. 200 U.S. Standard Sieve with a nominal opening of 74 microns.

Clays from the halite samples were obtained by dissolving core samples in deionized water, filtering and washing the insoluble residue, and drying at ambient temperature in air or vacuum. In experiments with rock-salt minerals, a 350 to 840 micron particle size range was used.

I-C Surface Area

Distribution coefficients can be expressed in units of volume per unit mass or volume per unit area. The former is used in this work, however, surface areas of some of the -200 mesh rock samples were measured using a gas adsorption (BET) technique and the results are given in Table 1. Also included are the results obtained in a Battelle study⁽²⁾ on similar samples. Their measurements were done on 44-149 micron powders using the ethylene glycol method.⁽³⁾ This method was developed for use with soil and clay samples and has been proposed for use in all surface area measurements relating to distribution coefficients.

The samples run by the ethylene glycol method were Culebra and Magenta from the 853' and 734' horizons of AEC #8 borehole, respectively. The Cherry Canyon #1, #2 and #3 were taken from the same outcropping as the Cherry Canyon #4 and #6 samples. Despite the difference in particle size and measuring technique used, the results compare reasonably well. The order of magnitude spread in the Cherry Canyon #1, #2 and #3 results may reflect heterogeneity in the outcropping, as the average value for the three determinations compares very well with the average of the Cherry Canyon #4 and #6 results.

The ethylene glycol method of surface area measurement appears to be more difficult and time consuming than the BET method. The general agreement in the data in Table 1 indicate that considerably more evidence of desirability should be available prior to any decision to use the ethylene glycol method as the "standard" in determining surface areas for use in Kd calculations.

Section II. Brine and Groundwater Simulants

The bulk of the Kd measurements reported herein were done using simulated brines and groundwater of the compositions given in Table 2. The

Brine A composition is based on that expected in an aqueous solution in contact with potash deposits found in the vicinity of the WIPP site. The Brine B composition is typical of water in contact with halite deposits in the repository horizons. The groundwater Solution C composition is based on analyses of shallow groundwaters from the Los Medanos area⁽⁴⁾ above the evaporites and is intended to represent an "average" composition.

In determining Kd values for halite particles, saturated brines prepared from the particular core sample from which the halite had been taken were used as the liquid phase.

Section III. Solution Chemistry

III-A Simulants

The use of simulated brines became necessary as both naturally occurring brines and core samples from repository horizons are currently available in very limited quantities. Simulants do offer the advantage of providing a reproducible matrix which allows for direct comparison of Kd data generated in different laboratories.

Potential problems in using simulants could arise from the absence of trace constituents which may be present in natural waters. If these are common inorganic species, the effect on Kd's would probably be negligible. However, trace quantities of organic compounds or dissolved gases such as hydrogen sulfide could produce significant changes in Kd values should they tend to form stable complexes with some nuclides. The effect of trace quantities of organics which may be introduced into the repository as rad-waste is being addressed and is discussed in Section VIII.

III-B Eh

In aqueous migration from a deep geologic storage site, nuclides would most likely encounter both anoxic and aerobic conditions, in that

order, as the biosphere is approached. The potential effect on Kd values could be many orders of magnitude; however, this should be limited to nuclides such as J, Np, and Pu which may undergo redox reactions in the potential range encountered.

Oxidizing conditions have been used to date as they are believed to produce the "worst case" with respect to migration, i.e., the higher valence states of the previously mentioned actinides tend to have lower Kd's. and they will be encountered in any scenario leading to contamination of the biosphere.

III-C pH

The effect of the pH is believed to be extremely important in both the solution chemistry and the adsorption mechanism involved in the Kd for a given geological media. Problems encountered in determining Kd values in systems where solution pH is varying are discussed in Section VII. Changes in the adsorption characteristics of clays, oxides, and some zeolite materials as a function of pH are well documented.⁽⁵⁾

The initial pH values of 6.5, 6.5 and 7.5 for Brine A, Brine B and Solution C simulants, respectively, were chosen as being representative of field pH measurements of natural brines and groundwaters in the Los Medanos area.

III-D Radionuclide Concentration

Ideally, a distribution coefficient should be independent of concentration. This condition usually exists only over a narrow concentration range and, therefore, nuclide concentrations should be chosen which are somewhat representative of those expected in a repository. The problem lies in the fact that little or no data exists to aid in estimating leaching rates under conditions expected after closure of a repository. These include

glass or other waste forms at elevated temperature (70-200°C) and lithostatic pressure (2000 psi) in contact with "wet" salt or brine. Another unknown, at present, is the effect of radiolysis on leaching mechanisms and rates. Available leaching data is primarily the result of laboratory leaching experiments with simulated waste in distilled water at ambient temperature.

In a study similar to this done for Sandia at Battelle Northwest Laboratories, nuclide concentrations were based in part on a 30 day static leach test of a monolithic Battelle high level zinc borosilicate glass waste in distilled water. Samples of simulated high level waste glass prepared at both Battelle and Sandia Labs using calcined high level waste oxide simulant and Battelle zinc borosilicate glass frit have been in a leach test at Sandia for the past year.⁽⁶⁾ These tests are being conducted in a quartz Soxhlet apparatus in which monolithic glass samples are in contact with freshly distilled water at 95°C. Leach rates of Cs, Sr, Mo, and the total weight loss are monitored on a monthly basis. The results are given in Table 3 along with some Battelle results for comparison. The Sandia La and Eu data represent leaching which occurred in the eleventh month of test, as no attempt was made to determine these elements in the earlier leachate samples.

Where direct comparisons are possible, the leach rates observed at 95°C are consistently greater by approximately one order of magnitude than those observed at ambient temperature. The presence of phosphate in the glass also appears to result in higher leach rates.

The purpose of including the data in Table 3 in this report is to provide some basis for estimating nuclide concentrations which might be found in water associated with or leaving a repository. The problem remains of choosing hypothetical contact times and volumes. The waste from one tonne

of commercial nuclear fuel fixed in a single cube of glass with a volume of 3 cubic feet is used as the nuclide source in the following discussion. On the order of 7.5 liters of brine originating from water in the surrounding 30 cm of halite could be expected to be in contact with the source per meter length canister.⁽⁷⁾ If the repository remains intact, contact time would be indefinite. Should breaching and water intrusion occur, contact times of months or years are possible as typical groundwater velocities of 0.01 foot per day are observed in the area of the repository.⁽⁹⁾

Using the hypothetical 23 liter contact volume for a 10 foot canister and a four month average contact time along with the source leach rates in Table 3, concentration ranges for nuclides in brine leaving the repository were calculated and are given in Table 4. Obviously, the liquid volume associated with the waste is dependent on the scenario envisioned for water intrusion and may be orders of magnitude larger, thus diluting nuclide concentrations. On the other hand, leach rates may be considerably higher due to temperature, pressure, and radiolysis effects or increased surface area resulting from cracking or devitrification, both of which would tend to increase nuclide concentrations.

In order to simplify both sampling and counting operations in the initial work, an activity of approximately 1 $\mu\text{Ci}/\text{ml}$ was used for all determinations unless stated otherwise. The corresponding nuclide concentrations based on the suppliers' analyses of the isotopes used are listed in Table 5. In general, they fall in or near the ranges given in Table 4, with the obvious exception of ^{131}I which has a very high specific activity and ^{106}Ru , which was thought to be carrier free, and subsequently found to contain a high percentage of stable isotope.

Unless otherwise stated, all distribution coefficient measurements were

done using a single nuclide in the brines or groundwater to eliminate competing ion effects. The effect of the nuclide concentration on K_d 's is of concern and some initial work in this regard is presented in Section VII.

Section IV. Experimental Procedure

IV-A Apparatus, Sample Size and Sampling

Samples of rock, clay, anhydrite, polyhalite, or halite were weighed directly into 30 ml capacity polyethylene dropping bottles and 20 to 25 ml volumes of doped brine or groundwater were added. The ratio of liquid to solid was typically in the range of 30 to 35. Due to limited quantities of the clay samples, higher ratios were used, i.e., 50 for the 2186' clay and 100-150 for the 2725' clay.

The bottles were sealed by placing a piece of polyethylene film over the opening and replacing the bottle top. Agitation was provided by orbital, reciprocating, or wrist-action shakers. Samples for analysis were taken by replacing the polyethylene film with a 0.8 μ pore size Gelman filter, tightening the dropping bottle top down over the filter, and squeezing the bottle to force 0.5 to 1.0 ml volumes into pre-weighed polyethylene vials. Quantitative volumes were determined from weight and density measurements. The filters were replaced with polyethylene film and the agitation continued.

Portions of all "feed" solutions were put in identical polyethylene dropping bottles, agitated, and sampled at the same time and in the same manner. The activity in the filtered "feed" samples were used as the initial solution activity in the K_d calculations.

IV-B Analyses

The activity in solutions containing ^{137}Cs , ^{85}Sr , ^{106}Ru , ^{59}Fe , ^{131}I , ^{125}Sb , ^{152}Eu , ^{144}Ce , or ^{153}Gd was determined by x-ray spectroscopy. A Harshaw 3" x 3" NaI(Tl) scintillation crystal or an Ortec VIP Series

Coaxial Ge(Li) solid state detector were used. Data was accumulated and processed by a PDP-11/20 computer system. ^{99}Tc beta activity was measured using a mica end-window Geiger tube or by liquid scintillation counting. Alpha activities were determined by liquid scintillation counting. Since only relative activities are needed to determine K_d 's, units of cpm/ml were used in all calculations.

IV-C Equilibration Time

Samples of fission product nuclides were generally taken after 14-20 and 30-35 day equilibration periods. In some instances, more frequent sampling was done. Variation in K_d 's between the two sampling times were generally within a factor of two and are believed to result from changes in concentration due to adsorption on container walls or pH changes in both the sample and feed solutions rather than from rock-nuclide sorption kinetics.

Equilibration times of 170 days were used in the actinide experiments. This extended period was dictated by delays in acquiring laboratory facilities rather than by experimental design.

Section V. K_d Data

The results of K_d measurements using the conditions described in previous Sections are given in Tables 6-15. Each table represents a different geological sample and contains the K_d 's determined for the various brine/groundwater-nuclide combinations listed and a pH range including the initial feed pH and final sample pH values. The K_d ranges given for the fission product nuclides include two or more measurements made during the course of the experiment. Error associated with these measurements is certainly the most significant at the high ($> 10^4$) and low (< 1) ends of the K_d range, where background to signal ratios are high or calculations are based on small differences in large numbers. Two-to-fivefold variations of K_d 's

between duplicate analyses in these regions were not uncommon. Another obvious source of uncertainty is sampling, both in picking a section of core to represent a geological formation and in taking small samples to represent the core. The magnitude of error due to heterogeneity in a given core sample is unknown, as multiple samples were not used in this survey.

Section VI. Discussion of Kd Data

VI-A Cesium

Cesium adsorption from brines "A" and "B" on Culebra and Magenta samples, representing a potential aquifer region overlying the repository horizons, is minimal or non-existent with Kd's ranging from 0 to 2. Adsorption from groundwater C is slightly higher (Kd's from 4 to 10). In the potential aquifers underlying the repository, Bell Canyon and Cherry Canyon formations, Kd's in the brines range from < 1 to 16 and those in "C" from 30 to 140. In general, Cs adsorption is slightly higher in "B" than in "A" brine and increases significantly in the groundwater "C" simulant. These trends tend to support an ion exchange mechanism for Cs adsorption.

Similar results are observed on the samples associated with the repository horizons, with the exception of the polyhalite sample, which did not adsorb Cs from any of the solutions used.

VI-B Strontium

The adsorption of Sr on the rock samples from potential aquifer regions was very low with a Kd of 5 being the highest value observed in both brines and groundwater simulant.

Of the materials associated with the repository horizons, only the polyhalite sample showed any appreciable adsorption of Sr from the brine solutions that would be associated with the region.

The interstitial clay in the halite formation shows no tendency to

adsorb Sr from the brine solutions (Tables 8 and 12), and this may be attributed in part to the relatively high concentration of stable Sr used in the simulants. However, the same behavior was observed in an experiment where a brine prepared by dissolving a halite core and doped with < 0.3 ppm ^{85}Sr was cycled through a column of the halite particles from the same core (Table 2). In this case, only a slight reduction in Sr activity was observed (which may have resulted from adsorption on the glass column or Tygon tubing used to circulate the brine), while ^{144}Ce was quantitatively removed by the halite.

VI-C Europium, Gadolinium and Cerium

These nuclides have been grouped together for discussion because their chemistries are very similar, particularly with respect to hydrolysis, and secondly, because they exhibited similar behavior in their interactions with the geomeedia from the WIPP site.

With the exception of polyhalite samples, Kd's of greater than 10^3 for these nuclides were observed on all the geological samples with which they were contacted. Any interpretation of these data with respect to mechanism or comparison of the effects of different brines or geological media is difficult because of the contribution of hydrolysis and subsequent precipitation to the overall adsorption observed in the experiments.

For example, the polyhalite sample which was singled out as having Kd's of less than 10^3 for these nuclides (Table 10), also had final pH values which were lower than the rock or clay samples. Thus, the apparent difference in Kd's may be a hydrolysis effect rather than be related to the polyhalite material. The effect of hydrolysis is further discussed in Section VII.

VI-D Technetium and Iodine

Both of these nuclides are expected to exist as anionic species

in natural groundwaters or brines and were used in the form of pertechnetate, TcO_4^- , and iodide, I^- , in this work.

Natural ion exchangers typically exhibit extremely low anion capacities, particularly in neutral or basic solution. In this work, the only material which showed significant adsorption of either of these species was a clay sample taken from a halite core (Table 13). The adsorption was observed in Brine A and groundwater C, but neither species appeared to be adsorbed from Brine B. This behavior is not explained and suggests that the measurements should be repeated. The relatively high concentration of Tc used may have far exceeded the anion exchange capacity of some or all of the samples and this possibility is being investigated.

VI-E Ruthenium and Antimony

Difficulty was encountered in preparing the doped "A", "B", and "C" solutions due to the high concentrations of stable Ru and acid ($4\text{NH}_4\text{Cl}$) in the ^{106}Ru solution used. Adjustment of pH after doping resulted in precipitation of > 95% of the Ru. The final feed solutions were estimated to contain approximately $0.10 \mu\text{Ci/ml}$ of ^{106}Ru in "B" and "C" or 25 ppm total Ru.

General trends observed in the Kd measurements include: 1) higher Kd's for the clay minerals than for the rock samples, 2) higher Kd's in simulants "B" and "C" than observed in "A". The latter effect may be the result of brine composition, but more likely is a hydrolysis effect as the final equilibrium pH of "B" and "C" is higher than that in the "A" brine.

Antimony was added to the group of nuclides being studied late in this work, and there are not sufficient data available on which to base any general statements.

VI-F Actinides

The actinides used in this work were supplied as Am(III), Cm(III), and Pu(IV) solutions and used at face value. No attempts were made to determine the Pu species present in the simulant solutions after doping. The nominal activity of the actinides in the solutions used in this work was $1\mu\text{Ci/ml}$, however, the final activities in the "feed" solutions were lower (Table 16). The doping was done by adding the isotope solutions to containers and evaporating to dryness at room temperature. The brines or groundwater solutions were then added to the containers and the solutions were set aside for several days. The amount of isotope used was sufficient to provide an activity of $1.0\mu\text{Ci}$ per milliliter of solution if the entire amount was dissolved. The actinide activity added to the feed solutions versus the activity found in the "feed" solutions after 170 days equilibration and sampling through an 0.8μ filter are compared in Table 16.

The actinide feed concentrations used in the Kd calculations are from 1 to 3 orders of magnitude less than the nominal actinide concentration. In general, the actinide concentration in groundwater "C" at a pH of 7.3-7.4 are greater than those in the brine solutions in the 6.9-7 pH range. This is particularly true for ^{244}Cm , where the concentrations are 2 to 3 orders of magnitude lower in the brine solutions.

Kd values for the actinides of 300 or greater are observed for all the geological samples if the halite Kd's are based on weight of insoluble material rather than the weight of the total halite sample. In general, the Kd values in the groundwater "C" are higher than in Brine "B" which could result from hydrolysis due to higher pH in the "C" solutions, however there are some cases where this Kd order is reversed.

The reasonably good agreement between the Kd values for the clay

samples (Table 9) and the halite containing interstitial clay particles (Tables 8 and 12) suggests that the halite in the vicinity of the repository can serve as a barrier to actinide migration.

VI-G Iron (Ferric)

The presence of iron from cannister or overpack corrosion in association with any radionuclides which may be leached from a waste form in a salt mine environment is very probable. Thus, it was decided to measure the Kd's of iron on some of the geological samples from the WIPP site as a basis for future ion interaction studies. Simulants A, B and C were doped at 1 $\mu\text{Ci/ml}$ with ^{59}Fe , resulting in solutions of pH equal 7.0, 6.7 and 4.7, respectively. No pH adjustments were made prior to use.

After a 14 day equilibration period, significant decreases were noted in the ^{59}Fe activity in the A and C simulant feeds and no activity was detected in the B simulant feed after sampling through a 1 micron pore size filter. No ^{59}Fe activity was detected in the liquid phases of any of the samples, which included the three simulant solutions in contact with Magenta, Culebra, 2186.6' Clay and 2725' Clay, implying a Kd of ∞ .

Section VII. pH and Nuclide Concentration Effect on Kd

The first investigation into the contribution of the pH of the aqueous phase and effect of nuclide concentration on the sorption coefficient involved ^{152}Eu sorption from brines A and B and groundwater C on samples from the Magenta and Culebra formations. The feed solutions used are described in Table 17.

The experimental procedure used was the same as that described previously, except two blank samples of each feed solution were included instead of one. At the end of a two week equilibration period, the pH of the samples and feed solutions were measured. One of the feed B and C solutions was then adjusted

so that its pH was equal to that observed in sample solutions containing that feed. A sodium carbonate solution was used for the pH adjustment, which was done over a period of three days. By the time analytical samples of the adjusted feeds were taken, the pH of some of them had increased and was higher than the corresponding sample (Table 18). The pH of the Brine A feeds was not adjusted as the final values were the same as those in the samples.

The pH of all the solutions was remeasured when the three month samples were taken for analyses. The pH of the adjusted feeds decreased significantly (Table 18) during this period, probably due to absorption of atmospheric carbon dioxide.⁽⁸⁾ The pH of the solutions contacting the rock also varied with some increasing and others decreasing; however, the change was consistent within a given set of samples containing the same rock and solution.

The ¹⁵²Eu activities in the 3 month samples of the feed solutions and pH adjusted feed solutions are given in Table 19. Distribution coefficients calculated from both the feed activities and pH adjusted feed activities after two week and three month periods are listed in Table 20.

Europium is apparently more soluble in Brine A than in Brine B at the same pH or in the C composition at higher pH. The effect of adjusting the pH in B and C solutions definitely resulted in hydrolysis and formation of some species which did not pass through an 0.8μ filter. It is also of interest that significant decreases in activity in the pH adjusted feeds were observed for all Eu concentrations used. Kd's calculated from feed activities at different pH varied as much as a factor of 18, but generally agreed within a factor of 3. Variation in Kd can also be observed as a function of sample pH.

Section VIII. The Effect of Trace Organic Contaminants on Kd's of ¹⁵²Eu, ¹⁵³Gd, and ¹⁴⁴Ce

One of the concerns in estimating migration rates of radionuclide in aqueous media is the ionic form of the nuclide of interest. Experiments have shown that the simple ionic forms of most polyvalent cations interact quite readily with geologic media from the WIPP site via ion exchange or other sorption phenomena. These interactions serve to retard the movement of the ionic species relative to the aqueous matrix containing them.

The extent of the nuclide-geologic media interaction can be significantly altered by changes in the ionic form of the nuclide. Examples of such changes are redox reactions which may result in species of zero or negative charge types and reactions with available inorganic or organic ligands to form complex species with different chemical properties.

A cooperative Sandia-UNM* study has been initiated to investigate both sources and effects of organic ligands which may reasonably be expected to be associated with the waste repository at the WIPP site in Southeastern New Mexico. One such source which may be present in large quantities in the repository is the plywood used in containers for shipping TRU waste. Samples of these containers are being refluxed in synthetic Brine B at 70°C, the maximum temperature expected in the TRU waste horizon in the repository. The initial samples of this brine, subsequently referred to as B*, were taken after 5 weeks of refluxing.

Although no significant physical degradation of the plywood was observed after this time period, chemical leaching did occur as evidenced by the coffee

* The principal investigator at the University of New Mexico is Dr. Robert T. Paine.

brown appearance of the brine. GC-MS analysis of the brine indicated the presence of organic material, but identification was inconclusive. Infrared spectroscopy was used to examine carbon tetrachloride and benzene-acetone extracts from the brine. The extracted organic material fell into the general class of esterified rosin compounds, but no specific identification was possible. Qualitative observation indicated that the brine contained extremely small amounts of organic material. Neither solvent system used extracted the colored species from the brine.

The effect of plywood extract on lanthanide distribution coefficients (K_d 's) was determined by measuring K_d 's for ^{153}Gd , ^{144}Ce and ^{152}Eu between five geologic media from the WIPP site and the brine B* containing the plywood extract, and comparing these values with K_d 's obtained in identical experiments using pure Brine B. Both brine solutions were doped with all three of the isotopes, approximately 1 $\mu\text{Ci}/\text{ml}$ of each, and the pH was readjusted to 6.5. Ten milliliter aliquots of the brines were added to one-half gram samples of the geologic media which had been reduced to -200 mesh size. Samples of the brines were taken for analysis after two-week and four-week equilibration periods during which time the samples were agitated on a shaker. Both the "feed" solutions and samples were filtered through an 0.8μ filter prior to counting. The results are given in Table 21.

Although both the B and B* brines were doped initially with the same concentrations of tracers, there is a significant difference in the activity of the feed samples taken. This could result from adsorption on the polyethylene containers or hydrolysis and subsequent filtration of hydrated oxides of the tracer elements through the 0.8μ filters. In either case, the effect occurs to a significantly lesser extent in the brine B*, which is probably the result of interaction between the tracers and some ligand

extracted from the plywood to form complexes which are less susceptible to hydrolysis. The feed activities in B* also appear to be decreasing with time at a faster rate than those in B.

A similar trend is observed for Kd's where lower values are generally associated with the brine B*. The exception is the 2186.6' clay material, which seems to sorb the tracers equally well or better from B*.

The difference in Kd values could also result from complex formation. The complexing ligand may be a rosin derivative, many of which form very stable compounds with heavy metals. It may also be the species which causes the brown coloration of the brine. Observation of the analytical samples taken from the brine B* samples showed that the clay material had completely decolorized the brine. The other materials decolorized the B* samples to varying degrees, as given below in order of decreasing intensity:

Feed > Magenta > Culebra $\approx$ Bell Canyon > Cowden > Clay solution

Work in this area will continue with attempts to identify the complexing ligands and a study involving higher extract concentrations and longer equilibration times. Similar work will be done using extracts which are being prepared from other organic materials expected to be associated with TRU waste such as rubber gloves, swipes, detergents, etc. Based on lanthanide results, an experimental matrix will be designed to study the actinide elements.

Section IX. Summary

A survey of the potential of geological media from the vicinity of the Waste Isolation Pilot Plant site in Southeastern New Mexico for retardation of radionuclide migration via an aqueous carrier has been completed. Solution simulants representing water in equilibrium with potash minerals or halite zones and a typical groundwater were spiked with radionuclides and contacted

with geological samples to obtain sorption coefficients, Kd's. The samples were taken from potential aquifers above and below the repository horizons and from bedded salt deposits in the repository horizons. The nuclides chosen for study represent those with a high potential for leaching and/or migration, high radiotoxicity, or those with a chemistry similar to nuclides with the aforementioned properties. They included ^{137}Cs , ^{85}Sr , ^{131}I , ^{99}Tc , ^{125}Sb , ^{144}Ce , ^{152}Eu , ^{153}Gd , ^{106}Ru , ^{243}Am , ^{244}Cm and ^{238}Pu .

A very general summation of the Kd results in brine simulants is as follows: Anionic species, TCO_4^- and I^- , showed little or no tendency to adsorb on any of the geological media ($\text{Kd}'s \leq 1$), with the possible exception of a clay material from a halite stratum ($\text{Kd} < 5$). Cs and Sr Kd's were also generally less than 1, but values in the range of 10-20 were observed on several minerals. Ru Kd's ranged from 25 to $> 10^3$, depending on the brine and geomedium. The lanthanide and actinide Kd's were typically $> 10^3$, with only polyhalite showing significantly lower adsorption.

In the groundwater simulant, Tc and I showed the same behavior. The Kd's of the other nuclides were slightly higher, particularly those of Cs and Sr. This would be expected if the sorption were due to an ion exchange mechanism, but, in the case of the lanthanides and actinides, may also result from an increased contribution of hydrolysis to the Kd due to the higher pH of the groundwater simulant.

Important parameters in Kd measurements include solid sample form, simulant composition, Eh and pH, and radionuclide concentration. In the Kd survey measurements, an initial set of these parameters was selected and, wherever possible, was used throughout the work. Parametric studies with Eu involving pH, trace organic constituents in the simulant solutions, and radionuclide concentrations have shown that significant differences in Kd's

can be observed by varying any of those parameters.

A general observation which can be made from data obtained to date is that a K_d represents an empirical value for nuclide adsorption, which includes the effects of physical adsorption, ion exchange, and hydrolysis or other precipitation processes. The utility of a given K_d value is unambiguous only for that set of conditions used in making the measurement. K_d information which is used in modeling radionuclide migration should be in the form of a range of values generated in parametric studies under the variety of conditions postulated for a specific repository site.

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Table 1

Surface Areas of Geological Samples

<u>Sample</u>	<u>Size Range, (μm)</u>		<u>Surface Area, m³/g</u>	
	<u>BET</u>	<u>Ethylene Glycol</u>	<u>BET</u>	<u>Ethylene Glycol</u>
Magenta	< 74	44 - 149	6.3	8.1
Culebra	< 74	44 - 149	4.2	7.1
Cherry Canyon #1	--	88 - 149		1.3
Cherry Canyon #2	--	88 - 149		5.2
Cherry Canyon #3	--	44 - 149		11.0
Cherry Canyon #4	< 74	---	6.3	--
Cherry Canyon #6	< 74	---	4.2	--

Table 2

REPRESENTATIVE BRINES/SOLUTIONS
FOR
WIPP EXPERIMENTATION

Ion	Brine "A" (mg/liter) (± 3%)	Brine "B" (mg/liter) (± 3%)	Solution "C" (mg/liter) (± 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

Table 3

Leaching Data For Zinc Borosilicate Glass Waste Forms

<u>Element</u>	95°C Leach ($\mu\text{g}/\text{cm}^2$ day)		Ambient Leach ($\mu\text{g}/\text{cm}^2$ day)
	<u>SIA</u> (1)	<u>BNW</u> (2)	<u>BNW</u> (3)
Cs	1.6	0.27	0.038
Sr	0.69	0.29	0.033
Mo	1.04	0.58	---
Eu	0.015	0.003	1×10^{-4}
La	0.02	0.046	---
Am	--	--	8.8×10^{-4}
Cm	--	--	9.6×10^{-7}
Pu	--	--	7×10^{-3}
Total Weight Loss	88	44	---

- (1) Prepared at Sandia using Battelle zinc borosilicate glass frit and a calcined high level waste oxide simulant containing phosphate.
- (2) Believed to be of the same composition as the SIA glass waste with the exception that phosphate was not added.
- (3) Calculated from data in Battelle document entitled "Batch Kd Measurements of Nuclides to Estimate the Migration Potential at the Proposed Waste Isolation Pilot Plant in New Mexico," by Serne, R. J., Rai, D., Mason, M. J., and Molecke, M. A., EML-2448/UC-70.

Table 4

Estimated Nuclide Concentration in Repository Brine

<u>Element</u>	<u>Concentration Range</u> ⁽¹⁾
Cs	16 - 710 $\mu\text{g/ml}$
Sr	16 - 310 $\mu\text{g/ml}$
Eu	3.3×10^{-3} - 6.6 $\mu\text{g/ml}$
Am	0.4 - 4 $\mu\text{g/ml}$
Cm	4.3×10^{-4} - 4.3×10^{-2} $\mu\text{g/ml}$
Pu	3.3 - 33 $\mu\text{g/ml}$

-
- (1) The lower values were estimated using the ambient temperature leaching data in Table 2. The higher values for Cs, Sr and Eu are based on the leach rates of SLA glass at 95°C and those for Am, Cm and Pu were estimated by assuming an increase of one order of magnitude in leach rate at the increased temperature.

Table 5

Nominal Concentration of Nuclides Used in Kd Measurements

<u>Nuclide</u>	<u>Concentration, ppm</u>
¹³⁷ Cs	0.012
Stable Cs	1.0
⁸⁵ Sr	0.03 - 0.3
Stable Sr	5 - 15
¹⁰⁶ Ru	2500
⁹⁹ Tc	59
¹⁵² Eu	0.1 - 1.0
¹⁴⁴ Ce	3×10^{-4}
¹³¹ I	5×10^{-5}
¹⁵³ Gd	0.2 - 2.0
¹²⁵ Sb	≤ 0.01
²⁴³ Am	5.4
²⁴⁴ Cm	0.012
²³⁸ Pu	0.058

Table 6

Distribution Coefficients on Samples From the Magenta Dolomite

Fission Product Distribution Coefficients						
	<u>pH range</u>	<u>Cs</u>	<u>Sr</u>	<u>I,Tc</u>	<u>Eu,Gd</u>	<u>Ru</u>
Brine A	6.5 - 6.9	< 1	1	0 - 1.5	$> 5 \times 10^3$	40-50
Brine B	6.5 - 7.5	< 1	1	< 1	$> 5 \times 10^3$	500-600
Sol'n C	7.5 - 8.2	4	5	0 - 1.5	$> 10^4$	400-550

Actinide Distribution Coefficients				
	<u>pH range</u>	<u>Pu</u>	<u>Am</u>	<u>Cm</u>
Brine B	6.5 - 7.8	5.4×10^3	3.1×10^2	1.3×10^3
Sol'n C	7.5 - 8.2	2.4×10^3	2.4×10^3	4.2×10^4

Table 7

Distribution Coefficients on Samples From the Culebra Dolomite

Fission Product Distribution Coefficients						
	<u>pH range</u>	<u>Cs</u>	<u>Sr</u>	<u>I,Tc</u>	<u>Ba,Gd</u>	<u>Ru</u>
Brine A	6.5 - 6.9	< 1	< 1	< 1	$> 10^4$	25 - 35
Brine B	6.5 - 7.6	1-2	1-2	< 1	$> 10^4$	640 - 660
Sol'n	7.5 - 8.2	7-10	4-5	< 1	$> 10^4$	240 - 400

Actinide
Distribution Coefficients

	<u>pH range</u>	<u>Pu</u>	<u>Am</u>	<u>Cm</u>
Brine B	6.5 - 7.8	2.1×10^3	2.6×10^3	1.2×10^4
Sol'n C	7.5 - 8.3	7.3×10^3	2.2×10^4	1.1×10^5

Table 8

Distribution Coefficients on Halite From The
2056' Horizon of ERDA #9 BoreholeActinide Distribution
Coefficients¹

<u>pH range</u>	<u>Pu</u>	<u>Am</u>	<u>Cm</u>
7.0 - 7.1	17	306	354
	(1.0×10^4)	(1.8×10^5)	(2.1×10^5)

- 1) The Kd values in parentheses were calculated from the weight of water insoluble material in the halite. The lower values are based on the total weight of halite taken.

Table 9

Distribution Coefficients on Samples of Clay From
The 2186.6' Horizon of AEC #8 Borehole

Fission Product Distribution Coefficients						
	<u>pH range</u>	<u>Cs</u>	<u>Sr</u>	<u>I,Tc</u>	<u>Gd,Eu</u>	<u>Ba</u>
Brine A	6.5 - 7.0	< 1	< 1	< 2	$> 2.5 \times 10^3$	150-180
Brine B	6.5 - 7.7	4-6	< 1	< 1	$> 10^4$	$> 2 \times 10^3$
Sol'n C	7.5 - 7.8	80-120	3-6	< 1	$> 10^4$	$> 1 \times 10^3$

Actinide
Distribution Coefficients

	<u>pH range</u>	<u>Am</u>	<u>Pu</u>	<u>Cm</u>
Brine B	6.5 - 8.0	1.1×10^3	4×10^4	1.9×10^4
Sol'n C	7.5 - 8.4	3.5×10^3	1.8×10^5	4.2×10^5

Table 10

Distribution Coefficients on Samples of Polyhalite
From the 2304' Horizon of ERDA #9 Borehole

Fission Product Distribution Coefficients						
	<u>pH range</u>	<u>Cs</u>	<u>Sr</u>	<u>Eu,Ce</u> ¹	<u>Sb</u>	<u>Tc</u>
Brine A	6.5 - 7.0	< 1	5-10	10-20	< 1	< 1
Brine B	6.5 - 7.2	< 1	19-22	430-700, 50-55	0.9-1.5	< 1
Sol'n C	7.5 - 7.6	< 1	35-40	100-200, 40-60	3-4	< 1

- 1) Where two ranges of values are given, the first refers to Eu and the second to Ce.

Table 11

Distribution Coefficients on Sample of Cowden Anhydrite
From the 2562' Horizon of AEC #8 Borehole

Fission Product
Distribution Coefficients

	<u>pH range</u>	<u>Gd, Eu, Ce</u>
Brine B	6.5 - 7.9	$> 10^3$

Actinide Distribution
Coefficients

	<u>pH range</u>	<u>Am</u>	<u>Pu</u>	<u>Cm</u>
Brine B	6.5 - 7.9	2.9×10^2	6.7×10^3	4.2×10^3
Sol'n C	7.5 - 8.2	2.2×10^3	7.7×10^4	1.8×10^5

Table 12

Distribution Coefficients on Halite Samples From the
2611' Horizon of ERDA #9 Borehole

Column Experiment

Column Bed: 7.5 g of Halite in 1 cm diameter column

Solution: Saturated Halite Solution, 200 ml

Flow: 1 Bed volume/min.

<u>Time (days)</u>	<u>% of Initial Activity in Solution</u>	
	<u>⁸⁵Sr</u>	<u>¹⁴⁴Ce</u>
0	100	100
1	98.0	26.7
4	96.8	0.9
8	98.4	0

Actinide
Distribution Coefficients⁽¹⁾

<u>pH range</u>	<u>Am</u>	<u>Pu</u>	<u>Cm</u>
7.0 - 7.3	11	59	56
	(3.8×10^3)	(2.11×10^4)	(2×10^4)

- (1) The Kd values in parentheses were calculated using the weight of water insoluble material in the clay. The lower values are based on the weight of halite taken.

Table 13

Distribution Coefficients on Samples of Clay from
the 2725' Horizon of AEC #8 Borehole

Fission Product Distribution Coefficients						
	<u>pH range</u>	<u>Cs</u>	<u>Sr</u>	<u>Eu, Gd</u> ¹	<u>Tc, I</u> ¹	<u>Ru</u>
Brine A	6.6 - 7.0	4-9	< 1	$> 10^3$, $2.8-4 \times 10^2$	3.5-4.5, 0-3.5	90-120
Brine B	6.7 - 7.4	3-6	< 1	$> 10^4$	< 1	$> 10^3$
Sol'n C	7.5 - 8.0	34-40	30-45	$> 10^4$, $> 3 \times 10^3$	0.7-1.5, 0.5-4	$> 10^3$

Actinide
Distribution Coefficients

	<u>pH range</u>	<u>Am</u>	<u>Pu</u>	<u>Cm</u>
Brine B	6.5 - 7.8	310	7.2×10^4	2.7×10^3
Sol'n C	7.4 - 8.4	2.3×10^3	4.0×10^4	1.6×10^5

- 1) Where two ranges of values are given, the first refers to the first element listed and the second range is for the second element listed.

Table 14

Distribution Coefficients on Samples of Bell Canyon Formation

Fission Product Distribution Coefficients						
	<u>pH range</u>	<u>Cs</u>	<u>Sr</u>	<u>Eu</u>	<u>Sb</u>	<u>Tc</u>
Brine B	6.5 - 7.4	14-16	< 1	$> 10^4$	5-8	< 1
Sol'n C	7.5 - 7.9	130-140	1-5	$> 10^4$	20-25	< 1

Table 15
Distribution Coefficients on Samples of the
Cherry Canyon Formation

Cs and Sr Distribution Coefficients		
	<u>Cherry Canyon #4</u>	
	<u>Cs</u>	<u>Sr</u>
Brine A	1-2	< 1
Brine B	10-15	< 1
Sol'n C	120-125	2.5-3.3
	<u>Cherry Canyon #6</u>	
	<u>Cs</u>	<u>Sr</u>
Brine A	< 1	< 1
Brine B	4-5	0.5-1.3
Sol'n C	29-33	2.7-2.9

Table 16

Actinide Concentrations in Feed Solutions

	<u>^{238}Pu</u>	<u>cpm/ml</u>	<u>Found</u>	<u>pH of Solution</u>
	<u>Nominal (cpm/ml)</u> ⁽¹⁾		<u>Anal. moles/l. Conc.</u>	
Brine B	2.35×10^6	1.18×10^5	1.2×10^{-8}	7.0
Sol'n	"	3.41×10^5	3.5×10^{-8}	7.4
2056' Halite Brine	"	1.39×10^5	1.4×10^{-8}	7.0
2611' Halite Brine	"	1.51×10^5	1.5×10^{-8}	7.0
	<u>^{243}Am</u>	<u>cpm/ml</u>	<u>Found</u>	<u>pH of Solution</u>
	<u>Nominal (cpm/ml)</u> ⁽¹⁾		<u>Anal. moles/l. Conc.</u>	
Brine B	2.73×10^6	1.99×10^5	1.6×10^{-6}	6.9
Sol'n	"	9.64×10^5	7.8×10^{-6}	7.3
2056' Halite Brine	"	4.37×10^5	3.5×10^{-6}	7.0
2611' Halite Brine	"	8.50×10^5	6.8×10^{-6}	7.0
	<u>^{244}Cm</u>	<u>cpm/ml</u>	<u>Found</u>	<u>pH of Solution</u>
	<u>Nominal (cpm/ml)</u> ⁽¹⁾		<u>Anal. moles/l. Conc.</u>	
Brine B	2.00×10^6	1.42×10^4	3.5×10^{-10}	7.0
Sol'n	"	4.31×10^5	1.1×10^{-8}	7.4
2056' Halite Brine	"	1.39×10^3	3.4×10^{-11}	7.0
2611' Halite Brine	"	6.19×10^3	1.5×10^{-10}	7.0

(1) These activities were determined by analyses of the actinide stock solutions, and correcting for dilutions made in preparing the feed solutions.

Table 17

¹⁵²Eu Concentration and pH of Feed Solution

<u>Simulant</u>	<u>Nominal ¹⁵²Eu Concentration</u>		<u>Initial pH</u>
	<u>μCi/ml</u>	<u>ppm</u>	
A	1.0	0.1 - 1	6.8
B	1.0	"	6.5
C	1.0	"	7.4
A	0.1	0.01 - 0.1	6.8
B	0.1	"	6.4
C	0.1	"	7.6
A	0.01	0.001 - 0.01	6.8
B	0.01	"	6.5
C	0.01	"	7.5

Table 18

pH of Feed and Sample Solutions

<u>Rock</u>	<u>Simulant</u>	Nominal ¹⁵² Eu(μ Ci/ml)	Final sample pH		Final feed pH		Adjusted Feed pH	
			2 wks.	3 mos.	2 wks.	3 mos.	2 wks.	3 mos.
Culebra	A	0.01	6.9	7.1	6.9	7.2	--	--
"	A	0.1	6.9	7.1	6.9	7.1	--	--
"	A	1.0	6.9	7.1	6.9	7.2	--	--
"	B	0.01	8.1	7.6	6.8	7.0	8.5	7.7
"	B	0.1	8.1	7.6	6.8	7.0	8.5	7.3
"	B	1.0	8.3	7.6	6.9	7.0	8.5	--
"	C	0.01	8.7	8.4	7.1	7.8	9.2	8.2
"	C	0.1	8.7	8.4	6.9	7.7	9.2	8.13
"	C	1.0	8.8	8.4	7.1	7.8	9.2	8.15
Magenta	A	0.01	6.9	7.2	6.9	7.2	--	--
"	A	0.1	6.9	7.1	6.9	7.1	--	--
"	A	1.0	6.9	7.1	6.9	7.2	--	--
"	B	0.01	7.8	7.6	6.8	7.0	8.5	7.7
"	B	0.1	7.8	7.6	6.8	7.0	8.5	7.3
"	B	1.0	7.9	7.6	6.9	7.0	8.5	--
"	C	0.01	8.4	8.4	7.1	7.8	9.2	8.2
"	C	0.1	8.4	8.4	6.9	7.7	9.2	8.1
"	C	0.01	8.4	8.3	7.1	7.8	9.2	8.2

Table 19

¹⁵²Eu Activity in Feed and pH Adjusted Feed Solutions
After 3 Months

<u>Sample</u>	<u>Simulant</u>	Nominal <u>¹⁵²Eu (μCi/ml)</u>	<u>pH</u>	<u>¹⁵²Eu (cpm/ml)</u>
Feed	A	1.0	7.2	9.97×10^4
Feed	A	0.1	7.1	$..09 \times 10^4$
Feed	A	0.01	7.2	8.53×10^2
Feed	B	1.0	7.0	5.94×10^4
Adjusted Feed	B	1.0	7.7	2.20×10^4
Feed	B	0.1	7.0	4.96×10^3
Adjusted Feed	B	0.1	7.3	1.85×10^3
Feed	B	0.01	7.0	5.94×10^2
Adjusted Feed	B	0.01	-	2.93×10^2
Feed	C	1.0	7.8	6.79×10^4
Adjusted Feed	C	1.0	8.2	5.7×10^4
Feed	C	0.1	7.8	1.02×10^4
Adjusted Feed	C	0.1	8.1	7.5×10^3
Feed	C	0.01	7.8	1.02×10^3
Adjusted Feed	C	0.01	8.2	7.8×10^2

Table 20

¹⁵²Eu Distribution Coefficients (Kd's)

Rock	Simulant	Nominal		Kd (1)		Kd (2)	
		¹⁵² Su (μCi/ml)	2 week	3 month	2 week	3 month	
Culebra	A	0.01	1.7x10 ⁴	1.5x10 ⁴	--	--	
"	A	0.1	3.6x10 ⁴	2.1x10 ⁴	--	--	
"	A	1.0	1.8x10 ⁴	4.3x10 ⁴	--	--	
"	B	0.01	3.4x10 ³	1.6x10 ³	--	7.6x10 ³	
"	B	0.1	1.1x10 ⁴	3.6x10 ³	--	1.3x10 ³	
"	B	1.0	3.7x10 ³	3.9x10 ³	8.8x10 ²	1.4x10 ³	
"	C	0.01	2.8x10 ⁴	1.3x10 ⁴	--	1.1x10 ⁴	
"	C	0.1	2.7x10 ⁴	2.6x10 ⁴	--	1.9x10 ⁴	
"	C	1.0	2.0x10 ⁴	1.4x10 ⁴	1.2x10 ³	9.6x10 ³	
Magenta	A	0.01	1.4x10 ⁴	6 x 10 ²	--	--	
"	A	0.1	1.9x10 ⁴	2.0x10 ⁴	--	--	
"	A	1.0	1.2x10 ⁴	1.4x10 ⁴	--	--	
"	B	0.01	2.8x10 ³	8.6x10 ²	--	4 x 10 ²	
"	B	0.1	8.3x10 ³	3.7x10 ³	--	1.3x10 ³	
"	B	1.0	1.1x10 ³	1.2x10 ³	3.5x10 ²	4.0x10 ²	
"	C	0.01	2.0x10 ⁴	1.7x10 ⁴	--	1.3x10 ⁴	
"	C	0.1	3.6x10 ⁴	2.2x10 ⁴	--	1.6x10 ⁴	
"	C	1.0	1.4x10 ⁴	1.5x10 ⁴	7.7x10 ²	1.3x10 ⁴	

(1) Kd based on activity in feed solutions.

(2) Kd based on activity in pH adjusted feed solutions.

Table 21

Comparison of ^{153}Gd , ^{144}Ce , and ^{152}Eu Kd's in
Brine B and Brine B* Containing Plywood Extract

14 Day Equilibration

Sample	Brine	^{153}Gd		^{152}Eu		^{144}Ce	
		cpm/ml	Kd	cpm/ml	Kd	cpm/ml	Kd
Feed	B	24,200	-	20,230	-	5,120	-
Feed	B*	38,090	-	38,090	-	7,080	-
Culebra	B		4.2×10^3		9.9×10^3		1.5×10^3
"	B*		6.3×10^2		6.6×10^2		6.0×10^2
Magenta	B		2.5×10^3		3.4×10^3		1.4×10^3
"	B*		6.5×10^1		7.0×10^1		1.1×10^2
Bell Canyon	B		3.4×10^3		3.4×10^3		3.2×10^3
"	B*		1.3×10^2		1.5×10^2		2.3×10^2
Cowden	B		2.6×10^3		2.2×10^4		2.2×10^3
"	B*		3.7×10^2		4.0×10^2		5.1×10^2
High Clay	B		6.8×10^3		8.5×10^4		1.2×10^3
"	B*		8.7×10^3		2.8×10^4		2.5×10^3

28 Day Equilibration

Feed	B	23,260	-	20,170	-	4,800	-
Feed	B*	33,350	-	35,210	-	5,910	-
Culebra	B		4.3×10^3		8.3×10^3		3.3×10^3
"	B*		2.1×10^3		1.8×10^3		1.3×10^3
Magenta	B		3.5×10^3		2.5×10^3		$\geq 10^4$
"	B*		1.4×10^2		1.6×10^2		2.5×10^2
Bell Canyon	B		4.2×10^3		2.7×10^3		3.2×10^3
"	B*		1.5×10^2		1.7×10^3		3.2×10^2
Cowden	B		$\geq 10^5$		5.4×10^3		1.8×10^3
"	B*		4.7×10^2		4.8×10^2		5.3×10^2
Hi Clay	B		6.5×10^3		8.7×10^3		6.1×10^3
"	B*		1.9×10^4		3.2×10^4		5.9×10^3

WIPP DRILL HOLE LOCATIONS

LEGEND

TD = Total Depth	● ERDA Potash Drill Holes (P1 - P21)
TA = Temporarily Abandoned	////// State Land
⊗ Deep Producing Gas	- - - - - Natural Gas Pipeline
⋈ Abandoned Well	— — — — — Land Withdrawal Boundary
⊗ Deep & Abandoned	
⊕ Potash Drill Holes	

FIGURE 1.

ALTITUDE
METERS FEET

GEOLOGIC SECTION THROUGH THE LOS MEDAÑOS AREA

Sandia Laboratories

FIGURE 2.

GENERALIZED SECTION

CLAYTON W. WILLIAMS, JR.
BADGER UNIT FEDERAL
SEC. 15, 22 S-31 E

FIGURE 3