INTERACTION OF RADIONUCLIDES WITH ARGILLITE FROM THE ELEANA FORMATION ON THE NEVADA TEST SITE

R. G. Dosch and A. W. Lynch

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ABSTRACT

Distribution coefficients have been determined for ^{137}Cs, ^{85}Sr, ^{144}Ce, ^{99}Tc, ^{152}Eu, ^{238}Pu, ^{244}Cm, and ^{243}Am between argillite from the Eleana Formation on the Nevada Test Site (NTS) and several aqueous phases. Radionuclide concentrations in the range of 1 to 0.001 $\mu Ci/ml$ were used with contact times of 14, 28, and 56 days.

Reaction mechanism, concentration effects, exchange capacity, equilibration times, and particle size effects were addressed in a more comprehensive study of the interaction of argillite with Cs in deionized water. The experimental parameters used in the distribution coefficient measurements were based in part on this work. The aqueous phases included a simulated groundwater with composition based on the analysis of a NTS groundwater, the same simulant and deionized water which were pre-equilibrated with powdered argillite, and a groundwater simulant with approximately the same qualitative composition of the NTS simulant, but with a higher ionic strength.

A system to provide continuous pH control by CO_2 addition during equilibration of the argillite-solution mixtures was designed and assembled. Initial experiments were done with Cs and Eu and the effects of pH on their distribution coefficients are discussed.

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THE ELEANA FORMATION ON THE NEVADA TEST SITE

I.   INTRODUCTION

The Eleana Formation located on the Nevada Test Site (NTS)
is undergoing preliminary evaluation as a medium for isolation
of high-level radioactive waste. As a part of this work, argillite
from the J subunit of the Eleana was studied to begin evaluation
of its potential for retardation of aqueous borne radionuclides.
Distribution coefficients (Kd) were determined for ^{137}Cs, ^{85}Sr,
^{99}Tc, ^{152}Eu, ^{144}Ce, ^{243}Am, ^{244}Cm, and ^{238}Pu between powdered
or crushed argillite and several different aqueous phases. These
included a simulated NTS groundwater, the same simulant after a
30 day equilibration with argillite, and deionized water
equilibrated with argillite for the same period of time. The
composition and preparation of the simulant are presented along
with the compositional changes which occurred during contact
with the argillite. Radionuclide concentrations in the range
of 1 to 0.001 μCi/ml were used with contact times of 14, 28, and
56 days.

As an aid in planning other Kd measurements, the interaction
of the argillite with Cs in deionized water was studied. Reaction
mechanism, concentration effects, exchange capacity, equilibration
time, and particle size effects were addressed, and are included
as a section of this report.

An apparatus used for continuous pH control by CO_2 addition
during equilibration periods used in Kd determinations is

described. The results of some initial experiments with ^{137}Cs and ^{152}Eu are included.

II.   ARGILLITE: SOURCE, COMPOSITION, AND PREPARATION

The argillite used in this work was a two inch diameter core sample from the 1805 foot level of Hole UE17e at NTS. Sample 1805 is an example of relatively hi-quartz argillite with approximately 45% quartz. The major constituents, based on x-ray diffraction analyses,[1] include quartz - SiO_2 and illite - a variable composition K-Al silicate along with lesser or trace quantities of chlorite - $(Mg, Fe, Al)_6 (Al\ Si_4)O_{10}(OH)_8$, ferroan dolomite - $Ca(Mg_xFe_{1-x})(CO_3)_2$, siderite - $FeCO_3$, microcline - $KAlSi_3O_8$, pyrophyllite - $Al_2Si_4O_{10}(OH)_2$ and sodic plagioclase - $(Na, Ca)(Al, Si)\ AlSi_2O_8$. A quantitative analyses is given in Table 1-A.

Unless stated otherwise, a -200 mesh (< 74μ) powder was used in this work. The core sample was reduced to 1/8" to 1/4" pieces using a small jaw crusher. Fifty to one-hundred gram samples of this material were taken as needed by quartering techniques and alternately ground in a tungsten carbide ball mill and sieved until the entire sample passed through a No. 200 U.S. Standard Sieve.

III. AQUEOUS PHASE COMPOSITIONS

Deionized water was used in preliminary work with stable Cs and ^{137}Cs. Distribution coefficients for ^{137}Cs and the other isotopes were also measured in a simulated NTS groundwater with a composition (Table 1-B) based on a preliminary analysis[2] of water from the Tippipah limestone and uppermost

quartzite within the Eleana. As such, the simulant composition is representative of groundwater compositions that might be expected in the event of a disastrous breach, in which inflowing water did not equilibrate with wall rock prior to contacting the waste. Other solutions included both the NTS simulant and deionized water which were equilibrated with the argillite prior to use. In each case, two liters of solution were shaken for 30 days with 40 grams of a -5 to +18 mesh fraction. The liquid to solid ratio was the same as that used in the bulk of the Kd measurements. The pre-equilibrated simulant composition should more closely resemble groundwater compositions in the event of a slower water ingress to a repository, in which the water is at least partially equilibrated with argillite prior to contact with waste.

The simulant was prepared by adding 187.1 mg of $CaCO_3$ and 32 mg of $MgCO_3$ to 800 ml of deionized water and bubbling CO_2 into the stirred solution until dissolution was complete. Then, the given amounts of the stock solutions #1 thru #5 listed in Table 2 were added and the total volume was adjusted to one liter. The final pH was 7.7 as opposed to the field measurement of 7.2. Addition of CO_2 dropped the pH to about 6.8, however, when CO_2 addition ceased, the pH slowly increased to 7.7 to 7.8 as the gas escaped from solution.

All the solutions were analyzed prior to use and the results are given in Table 1-B. Significant differences in the experimentally determined concentrations versus those added are observed for bicarbonate, sulfate, strontium, and iron.

The high bicarbonate resulted from the presence of sodium
hydroxide in solution 2 (Table 2) which reacted with CO_2
in the simulant. The excess correlated well with the sodium
added via that solution. The sulfate and strontium deviations
are probably due to addition as impurities in other compounds
which were used, while the decrease in iron content to below
atomic absorption detection limits is most likely the result
of hydrolysis and subsequent precipitation.

Equilibration of the simulant with argillite resulted
in compositional changes (Table 1-B) which appear to be associated
with ion exchange reactions in which Ca, Mg, and K ions
replaced Na and Sr in the argillite. The net change in concentration
of the former was -1.1 meq/liter as opposed to +1.2 meq/liter
for the Na and Sr. After equilibration with argillite, the
deionized water can be described as a dilute solution ($\sim 10^{-4}$M)
of sodium bicarbonate containing trace quantities of Si, K^+, and
F^-.

IV. INITIAL Kd SURVEY

The initial work with the Eleana argillic was a "survey"
experiment designed to determine if the formation had any
significant potential for retardation of radionuclide migration.
At the time the initial measurements were carried out, an
analysis of water associated with the Eleana formation was not
available and a simulant based on the composition of groundwater
in the Delaware Basin in Southeastern New Mexico was used
(Table 3). The work is included as an independent section in
the report because the groundwater simulant and, in some cases

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the nuclide concentrations, were different than those used in the bulk of the measurements. Some of the effects of these differences are discussed in subsequent sections of this report. Also, since Delaware Basin simulant Kd's for geological media associated with the proposed WIPP site are available,[4] some comparison of the two sites can be made in terms of potential for nuclide migration in sub-surface waters.

The Delaware Basin simulant was doped with ^{137}Cs, ^{85}Sr, ^{152}Eu, ^{125}Sb, ^{144}Ce, or ^{99}Tc at an activity of 1 µCi/ml. Analytical concentrations associated with this activity were calculated from information provided by suppliers and are listed in Table 4 along with similar data for some isotopes used in subsequent work. In the case of Cs and Sr, the concentration of stable isotopes in the simulant was much greater than the radioisotope concentrations. The isotopes were chosen because they have a high potential for leaching and migration, or because their chemistry is similar to other nuclides of more interest because of high toxicity combined with long half-lives, such as the actinides. In all measurements, a single isotope was used in the liquid phase to preclude competing ion effects.

The experimental and calculational methods used are described in detail in Section VIA and VIB of this report. The results of the Kd measurements are given in Table 5 along with the pH of the solutions at the end of the four week equilibration period. The Kd values are of the same magnitude as those observed for geological samples from the WIPP site under the

same experimental conditions with the exception of ^{137}Cs, which is considerably higher for the Eleana argillite as compared to WIPP samples.

V. INTERACTION OF Cs WITH ARGILLITE

A preliminary study of a more comprehensive nature was done to provide knowledge necessary for planning and interpreting nuclide migration studies in the Eleana argillite. A simple system - a monovalent cation, Cs, in deionized water - was picked as a starting point.

The initial experiment was done to determine the capacity and absorption rate of Cs on argillite. The material used was part of a 100 gram portion of the UE17e 1805 core sample which was reduced to a powder as previously described. One gram samples were added to 20 ml volumes of deionized water containing 25, 100, 500, 1000, and 2000 ppm of Cs, added as CsCl, and the samples were agitated on a wrist action shaker. At the same time, a set of samples containing 5 grams each of argillite and 100 ml of 0, 25, 100, 500, 1000, and 2000 ppm Cs$^+$ solution were also started.

The 20 ml bottles were sampled at 5, 24, and 95 hour periods and the 100 ml bottles at 120 and/or 168 hours. Cesium uptake in meq/g and Kd values are given in Table 6. The pH of the larger sample solutions was monitored periodically and this data is in Table 7. The Na$^+$, K$^+$, Ca^{++}, Mg^{++}, and Sr^{++} concentrations in the large sample volumes were determined after 120 or 168 hours by atmoic absorption analyses. These

results are given in Table 8. Table 9 lists the total milli-equivalents of Na^+, K^+, Mg^{++}, Ca^{++}, and Sr^{++} found in the 100 ml. sample and the number of milliequivalents of Cs^+ adsorbed from the same volume on 5 g of argillite.

The results in Tables 6-9 indicate that the primary Cs absorption mechanism is ion exchange and that maximum Cs absorption occurs within the first few hours of contact with the liquid phase. The primary reaction occurring when argillite is contacted with deionized water appears to be sodium - hydrogen ion exchange as evidenced by initial increases in both the Na^+ and OH^- concentrations. As the Cs^+ concentration in solution increases, the H^+ ion concentration also increases (Table 7) indicating that Cs^+ is replacing H^+ ion. At concentrations up to 100 ppm Cs^+, the primary reaction is exchange with Na^+ and H^+. At higher concentrations, K^+, Ca^{++}, Mg^{++}, and Sr^{++} enter the exchange reaction (Table 8) in addition to Na^+ and H^+. The Kd results in the 500 ppm Cs^+ solution (Table 6) are quite interesting. A Kd of 80 ml/g is observed after 5 hours which decreases to 62 at longer contact times. This suggests that the ion exchange reactions occur rapidly, but the final Cs^+ distribution is a function of the overall system equilibrium, which is approached at a slower rate. The limiting step is probably the establishment of the carbonate-bicarbonate - carbon dioxide equilibria as evidenced by the gradual change in pH with time (Table 7).

The effect of various size fractions of argillite on Kd's was also investigated. The fractions were obtained by

putting a 450 gram piece of the core sample through a jaw
crusher and passing the crushed material through a series of
U.S. Standard Seives. The size fractions and quantities of
each fraction collected are listed in Table 10. With the
exception of the < 37µ fraction, each fraction was washed on
the screen with deionized water to remove any "fines" adhering
to larger particles and then air dried at ambient temperature
for 60 hours prior to use.

Five gram samples of the > 4000µ and the 4000 - 1000µ
particles were contacted with 100 ml of Cs^+ solution and one
gram samples of the other fractions were contacted with 20 ml
of the same solution. A 2000 ppm Cs^+ solution was used with
all samples as the purpose was simply to determine if the
particle size had any influence on the rate of absorption and/or
the total Cs^+ capacity. Samples were taken for analysis after
5, 28, and 175 hour equilibration times. The results are
listed in Table 11.

With the exception of the 5 hr. data for the > 4000µ
particles, there is no evidence that particle size is a sig-
nificant factor in either the rate or amount of Cs^+ absorption
on the argillite. Small differences appear in the various size
fractions, but the only general trend which is evident is a
small decrease in Kd value with time as observed previously
(Table 5).

Tracer experiments with ^{137}Cs were done to compare Kd
results over a wider concentration range and at levels which
may be more typical of water associated with a repository.

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One gram samples of < 74μ powder were equilibrated for 120 hours with ^{137}Cs and mixtures of stable cesium and ^{137}Cs giving the analytical Cs concentrations shown in Table 12. The Kd results are also in Table 12 along with some results from higher concentration experiments for comparison.

The Kd values observed are relatively constant in the 0.0.12 to 0.2 ppm range, but decrease as concentration increases in the higher concentration range. Comparison of the Kd of the 1.12 ppm Cs$^+$ solution with that in Table 5 determined at about the same Cs$^+$ concentration shows a decrease of a factor of two, most likely due to different ionic strengths in the two solutions. This effect is small compared to that of increasing Cs$^+$ concentrations, and suggests that the reaction which results in Cs absorption in solutions containing 1 ppm Cs or less is very specific for Cs.

The effect of particle size on the Kd of Cs in the 0.1 ppm concentration range is shown in Table 13. One-gram samples of the various size ranges were equilibrated 288 hours with 20 ml of water containing 10 μCi/ml of ^{137}Cs or a concentration of 0.12 ppm. In this case, the dependence of Kd on the particle size is obvious. The higher Kd's on the larger particle sizes are an unexpected result. In general, the Kd's decrease with time. The obvious exception is the largest particle size fraction. This phenomena was not observed in the higher concentration Cs solutions after the first 28 hours of contact. The differences in Kd's among the particle size ranges probably results from segregation occurring in the crushing and sieving

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operations. It is apparent that care must be exercised in using a specific size fraction in Kd measurements, as results can differ by as much as a factor of sixteen.

VI. DISTRIBUTION COEFFICIENT (Kd) MEASUREMENTS IN NTS GROUNDWATER SIMULANT AND PRE-EQUILIBRATED DEIONIZED WATER

A. Experimental Procedure

The volumes of isotope stock solutions used in doping the simulants were measured into plastic cups and evaporated to dryness under ambient conditions. The simulants were then added to the cups, and after allowing 4 to 24 hours for dissolution, were filtered through an 0.8μ pore size filter (Acropor^{TM}, Gelman Instrument Co., Ann Arbor, MI). Aliquots were put into 25 ml capacity polyethylene dropper bottles containing argillite in the form of a -200 mesh powder prepared as previously described. A ratio of solution volume to weight of argillite of 50 ml/g was used in all measurements. Contact periods were 2, 4, and 8 weeks, during which time the samples were agitated on shakers. Polyethylene film placed over the bottle openings prior to replacing the caps prevented liquid from entering the spout.

Sampling involved placing an 0.8μ filter over the bottle opening, replacing the cap, and collapsing the bottle to force the liquid through the filter. Known volumes of the clarified solutions were used for analyses. Problems associated with multiple sampling and competing ion effects were circumvented by using a different simulant-argillite mixture containing

a single radionuclide for each measurement. Control volumes of each different doped simulant solution were carried through an experimental and sampling procedure identical to that used for the mixtures.

The fission product activities were determined by gamma ray spectroscopy, using a NaI well-crystal with a PDP 11 to accumulate and process the data. Actinide activities were determined by liquid scintillation counting.

B. Nomenclature

Since only relative concentrations are necessary for Kd calculations, the analytical data in Tables 13-22 is given in counts per minute per milliliter, cpm/ml. Counting efficiency can be estimated from the "activity added" data, which represents the activity in cpm/ml measured in 1 $\underline{M}$ HNO$_3$ or 1 $\underline{M}$ HCl solutions doped at the given levels based on the nominal concentration of the same isotope stock solutions used in the Kd measurements. Samples of simulants taken immediately after doping and filtering are referred to as "standard feed" and those taken at the 2, 4, and 8 week intervals as "feed" and "sample" for the control samples and simulant-argillite mixtures, respectively. The pH measurements were made at the same time as the analytical samples were taken.

All Kd's herein were calculated using Equation 1,

$$Kd = \frac{\text{Initial Activity} - \text{Final Activity}}{\text{Final Activity}} \times \frac{\text{Simulant Volume, ml}}{\text{Weight Argillite, g}} \quad \text{Eq. 1}$$

where activities refer to solution phase activity and the initial

and final activities refer to those in the control simulant and simulant-argillite mixture, respectively, at the time when the samples were taken.

The traditionally used symbol, Kd, implies an equilibrium condition for the distribution of a solute between two phases. This does not apply to this set of measurements, since the second or solid phase is an assemblage of at least seven minerals of which four[3] or more undergo ion exchange reactions. Other factors such as hydrolysis, absorption on container surfaces, and co-precipitation can contribute to overall absorption and thus to the Kd value as evidenced by the decrease of activity with time in some of the control solutions. The values given as Kd's actually represent sorption coefficients which describe the behavior of a given nuclide under the particular set of conditions used in making the measurement. The activity of the control simulant was used as the initial activity to try to isolate the contribution of the argillite-nuclide interaction to the overall sorption coefficient from reactions occurring in the simulants themselves. These Kd's are listed without parentheses in Tables 21 and 22. Values in parentheses were calculated using the total activity actually added to the simulants as the initial activity in Eq. 1 and thus include the effects of all mechanisms which result in the removal of the radionuclides from the liquid phase. These values are referred to as overall Kd's.

C. Distribution Coefficients

^{137}Cs

The Kd's for ^{137}Cs (Table 14) fall in the range of
$1.1-4.1 \times 10^3$ for all simulants, equilibration times, and
doping levels used. A slight trend toward increasing Kd's
with both increasing equilibration time and decreasing
doping levels is observed for all samples. A similar trend
is observed in comparing the pre-equilibrated water, the
pre-equilibrated simulant, and the as-prepared simulant. A
higher Kd would be expected in the water than in either of
the simulants because of its lower ionic strength. The
observed behavior may well be an effect of different solu-
tion pH.

The Kd's in Table 14 agree closely with those measured
in deionized water (Table 12). The decrease in Kd with time
was not apparent, probably because equilibrium is established
more rapidly in the simulants which already contain bicarbonate
or in the pre-equilibrated solutions. The lower Kd in the
Delaware Basin simulant (Table 5) is probably due to both
the higher ionic strength and the stable cesium concentration
in that simulant.

^{85}Sr

The ^{85}Sr Kd's in the simulant solutions fall in the range
of 21 to 60 (Table 15) and, in general, increase with both
time and decreasing Sr concentration. Relative changes in con-
centration were smaller in the case of Sr as compared to other

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isotopes because of the presence of stable Sr in most of the simulants used and in the argillite itself. The higher values in the pre-equilibrated water may result from the higher pH, but more likely reflect the lower analytical concentration of Sr in solution (Table 1). A greater loss of ^{85}Sr during preparation and initial filtering is seen in the pre-equilibrated solutions than in the as-prepared simulant. The reason for this and the large decrease in activity in the pre-equilibrated simulant control sample between the 2 and 4 week samples are not known. Comparison of the Kd's in Table 15 with those for Sr in the Delaware Basin simulant (Table 5) reaffirm the dependence of Kd's on the nuclide concentration.

^{152}Eu and ^{144}Ce

The most important factor in measuring Kd's for ^{152}Eu and ^{144}Ce (Tables 16 and 17, respectively) seems to be the mechanism other than sorption on the argillite which contributes to removal of the nuclides from the control solutions. Significant amounts of the activity added are lost both during preparation of the solutions and from the control solutions during equilibration periods resulting in apparent Kd's which range from 1.8×10^1 to 10^5 for Eu and 2.6×10^1 to 6×10^4 for Ce.

The overall Kd's for ^{152}Eu in the NTS simulant solutions range from 3×10^4 to 2×10^5 and appear to increase with time and with decreasing Eu concentration (Table 22). The overall values for the pre-equilibrated simulant are about one order of magnitude greater than those in the as-prepared

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simulant, while the values in the pre-equilibrated water
are about one order of magnitude lower for the same comparison.
The same range and trends also apply to the overall Kd's for
^{144}Ce listed in Table 22.

^{99}Tc

The apparent Kd's for ^{99}Tc range from 15 to 196 (Table
18). Considering that the Kd equals zero in the Delaware
Basin simulant (Table 5) doped at 1 μCi/ml, a range of 0
to 196 is seen for the concentration range of 1 to 0.001 μ
~i/ml. At constant doping level, 0.001 μCi/ml, a general
decrease in Kd occurs in the various solution phases. as-
prepared simulant > pre-equilibrated simulant > pre-equilibrated
water. The lack of explanation of this trend reflects a
lack of knowledge about the mechanisms involved in anion
sorption in geomedia, or chemical effects which may result
in reduction of the pertechnetate ion.

^{238}Pu

After the initial two week period, the 238 Pu Kd's
(Table 19) in the NTS simulants fell in the range of
1.7-5.9 x 10^4 while that in the pre-equilibrated water was
1.7 x 10^3. During the second two week period, the activity
in the argillite samples continued to decrease, but at a
slower relative rate than the activity in the control
solutions thus lowering the apparent Kd's to a range of 1.4 x 10^2
to 3.3 x 10^4. A precipitous decrease in activity occurred
in the pre-equilibrated simulant over the same time period.
Similar decreases in control or feed solution activity are

noted during the final four weeks for the two lower Pu concentrations resulting in apparent Kd's as low as 17. The former decrease was associated with a decrease in pH and the latter with increasing pH.

The overall Kd's (Table 23) for the as-prepared NTS simulant show an increase with both time and decreasing doping level. Conversely, the Kd's in the pre-equilibrated solutions decreased with time. The Kd's in the three different solutions doped at 0.1 μci/ml decrease in the order: as-prepared simulant > pre-equilibrated simulant > pre-equilibrated water.

^{243}Am

The apparent Kd's for ^{243}Am are similar in magnitude (Table 20) and trends to the Pu results. The overall Kd's (Table 23) for the as-prepared simulant show the trend toward increasing values with time and decreasing Am concentration. In comparing the different solutions used, the lowest Kd's are associated with the pre-equilibrated water.

^{244}Cm

After the first two week period, the apparent Kd's in the NTS simulant solutions are in the range of 10^4 to 10^5 (Table 21), after which time the values decrease due to the significant loss of activity in the control solutions. The overall Kd's (Table 23) show the same range of values and trends as previously described for both ^{243}Am and ^{238}Pu.

D. pH Effects

The solution phase pH can be expected to influence radio-nuclide migration in two general areas; 1) solute effects, and 2) solid phase effects. In the former, increasing pH can result in either partial hydrolysis which may alter the effective charge on a given species and thus change its chemistry with respect to sorption phenomena or complete hydrolysis which results in precipitation or the formation of neutral species. In the latter, changes in pH are known to effect the ion exchange properties of inorganic ex-changers[3], where in general increasing pH enhances cation exchange and decreasing pH is more favorable to anion exchange.

In measuring Kd's in the laboratory, the equilibrium pH of both the control solutions and those in contact with the geomedia are typically higher than those measured in the field due to loss of dissolved CO_2. A system was designed and built for use in controlling the pH continuously during equilibration periods. This was accomplished by constantly monitoring the pH with a glass electrode and using the recorder output of a pH meter (Model 4500, Beckman Instrument Co., Fullerton, CA) to control the addition of CO_2. The output is amplified by an operational amplifier (Model 741) and controls relays which activate a solenoid valve, which when open, allows CO_2 to flow through a variable leak into the sample solution. A diagram of the system is shown in Figure 1. The pH can be controlled to plus or minus 0.6 pH unit in the range of 5.5 to 8.

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Initial experiments using pH control were done with stable Cs and ^{152}Eu. The Cs was chosen because it does not undergo hydrolysis in the pH regime of interest and thus, changes in sorption should reflect the pH effect on the structural or chemical properties of the argillite. Eu was chosen to represent the trivalent lanthanides and actinides, which do undergo significant hydrolysis in the pH range of the CO_2-HCO_3^- equilibrium.

The cesium work was done with a pre-equilibrated NTS simulant containing 25 ppm of stable Cs. Fifty ml were contacted with 0.5g of a < 18 to > 40 mesh fraction of argillite. The pH was controlled in the range of 5.8 to 6.3 for 72 hours, when samples were taken for atomic absroption analysis. The results showed a Kd for Cs of 40 in the lower pH solution as compared to 68 in a control experiment done without pH control where the final pH was 8.5.

The ^{152}Eu experiments involved contacting 0.5g of the same size fraction of argillite with fifty ml of pre-equilibrated simulant doped at 0.1 μCi/ml. The initial pH, 8.3, was lowered and maintained between 5.7 and 6.6 by CO_2 addition. Samples were taken after 1 week, 2 week, and 4 week periods. A control sample was treated in an identical manner, except that the pH was not controlled. The results are given in Table 24. The Kd calculations were based on the activity of the feed solutions sampled at the same time intervals but not pH controlled. The overall Kd's, in

parentheses, were calculated using the activity initially
added to the feed solution.

The activity in the pH controlled sample remained
relatively constant while that in the feed and control
samples decreased with time as previously observed (Table 16).
The Kd's in the lower pH solution were consistently lower
than those in the control, by factors ranging from four after
one week to about seven after one month. After the final
samples were taken, the two argillite samples were thoroughly
washed by decantation with deionized water and counted under
identical conditions. The total activity associated with the
argillite from the pH controlled simulant was 6.3×10^5 cpm
as compared to 2.8×10^5 for the argillite from the higher
pH simulant.

A second experiment was done in the same manner except
that the simulant was added to the argillite and the pH was
decreased to less than 6 prior to doping with ^{152}Eu. The pH
of the feed solution was also controlled in the same range
as the sample.

The 1 week Kd values were higher than those in the pre-
vious pH controlled solution (Table 24), but lower than that
in the pH = 8.3 solution. The activity associated with the
argillite, 6.6×10^5, was slightly higher than previously
observed.

Although a lot remains to be understood about the effect
of pH on sorption, several general statements concerning the

argillite behavior can be made. The overall Kd's tend to be somewhat lower in solutions of lower pH and the difference may depend on how the experimental measurement was initiated. In the case of Eu, hydrolysis or sorption on container walls makes a significant contribution to the overall Kd, especially at long equilibration times. Whether the increased sorption on the argillite at lower pH is due to changes in the argillite or solute form is not known.

VII. SUMMARY

The work described in the body of this report can be divided into two general areas which, although interrelated, can be summarized in a somewhat independent manner. These include; 1) A detailed study of the interaction of Cs in deionized water with argillite from the Eleana Formation at the Nevada Test Site, and 2) Distribution coefficient measurements for some fission products and actinides of interest because of their estimated potential for migration to the biosphere or their impact on the biosphere should such migration occur.

At Cs concentrations of less than 100 ppm in deionized water, the primary Cs sorption method is ion exchange with hydrogen and sodium ions. This reaction is specific for Cs, since the presence of much higher concentrations of other mono- and divalent cations, such as in the Delaware Basin and NTS simulants, result in a twofold or less decrease in distribution coefficients at comparable Cs concentrations.

The maximum sorption occurs in the first few hours of contact
with argillite. Subsequent decreases in Kd probably result
from pH or other changes associated with establishment of
equilibrium in the mixtures.

At the higher Cs levels, ion exchange reactions involving
K^+, Mg^{++}, Ca^{++}, and Sr^{++} become significant. In the range
of 0.001 to 1 ppm Cs, the effect of concentration is minimal.
In the range of 1 to 2000 ppm, Kd's decrease significantly
with increasing Cs concentration which provably results in
part from different equilibria governing the ion exchange
reactions at higher concentrations. A stoichiometric excess
of Cs in solution would also be evidenced by an apparent
decrease in Kd, however, the milliequivalents of Cs sorbed
per gram of argillite continued to increase with concentration
through the entire range used.

The particle size of argillite in the range of > 4000
μm to < 37 μm, had a negligible effect on kinetics or total
Cs sorbed (meq/g) in solutions containing more than 1 ppm
Cs. However, at tracer level concentrations up to sixteenfold
differences in Kd's are observed on different size fractions.
This is most likely due to segregation of a minor phase(s)
during crushing and sieving operations.

For the Kd measurements, a complete piece of the core
sample was reduced entirely to a -200 meah (< 74u) powder to
minimize or eliminate particle size/segregation effects. Each
measurement was made in a different sol'cion-argillite mixture

containing a single radionuclide and Kd's were determined at two or more concentrations of each radionuclide.

The following is a summary of the overall Kd's (Tables 22-23) which are based on the initial quantity of radionuclide added to the solution phase, where the range of values includes all concentrations and simulants: ^{137}Cs - 1 X 10^3 to 4.4 x 10^3, ^{85}Sr - 5.6 X 10^1 to 4.8 X 10^3, ^{99}Tc - 2.8 x 10^1 to 2.4 x 10^2, ^{152}Eu - 3 x 10^3 to 1.8 x 10^5, ^{144}Ce - 5 x 10^3 to 2 x 10^5, ^{238}Pu - 2 x 10^4 to 5 x 10^5, ^{243}Am - 7.3 x 10^3 to 6 x 10^6, and ^{244}Cm - 8 x 10^3 to 5.8 x 10^5. The general trends observed were an increase in Kd with increasing equilibration time and decreasing nuclide concentration, and lower Kd's in the pre-equilibrated deionized water as compared to both pre-equilibrated and as-prepared NTS simulants. The exceptions, however, are numerous as exemplified by the ^{85}Sr Kd's in the pre-equilibrated water (Table 16) and the apparent decrease of the actinide Kd's with time in both of the pre-equilibrated simulants. The apparent Kd's, which are based on the activity of a control solution at the end of each equilibration period, are difficult to summarize. For nuclides which do not undergo hydrolysis in the pH range of interest (Cs, Sr, and Tc), agreement with the overall Kd's is generally well within an order of magnitude. However, differences between overall and apparent Kd's of up to five orders of magnitude were not uncommon in the lanthanide and actinide results.

VIII. CONCLUSIONS

The results of the work with Cs in deionized water
point out that care should be exercised in choosing nuclide
concentrations or using specific size fractions in Kd mea-
surements. Striking examples of concentration effects are
also seen for ^{99}Tc, where a Kd range of 0 to 240 was observed
over a concentration range of 59 to .059 ppm Tc, and for ^{85}Sr
which had a Kd of 5 in a solution containing 15 ppm Sr and
a Kd of 10^3 in a solution containing less than 1 ppm Sr.

The dominating factor in the actinide and lanthanide Kd
determinations is the mechanisms which results in the loss
of activity from the control solutions. Hydrolysis and
precipitation due to high pH is a possibility, however, neither
the loss of activity from control solutions nor the final
activity in the argillite-solution mixtures can be directly
correlated with pH or pH changes during equilibration. Mass
balance experiments would determine whether the actinides/
lanthanides were associated with the container walls, solution
(as a colloidal suspension or precipitate), or the argillite.
They would not differentiate between ion exchange and pre-
cipitation on the surface of the argillite due to localized
hydrolysis. The controlled pH experiment, where solutions
at pH=8 and pH=5.8-6.3 showed approximately the same decrease
in solution activity but a factor of three difference in
activity associated with the argillite suggests that both
reactions are occurring and that their relative importance
is pH dependent. The overall Kd's, which vary only with

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activity in the solution contacting the argillite, appear to be the most useful in comparing Kd data for different solutions and geological samples. The value of pre-equilibrating simulants used in Kd determinants is arbitrary as both the time scale and solution-rock ratios do not represent geological processes. The effects of pre-equilibrating simulants with argillite prior to contact with a doped simulant in this study are inconclusive. The Kd's in the as-prepared and pre-equilibrated NTS simulant generally agree within an order of magnitude, and no definitive trend can be identified. A trend toward lower Kd's in the pre-equilibrated deionized water is apparent.

A survey of distribution coefficients involving ten samples from various geological media associated with the Waste Isolation Pilot Plant (WIPP) site in New Mexico was completed prior to this study[4]. If distribution coefficients are used as a criteria, the Eleana Formation on the Nevada Test Site appears to have an equally high potential for retardation of aqueous-borne radionuclides, as the argillite Kd values for the nuclides involved in this study are typically comparable to or higher than those observed on the variety of WIPP materials.

REFERENCES

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2. Dinwiddie, G., USGS, Preliminary Analytical Results

3. Amphlett, C. B., Inorganic Ion Exchangers, Elsevier, Amsterdam, 1964.

4. Dosch, R. G., and Lynch, A. W., Interaction of Radio-nuclides With Geomedia Associated With the Waste Isolation Pilot Plant Site in New Mexico, SAND 78-0297, June, 1978.

Table 1-A

Composition of Argillite[1] From 1805 Foot Level
of the J Subunit of the Eleana Formation

	% by Weight		% by Weight
SiO_2	65.4	K_2O	1.13
Al_2O_3	16.6	$H_2O^+ + CO_2$	7.11
Fe_2O_3	0.69	H_2O^-	0.67
FeO	4.5	TiO_2	0.81
MgO	1.5	P_2O_5	0.27
CaO	0.64	MnO	0.041
Na_2O	0.73	SrO	0.011

(1) Analysis provided by J. Hustler of the Geology Department at
the University of New Mexico

Table 1-B

Solution Phase Compositions

Species	Groundwater[1] Analysis, mg/l	Groundwater[2] Simulant, mg/l	Argillite Equilibrated Simulant, mg/l	Water, mg/l
HCO_3^-	280	363	378	51
Ca^{++}	79	75	60	ND < 1
CO_3^{--}	0	0	0	0
Cl^-	13	14	14	ND < 0.5
F^-	0.6	0.6	1.3	0.4
Mg^{++}	25	24	20	ND < 1
K^+	6.6	6.4	5.8	0.02
Si	31	31	27	1.2
Na^+	30	30	57	20
SO_4^{--}	62	72	71	ND < 5
Fe^{+++}	0.03	ND < 0.01	ND < 0.01	ND < 0.01
Sr^{++}	0.42	0.59	1.1	ND < 0.05
pH	7.2	7.7		

(1) Preliminary Analytical Results from G. Dinwiddie of USGS.

(2) ND = Not Detected.

Table 2

Stock Solutions for Simulant Preparation

Stock Solution	Volume	Composition	Volume of Stock Solution per liter of Simulant
#1	100 ml	0.126g NaF	1 ml
#2*	100 ml	1.347g $Na_2SiO_3 \cdot 5H_2O$ 0.35g $SiO_2 \cdot xH_2O$ (80% SiO_2)	10 ml
#3	500 ml	0.127g KCl 0.111g $CaCl_2$ 0.782g $MgSO_4$	50 ml
#4	100 ml	0.0145g $FeCl_3 \cdot 6H_2O$	1 ml
#5	100 ml	0.1278g $SrCl_2 \cdot 6H_2O$	1 ml

*This solution was prepared by adding 20 ml of H_2O to the solids and heating until dissolution was complete, then diluting to 100 ml.

Table 3

Composition of Simulant Used in Kd Survey Experiment Based on Composition of Groundwater of the Los Medanos Area in Southeastern New Mexico

Species	Concentration (mg/liter)
Na^+	100
K^+	5
Mg^{++}	200
Ca^{++}	600
Fe^{+++}	≤ 1
Sr^{++}	15
Rb^+	1
Cs^+	1
Cl^-	200
$SO_4^=$	1750
HCO_3^-	100
$NO_3^=$	20
pH (adjusted)	7.5

Table 4

Analytical Concentrations of Radioisotopes in

Simulant Solutions

| Isotope | Concentration[1] | |
	ppm	moles/liter
^{137}Cs	0.012	8.8×10^{-8}
^{85}Sr	0.03-0.3	$3.5 \times 10^{-6} - 3.5 \times 10^{-7}$
^{152}Eu	0.1 - 1	$6.6 \times 10^{-6} - 6.6 \times 10^{-7}$
^{125}Sb	≤0.01	$\leq 8 \times 10^{-8}$
^{144}Ce	3×10^{-4}	2.1×10^{-9}
^{99}Tc	59	6×10^{-4}
^{238}Pu	0.06	2.5×10^{-7}
^{243}Am	5.4	2.2×10^{-5}
^{244}Cm	0.012	4.9×10^{-8}

(1) The radionuclide concentrations are for doping
     levels of 1 µCi/ml based on the suppliers analysis
     of the stock solutions.

Table 5

Distribution Coefficients for Eleana Argillite

| Nuclide | Kd | | pH (final) | |
	2 weeks	4 weeks	Feed	Sample
^{137}Cs	600	660	7.4	7.7
^{85}Sr	5.3	4.2	7.4	7.7
^{152}Eu	$\geq 7.7 \times 10^5$	$\geq 7.7 \times 10^5$	5.8	7.7
^{144}Ce	820	1.3×10^3	7.0	7.7
^{125}Sb	52	71	7.4	7.7
^{99}Tc	0	0	7.1	7.7

Table 6

Cesium Adsorption of Eleana Argillite

Cs^+ Initial Concentration	Cesium Adsorption							
	5 hrs.		24 hrs.		95 hrs.		120-168 hrs.	
	meqCs/g	Kd	meqCs/g	Kd	meqCs/g	Kd	meqCs	Kd
25 ppm[1]	--	--	--	--	--	--	0.0036	419
100 ppm[1]	--	--	--	--	--	--	0.014	270
500 ppm	0.060	80	0.059	74	0.058	66	0.057	62
1000 ppm	0.082	24	0.082	24	0.080	23	0.080	23
2000 ppm	0.11	11	0.11	11	0.11	11	0.097	10

(1) The sample volumes taken for analysis at the 5, 24, and 95 hour times were not sufficient for detection of Cs by atomic absorption analysis.

Table 7

pH of Eleana Argillite Samples

Initial Cs Concentration[1]	20 min.	20 hrs.	168 hrs.	210 hrs.	520 hrs.
0 ppm	9.6	9.8	--	8.9	8.5
25 ppm	--	--	--	--	--
100 ppm	9.3	9.6	--	8.7	8.3
500 ppm	--	--	8.1	--	8.0
1000 ppm	--	--	8.0	--	8.0
2000 ppm	--	--	8.0	--	7.9

(1) 5 g of -200 mesh Eleana Argillite in 100 ml of deionized water containing Cs^+ as CsCl.

Table 8

Na^+, K^+, Ca^{++}, Mg^{++}, and Sr^{++} Concentrations in Water or Cs Solutions in Contact With Eleana Argillite

Initial Cs^+ Concentration	Concentration (meq/100 ml)				
	Na^+	K^+	Ca^{++}	Mg^{++}	Sr^{++}
0	0.26	$1.3x10^{-2}$	$9x10^{-3}$	$2.1x10^{-3}$	$2.7x10^{-4}$
25	0.28	$1.3x10^{-2}$	$9.4x10^{-3}$	$2.1x10^{-3}$	$1.8x10^{-4}$
100	0.29	$1.2x10^{-2}$	$9.8x10^{-3}$	$2.3x10^{-3}$	$1.8x10^{-4}$
500	0.34	$2.4x10^{-2}$	$5.2x10^{-2}$	$2.2x10^{-2}$	$9.2x10^{-4}$
1000	0.35	$3.4x10^{-2}$	$1.2x10^{-1}$	$4.6x10^{-2}$	$2.4x10^{-3}$
2000	0.36	$4.1x10^{-2}$	$1.9x10^{-1}$	$6.8x10^{-2}$	$4x10^{-3}$

Table 9
C$_s$ Ion Exchange on Argillite

Initial Cs Concentration	Total Meq/100 ml of Na$^+$, K$^+$, Ca^{++}, Mg^{++}, Sr^{++}	Total Meq of Cs Adsorbed
0	0.28	0
25	0.30	0.018
100	0.31	0.070
500	0.44	0.28
1000	0.56	0.40
2000	0.66	0.49

Table 10
Size of Crushed Eleana Argillite

Size Range (μ)	Weight of Fraction(g)	% of Total Sample in Size Range
≥ 4000	93.6	20.8
4000 - 1000	272.2	60.6
1000 - 420	38.9	8.7
420 - 210	17.6	3.9
210 - 105	9.6	2.1
105 - 74	3.9	0.87
74 - 37	5.8	1.3
≤ 37	7.5	1.7
	449.1 g	

Table 11

Adsorption of Cs^+ on Eleana Argillite as a Function of Particle Size

Particle Size,μ	5 hr meqCs/g	Kd	28 hr meqCs/g	Kd	175 hr meqCs/g	Kd
> 4000	0.055	4.5	0.084	7.9	0.080	7.4
4000 - 1000	0.081	7.3	0.088	8.2	0.083	7.6
1000 - 420	0.093	9.0	0.089	8.4	0.088	8.2
420 - 210	0.094	9.1	0.092	8.8	0.086	8.1
210 - 105	0.088	8.1	0.093	8.8	0.081	7.2
105 - 74	0.085	7.9	0.084	7.8	0.081	7.4
74 - 37	0.081	7.2	0.078	6.9	0.071	6.0
< 37	0.099	9.8	0.095	9.1	0.086	7.9

Table 12

Concentration Dependence of Cs Distribution Coefficients on Eleana Argillite

[137]Cs Activity	Analytical Cs Concentration	Kd
0.1 μCi/ml	0.0012 ppm	1666
1.0 μCi/ml	0.012 ppm	1316
10 μCi/ml	0.12 ppm	1720
10 μCi/ml	0.21 ppm	1503
10 μCi/ml	1.12	1177
---	25	419
---	100	270
---	500	62
---	1000	24
---	2000	9.6

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Table 13

Effect of Particle Size of Eleana Argillite on Cs Kd's at Low Cs Concentration

Particle Size Range	[Cs$^+$]	Kd	
		120 hrs	288 hrs
≥ 4000μ	0.12 ppm	1937	6553
4000 - 1000μ	"	1849	1156
1000 - 420μ	"	808	618
420 - 210μ	"	669	416
210 - 105μ	"	1116	739
105 - 74μ	"	1069	693
74 - 37μ	"	803	611
≤ 37μ	"	1450	1447

Table 14. ^{137}Cs - Activities, pH Data, and Distribution Coefficients

NTS Simulant

^{137}Cs - 1.0 µCi/ml

	2 week	4 week	8 week
Activity Added, cpm/ml	2.22×10^5	2.22×10^5	2.22×10^5
Feed Activity, cpm/ml	1.89×10^5	1.89×10^5	1.83×10^5
Feed pH	8.2	8.2	8.2
Sample Activity, cpm/ml	3.36×10^3	2.97×10^3	2.85×10^3
Sample pH	8.2	8.0	8.3
Kd, ml/gm	2.7×10^3	3.1×10^3	3.0×10^3

^{137}Cs - 0.1 µCi/ml

	2 week	4 week	8 week	Argillite Equilibrated Solutions			
				NTS Simulant		Deionized H₂O	
				2 week	4 week	2 week	4 week
Activity Added, cpm/ml	2.22×10^4	2.22×10^4	2.22×10^4	2.22×10^4	2.22×10^4	2.22×10^4	2.22×10^4
Standard Feed Activity, cpm/ml	--	--	--	2.18×10^4	2.20×10^4	2.29×10^4	2.36×10^4
Feed Activity, cpm/ml	2.06×10^4	2.02×10^4	2.02×10^4	2.18×10^4	2.24×10^4	2.27×10^4	2.17×10^4
Feed pH	8.2	8.2	8.2	8.2	8.4	7.9	8.2
Sample Activity, cpm/ml	2.93×10^2	2.67×10^2	2.56×10^2	5.49×10^2	4.83×10^2	9.88×10^2	8.16×10^2
Sample pH	8.1	7.9	8.3	8.2	8.4	9.0	8.8
Kd, ml/gm	3.3×10^3	3.3×10^3	3.8×10^3	1.9×10^3	2.2×10^3	1.1×10^3	1.3×10^3

^{137}Cs - 0.01 µCi/ml

	2 week	4 week	8 week
Activity Added, cpm/ml	2.22×10^3	2.22×10^3	2.22×10^3
Feed Activity, cpm/ml	2.12×10^3	2.15×10^3	2.07×10^3
Feed pH	8.3	8.3	8.3
Sample Activity, cpm/ml	3.36×10^1	2.64×10^1	2.52×10^1
Sample pH	8.1	8.0	8.3
Kd, ml/gm	3.1×10^3	4.0×10^3	4.1×10^3

Table 15. ^{85}Sr - Activities, pH Data, and Distribution Coefficients

NTS Simulant

^{85}Sr - 1.0 µCi/ml	2 week	4 week	8 week				
Activity Added, cpm/ml	1.44×10^5	1.44×10^5	1.44×10^5				
Feed Activity, cpm/ml	1.14×10^5	1.21×10^5	1.26×10^5				
Feed pH	8.4	8.4	8.4				
Sample Activity, cpm/ml	6.08×10^4	6.61×10^4	6.38×10^4				
Sample pH	8.1	8.0	8.2	· Argillite Equilibrated Solutions			
Kd, ml/gm	40.0±0.6	40.9±0.5	48.5±2	NTS Simulant		Deionized H_2O	
^{85}Sr - 0.1 µCi/ml				2 week	4 week	2 week	4 week
Activity Added, cpm/ml	1.44×10^4	1.44×10^4	1.44×10^4	1.44×10^4	1.44×10^4	1.44×10^4	1.44×10^4
Standard Feed Activity, cpm/ml	--	--	--	4.65×10^3	4.75×10^3	3.86×10^3	3.92×10^3
Feed Activity, cpm/ml	1.22×10^4	1.34×10^4	1.30×10^4	3.59×10^3	1.12×10^3	3.30×10^3	3.12×10^3
Feed pH	8.3	8.3	8.3	8.3	8.5	7.9	8.3
Sample Activity, cpm/ml	6.64×10^3	6.49×10^3	5.97×10^3	2.26×10^3	2.07×10^3	1.47×10^2	3.29×10^2
Sample pH	8.1	8.0	8.3	8.3	8.4	8.9	8.7
Kd, ml/gm	40.6±0.5	50.3±0.7	59.7±0.7	21.2±1.2	--	$1.05±.01 \times 10^3$	$4.09±.03 \times 10^2$
^{85}Sr - 0.01 µCi/ml							
Activity Added, cpm/ml	1.44×10^3	1.44×10^3	1.44×10^3				
Feed Activity, cpm/ml	1.21×10^3	1.24×10^3	1.28×10^3				
Feed pH	8.2	8.2	8.2				
Sample Activity, cpm/ml	6.66×10^2	6.60×10^2	5.79×10^2				
Sample pH	8.1	8.0	8.3				
Kd, ml/gm	39.3±1.2	43±1.8	56.9±0.5				

Table 16. ^{152}Eu - Activities, pH Data, and Distribution Coefficients

NTS Simulant

	2 week	4 week	8 week	Argillite Equilibrated Solutions NTS Simulant 2 week	Argillite Equilibrated Solutions NTS Simulant 4 week	Deionized H_2O 2 week	Deionized H_2O 4 week
^{152}Eu - 0.1 μCi/ml							
Activity Added, cpm/ml	1.39×10^4	1.39×10^4	1.39×10^4	1.39×10^4	1.39×10^4	1.39×10^4	1.39×10^4
Standard Feed Activity, cpm/ml	--	--	--	1.29×10^4	1.52×10^4	5.25×10^3	5.11×10^3
Feed Activity, cpm/ml	3.91×10^3	4.52×10^3	4.85×10^3	1.18×10^4	6.9	2.78×10^2	2.80×10^2
Feed pH	8.6	8.6	8.6	8.6	8.2	8.1	8.2
Sample Activity, cpm/ml	19.8	16.7	11.6	5.4	4.0	1.10×10^2	2.05×10^2
Sample pH	8.2	8.0	8.3	8.3	8.4	8.9	8.8
Kd, ml/gm	$9.5 \pm 0.2 \times 10^3$	$1.35 \pm .02 \times 10^4$	$1.94 \pm .06 \times 10^4$	$1.08 \pm .04 \times 10^5$	37 ± 4	72.5 ± 1.3	18.1 ± 0.7
^{152}Eu - 0.01 μCi/ml							
Activity Added, cpm/ml	1.39×10^3	1.39×10^3	1.39×10^3				
Feed Activity, cpm/ml	58.1	81.2	78				
Feed pH	8.4	8.4	8.4				
Sample Activity, cpm/ml	1.4	0.88	0.4				
Sample pH	8.2	8.0	8.3				
Kd, ml/gm	$2.1 \pm .3 \times 10^3$	$4.5 \pm .8 \times 10^3$	$8.9 \pm 4.1 \times 10^3$				

Table 17. ^{144}Ce - Activities, pH Data, and Distribution Coefficients

	NTS Simulant			Argillite Equilibrated Solutions			
				NTS Simulant		Deionized H_2O	
	2 week	4 week	8 week	2 week	4 week	2 week	4 week
^{144}Ce - 0.1 µCi/ml							
Activity Added, cpm/ml	$3.17x10^3$	$3.17x10^3$	$3.17x10^3$	$3.17x10^3$	$3.17x10^3$	$3.17x10^3$	$3.17x10^3$
Standard Feed Activity, cpm/ml	--	--	--	$1.94x10^3$	$1.96x10^3$	$1.02x10^3$	$9.84x10^2$
Feed Activity, cpm/ml	$1.43x10^3$	$1.54x10^3$	$2.10x10^3$	$1.70x10^3$	$9.86x10^2$	49.8	40.7
Feed pH	8.6	8.6	8.6	8.5	8.8	7.9	8.3
Sample Activity, cpm/ml	5.7	1.7	1.6	2.6	1.6	29.3	26.7
Sample pH	8.2	8.0	8.3	8.3	8.4	8.9	8.8
Kd, ml/gm	$1.2\pm0.1x$ 10^4	$4.4\pm0.6x$ 10^4	$6.5\pm0.6x$ 10^4	$6.3\pm.5x$ 10^4	$2.9\pm0.3x$ 10^4	36.7 ± 2.5	26 ± 3
^{144}Ce - 0.01 µCi/ml							
Activity Added, cpm/ml	$3.17x10^2$	$3.17x10^2$	$3.17x10^2$				
Feed Activity, cpm/ml	38.2	40.1	37.6				
Feed pH	8.5	8.5	8.5				
Sample Activity, cpm/ml	0.22	not detected	0.12				
Sample pH	8.1	8.0	8.3				
Kd, ml/gm	$8.4\pm5.8x$ 10^3	•	$1.5\pm2.6x$ 10^4				

Table 18. ^{99}Tc - Activities, pH Data, and Distribution Coefficients

NTS Simulant

^{99}Tc - 0.01 µCi/ml	2 week	4 week	8 week
Activity Added, cpm/ml	$2.04x10^4$	$2.04x10^4$	$2.04x10^4$
Feed Activity, cpm/ml	$1.68x10^4$	$1.68x10^4$	$1.67x10^4$
Feed pH	8.3	8.3	8.3
Sample Activity, cpm/ml	$1.29x10^4$	$1.29x10^4$	$1.29x10^4$
Sample pH	8.2	8.0	8.4
Kd, ml/gm	15.0±0.1	16±0.1	15.2±0.1

Argillite Equilibrated Solutions

^{99}Tc - 0.001 µCi/ml	2 week	4 week	8 week	NTS Simulant 2 week	NTS Simulant 4 week	Deionized H$_2$O 2 week	Deionized H$_2$O 4 week
Activity Added, cpm/ml	$2.04x10^3$	$2.04x10^3$	$2.04x10^3$	$2.04x10^3$	$2.04x10^3$	$2.04x10^3$	$2.04x10^3$
Standard Feed Activity, cpm/ml	--	--	--	--	--	--	--
Feed Activity, cpm/ml	$1.70x10^3$	$1.70x10^3$	$1.71x10^3$	$2.00x10^3$	$2.01x10^3$	$2.02x10^3$	$2.06x10^3$
Feed pH	8.3	8.3	8.3	8.1	8.5	7.9	8.8
Sample Activity, cpm/ml	$4.70x10^2$	$3.35x10^2$	$4.14x10^2$	$8.54x10^2$	$8.24x10^2$	$1.27x10^3$	$1.17x10^3$
Sample pH	8.2	7.9	8.3	8.3	8.3	7.9	8.1
Kd, ml/gm	133±3	196±1.5	144±1	64.6±.7	71.8±.6	28.5±.5	37.8±.5

Table 19. ^{238}Pu - Activities, pH Data, and Distribution Coefficients

NTS Simulant

^{238}Pu - 1.0 µCi/ml

	2 week	4 week	8 week
Activity Added, cpm/ml	2.45×10^6	2.45×10^6	2.45×10^6
Feed Activity, cpm/ml	7.94×10^5	7.22×10^5	3.70×10^4
Feed pH	--	8.5	8.4
Sample Activity, cpm/ml	2.34×10^3	1.12×10^3	4.06×10^2
Sample pH	7.8	7.9	8.0
Kd, ml/gm	1.7×10^4	3.3×10^4	3.9×10^2

^{238}Pu - 0.1 µCi/ml

	NTS Simulant			Argillite Equilibrated Solutions			
				NTS Simulant		Deionized H$_2$O	
	2 week	4 week	8 week	2 week	4 week	2 week	4 week
Activity Added, cpm/ml	2.45×10^5	2.45×10^5	2.45×10^5	2.45×10^5	2.45×10^5	2.45×10^5	2.45×10^5
Standard Feed Activity, cpm/ml	--	--	--	4.01×10^4	4.01×10^4	7.22×10^4	7.22×10^4
Feed Activity, cpm/ml	7.51×10^4	4.22×10^3	90.1	2.80×10^4	85.9	2.16×10^4	1.37×10^4
Feed pH	--	7.9	8.4	8.4	8.0	7.7	7.9
Sample Activity, cpm/ml	2.13×10^2	1.0×10^2	67.3	23.2	22.2	6.13×10^2	7.08×10^2
Sample pH	7.9	7.9	8.1	8.1	8.1	9.0	8.6
Kd, ml/gm	1.7×10^4	2.0×10^3	17 ± 3	$5.9 \pm .7 \times 10^4$	$1.4 \pm .3 \times 10^2$	1.7×10^3	$9.3 \pm .3 \times 10^2$

^{238}Pu - 0.01 µCi/ml

	2 week	4 week	8 week
Activity Added, cpm/ml	2.45×10^4	2.45×10^4	2.45×10^4
Feed Activity, cpm/ml	8.02×10^3	3.1×10^2	3.6
Feed pH	--	7.9	8.4
Sample Activity, cpm/ml	12.4	10.5	2.4
Sample pH	7.9	8.0	8.0
Kd, ml/gm	$3.1 \pm 0.5 \times 10^4$	$1.1 \pm 0.3 \times 10^3$	24 ± 57

Table 20. ^{243}Am - Activities, pH Data, and Distribution Coefficients

NTS Simulant

^{243}Am - 1.0 µCi/ml

	2 week	4 week	8 week
Activity Added, cpm/ml	2.79×10^6	2.79×10^6	2.79×10^6
Feed Activity, cpm/ml	1.55×10^5	1.40×10^5	1.22×10^5
Feed pH	--	8.6	8.7
Sample Activity, cpm/ml	9.71×10^2	1.14×10^3	3.65×10^2
Sample pH	7.9	8.0	8.1
Kd, ml/gm	7.6×10^3	5.9×10^3	1.5×10^4

^{243}Am - 0.1 µCi/ml

	NTS Simulant			Argillite Equilibrated Solutions			
				NTS Simulant		Deionized H$_2$O	
	2 week	4 week	8 week	2 week	4 week	2 week	4 week
Activity Added, cpm/ml	2.79×10^5	2.79×10^5	2.79×10^5	2.79×10^5	2.79×10^5	2.79×10^5	2.79×10^5
Standard Feed Activity, cpm/ml	--	--	--	1.05×10^5	1.65×10^5	9.87×10^4	9.87×10^4
Feed Activity, cpm/ml	3.55×10^4	2.50×10^4	117.3	1.07×10^5	1.05×10^5	1.12×10^4	4.85×10^3
Feed pH	--	8.3	8.2	8.5	8.6	8.0	7.9
Sample Activity, cpm/ml	2.2	51	N.D.	18	164	1.14×10^3	1.89×10^3
Sample pH	7.9	8.0	8.0	8.1	8.1	9.0	8.6
Kd, ml/gm	7.6×10^5	2.3×10^4	∞	3×10^5	3.2×10^4	4.4×10^2	78

^{243}Am - 0.01 µCi/ml

	2 week	4 week	8 week
Activity Added, cpm/ml	2.79×10^4	2.79×10^4	2.79×10^4
Feed Activity, cpm/ml	3.28×10^3	36	13.2
Feed pH	--	7.9	8.2
Sample Activity, cpm/ml	N.D.	14	N.D.
Sample pH	7.9	7.9	8.1
Kd, ml/gm	∞	77	∞

Table 21. ^{244}Cm - Activities, pH Data, and Distribution Coefficients

NTS Simulant

^{244}Cm - 1.0 µCi/ml	2 week	4 week	8 week
Activity Added, cpm/ml	2.09×10^6	2.09×10^6	2.09×10^6
Feed Activity, cpm/ml	1.09×10^6	3.51×10^5	1.02×10^4
Feed pH	--	8.3	8.3
Sample Activity, cpm/ml	1.73×10^2	3.63×10^2	2.89×10^2
Sample pH	7.9	7.9	8.1
Kd, ml/gm	2.9×10^5	4.8×10^4	1.6×10^3

^{244}Cm - 0.1 µCi/ml	2 week	4 week	8 week	Argillite Equilibrated Solutions NTS Simulant 2 week	4 week	Deionized H$_2$O 2 week	4 week
Activity Added, cpm/ml	2.09×10^5	2.09×10^5	2.09×10^5	2.09×10^5	2.09×10^5	2.09×10^5	2.09×10^5
Standard Feed Activity, cpm/ml	--	--	--	8.5×10^4	8.5×10^4	3.4×10^4	3.4×10^4.
Feed Activity, cpm/ml	1.05×10^5	5.76×10^2	6.17×10^2	6.58×10^4	9.01×10^2	2.23×10^3	2.41×10^3
Feed pH	--	7.9	8.3	8.3	8.0	7.6	7.8
Sample Activity, cpm/ml	50.6	1.20×10^3	1.02×10^2	53.1	46.9	4.30×10^2	7.26×10^2
Sample pH	7.9	8.2	8.2	8.1	8.2	9.0	8.6
Kd, ml/gm	$9.6 \pm .3 \times 10^4$	(--)	2.4×10^2	$6.1 \pm .3 \times 10^4$	$9.0 \pm .3 \times 10^2$	2.0×10^2	1.2×10^2

^{244}Cm - 0.01 µCi/ml	2 week	4 week	8 week
Activity Added, cpm/ml	2.09×10^4	2.09×10^4	2.09×10^4
Feed Activity, cpm/ml	8.49×10^3	57.8	33
Feed pH	--	7.9	8.1
Sample Activity, cpm/ml	7.2	8.3	Not detected
Sample pH	7.8	8.0	8.1
Kd, ml/gm	$5.9 \pm 1.5 \times 10^4$	$2.6 \pm .4 \times 10^2$	(-)

Table 22. Summary of Apparent and Overall Kd's for Fission Products and Eleana Argillite

	NTS Simulant[1]			NTS Simulant[1]		Deionized Water[1]	
	14 day	28 day	56 day	14 day	28 day	14 day	28 day
^{137}Cs - 1 μCi/ml	2.7×10^3 (3.2×10^3)	3.1×10^3 (3.6×10^3)	3.0×10^3 (3.7×10^3)				
0.1 μCi/ml	3.3×10^3 (3.5×10^3)	3.3×10^3 (3.6×10^3)	3.8×10^3 (4.2×10^3)	1.9×10^3 (2.0×10^3)	2.2×10^3 (2.2×10^3)	1.1×10^3 (1.0×10^3)	1.3×10^3 (1.3×10^3)
0.01 μCi/ml	3.1×10^3 (3.3×10^3)	4.0×10^3 (4.2×10^3)	4.1×10^3 (4.4×10^3)				
^{85}Sr - 1 μCi/ml	40 (62)	40.9 (58)	48.5 (63)				
0.1 μCi/ml	40.6 (57)	50.3 (58)	59.7 (72)	21.2 (270)	<0 (287)	1.1×10^3 (4.8×10^3)	4.1×10^2 (2.1×10^3)
0.01 μCi/ml	39.3 (56)	43 (57)	56.9 (70)				
^{152}Eu - 0.1 μCi/ml	9.5×10^3 (3.4×10^4)	1.35×10^4 (4.2×10^4)	1.94×10^4 (5.6×10^4)	1.1×10^5 (1.3×10^5)	37 (1.7×10^5)	72.5 (6×10^3)	18 (3.3×10^3)
0.01 μCi/ml	2.1×10^3 (5.0×10^4)	4.5×10^3 (7.8×10^4)	8.9×10^3 (1.75×10^5)				
^{144}Ce - 0.1 μCi/ml	1.2×10^4 (2.6×10^4)	4.4×10^4 (9.0×10^4)	6.5×10^4 (1.0×10^5)	3.3×10^4 (6.1×10^4)	2.9×10^4 (1.5×10^5)	36.7 (5.4×10^3)	26 (5.8×10^3)
0.01 μCi/ml	8.4×10^3 (7.0×10^4)	∞ (∞)	1.5×10^4 (1.2×10^5)				
^{99}Tc - 0.01 μCi/ml	15.0 (28)	16.0 (30)	15.2 (29)				
0.001 μCi/ml	133 (171)	196 (244)	144 (181)	64.6 (67.4)	71.8 (79.8)	28.5 (29.1)	37.8 (36.1)

(1) Overall Kd's based on total activity added are in ( ).

Table 23. Summary of Apparent and Overall Kd's for Actinides on Eleana Argillite

	NTS Simulant[3]			NTS Simulant[3]		Deionized Water[3]	
	14 day	28 day	56 day	14 day	28 day	14 day	28 day
^{238}Pu - 1 µCi/ml	1.7×10^4 (5.1×10^4)	3.3×10^4 (1.1×10^5)	3.9×10^2 (3×10^5)				
0.1 µCi/ml	1.7×10^4 (5.5×10^4)	2.0×10^3 (1.2×10^5)	17 (1.8×10^5)	5.9×10^4 (5.2×10^5)	1.4×10^2 (5.5×10^4)	1.73×10^3 (2×10^4)	9.3×10^2 (1.8×10^4)
0.01 µCi/ml	3.1×10^4 (9.3×10^4)	1.1×10^3 (1.1×10^5)	24 (5.0×10^5)				
^{243}Am - 1 µCi/ml	7.6×10^3 (1.4×10^5)	5.9×10^3 (1.2×10^5)	1.6×10^4 (3.6×10^5)				
0.1 µCi/ml	7.6×10^5 (5.9×10^6)	2.3×10^4 (2.6×10^5)	∞[1] (∞)[1]	3×10^5 (7.7×10^5)	3.2×10^4 (8.5×10^4)	4.4×10^2 (1.2×10^4)	78 (7.3×10^3)
0.01 µCi/ml	∞[1] (∞)[1]	77 (8.8×10^5)	∞[1] (∞)[1]				
^{244}Cm - 1 µCi/ml	2.9×10^5 (5.5×10^5)	4.8×10^4 (2.8×10^5)	1.6×10^3 (3.4×10^5)				
0.1 µCi/ml	9.6×10^4 (1.9×10^5)	(--) (8.0×10^3)	2.4×10^2 (9.9×10^4)	6.1×10^4 (2×10^5)	9.0×10^2 (2.2×10^5)	2.0×10^2 (2.3×10^4)	1.2×10^2 (1.5×10^4)
0.01 µCi/ml	5.9×10^4 (1.5×10^5)	2.6×10^2 (1.1×10^5)	∞[2]				

(1) Sample Activity slightly greater than Feed Activity.
(2) Activity above background was not detected in sample.
(3) Overall Kd's based on Total Activity Added are in ( ).

Table 24

pH Effects on ^{152}Eu Distribution Coefficients

	1 week		2 week		4 week	
	cpm/ml	Kd	cpm/ml	Kd	cpm/ml	Kd
Activity Added	1.4×10^4	--	1.4×10^4	--	1.4×10^4	--
Feed Solution	1.2×10^4	--	1.1×10^4	--	75	--
Argillite (Control Sample)	88	6.9×10^3 (7.8×10^3)	71	6.6×10^3 (8.7×10^3)	49	22 (1.1×10^4)
Argillite (pH Controlled)	341	1.8×10^3 (2.0×10^3)	324	1.4×10^3 (1.9×10^3)	341	-- (1.6×10^3)

Figure 1. APPARATUS FOR pH CONTROL