SAND98-2685 J

Laboratory Column Experiments for Radionuclide Adsorption Studies of the Culebra Dolomite at the Waste Isolation Pilot Plant

Glenn O. Brown
(Corresponding author)
Biosystems and Agricultural Engineering Department
Oklahoma State University, Stillwater, OK 74078
Phone: 405-744-8425 / Fax: 405-744-6059
E-mail: gbrown@okstate.edu

Daniel A. Lucero
WIPP Test and Analysis Department
Sandia National Laboratories, Albuquerque, NM 87185-1320
Phone: 505-844-3462 / Fax: 505-845-3467
E-mail: dalucer@sandia.gov

Hsuan-Tsung Hsieh
Biosystems and Agricultural Engineering Department
Oklahoma State University, Stillwater, OK 74078
Phone: 405-612-1056 / Fax: 405-744-6059
E-mail: hsieh@okstate.edu

Submitted for Sandia Review
October 23, 1998

First Revision
November 19, 1998
(Incorporating George Perkins review)

Second Revision
December 18, 1998
(Incorporating Carol Crawford reference review)

Third Revision
August 31, 1999
(Incorporating CAO review)

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of energy under Contract DE-AC04-94AL85000.

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

Radionuclide transport experiments were carried out using cores from the Culebra member of the Rustler Formation collected inside the Air Intake Shaft of the Waste Isolation Pilot Plant. Twenty-six tests include experiments with ^{3}H, ^{22}Na, ^{241}Am, ^{239}Np, ^{228}Th, ^{232}U, ^{241}Pu, and two brine types. ^{3}H and ^{22}Na were conservative tracers. ^{239}Np and ^{232}U eluted but were moderately retarded. ^{241}Am, ^{228}Th and ^{241}Pu were not detected in column effluent even after extended flow times. Breakthrough curves for eluting species were fitted to single and dual porosity models. Fitted porosity for the conservative solutes ^{22}Na and ^{3}H showed little difference between models. That indicates limited effective distinction between the two implying significant preferential flow occurred in the columns. Fitted retardation factors, *R*, ranged from 30 to 78 for ^{239}Np and from 2 to 18 for ^{232}U, using the single porosity model. The dual porosity fit for ^{232}U and ^{239}Np yielded matrix retardation values one to two orders of magnitude greater than the single porosity model. Theoretical analysis for the non-eluting species, ^{241}Am, ^{228}Th and ^{241}Pu provided minimum retardation estimates. Minimum *R* values were 520 to 25,000 for ^{241}Am, 9.1 to 47 for ^{228}Th, and 800 to 20,000 for ^{241}Pu.

Keywords: column experiment, radionuclide, adsorption, retardation, Culebra dolomite, Waste Isolation Pilot Plant.

INTRODUCTION

Under the authorization of Public Law 96-164 (1979), the U.S. Department of Energy (DOE) has developed a nuclear waste disposal facility, the Waste Isolation Pilot Plant (WIPP), located approximately 42 km east of Carlsbad, New Mexico(U.S. DOE, 1996). The WIPP is designed to demonstrate the safe disposal of transuranic wastes produced by the defense nuclear-weapons program and is regulated by the U.S. Environmental Protection Agency under 40 CFR Part 191 (U.S. EPA, 1993). These regulations place limits on cumulative radioactive release to the accessible environment over 10,000 years and require that Performance Assessment analyses be executed to demonstrate the WIPP facility compliance with the regulations. Initial Performance Assessment calculations and sensitivity analyses (Helton et al., 1991 and 1992; Bertram-Howery et al., 1990) identified the radionuclide retardation factor, *R*, in the Culebra Dolomite as an important parameter in assuring the safe performance of the repository over its regulated life of 10,000 years.

While laboratory column transport tests have been carried out for many years, little information is available on procedures and results for experiments using actinides in general and within dolomite samples specifically. Reported laboratory column tests with actinides include Toulhoat (1986), Casas et al. (1994) and Vandergraaf et al. (1997) testing with fractured granite, Sims et al. (1996) work with intact sandstone, and Hölttä et al. (1991) experiments with fractured tonalite. The Culebra is a much more complex porous medium than the simple fracture systems examined by other researchers. It contains multiple porosity types which differ in both size and shape (Holt, 1997). Only limited transport experiments have been carried out using Culebra

sample with non-actinide solutes (Lynch, 1979). Thus, none of the previous work was considered adequate to address the site-specific actinide transport questions at WIPP.

Intact rock column experiments were designed as part of the larger Culebra retardation studies program to demonstrate retardation in the Culebra Dolomite. Experiments with large diameter intact core simulate the subsurface environment (albeit at an intermediate scale smaller than the field) and provide a means to quantify some effects of coupled transport processes under simulated flow conditions. This paper presents the procedures, analysis and results of the intact core column experiments. Brush (1998b) used all of those results, along with results of semi-empirical batch sorption experiments, to develop the sorption distributions used in WIPP Performance Assessment. Lucero et al. (1998) have also presented experimental results of colloid-assisted transport with the same materials used here.

MATERIALS AND PROCEDURES

Detailed information on test materials, equipment and procedures are presented in Lucero et al. (1998). Procedures where developed to address several concerns. The use of actinides always requires concessions to lab safety. Some typical lab practices are just not possible if a column is inside a glove box. Low actinide solubility restricts both the total mass injected and the method of injection. Running multiple concurrent tracers required the careful consideration of the isotopes used to minimize analysis interference. Finally, while most published research is based on just a handful of tests, this program was required to carry out dozens of tests to provide an adequate data set for Performance Assessment needs. The following section summarizes the general procedures used and parameters specific to these tests.

Drilling inside the air-intake shaft at a depth of 220 m as shown in Figure 1, provided representative 145 mm core samples. Each borehole was drilled in a north-south direction,

which is the probable direction of ground-water flow at the air-intake shaft (Ramsey et al., 1996). Figure 1 also shows the approximate position of the tested core sections. Core sections tested were relatively solid and intact, but demonstrated the fractures, gypsum infilling and vugs typical of WIPP Culebra cores. Core C had a fracture going almost entirely through the sample. It is not believed to be a drilling artifact, but may be a natural unloading fracture that is partly cemented. Table 1 lists dimensions, weights and density of the sample used in each test. Surprisingly, the cores had equivalent porosity although they appeared quite dissimilar.

Cores were cut to the desired length on a dry diamond saw and a urethane liner was poured around each. After mounting in their holders, the cores where preconditioned to achieve chemical equilibrium by leaching with their matching air-intake shaft brine for two to eight pore volumes.

Synthetic solutions matching the measured composition of water taken from the boreholes were used in most of the test series. In two tests, a brine matching the composition of the deeper, Salado Formation (ERDA 6) was used to determine if transport is influenced by intrusion of those waters. Table 2 lists the composition of both synthetic brines.

A schematic of the test apparatus is shown in Figure 2. Its major components were a column core holder, a syringe pump, a brine injection reservoir and an effluent collector. Aluminum was used to construct the column barrel and the end fittings were made of brass. Overburden loads are simulated by applying a confining pressure of 35 kN/m^2 in the annulus between the column and the liner. That pressure is also applied to the top distributor plate that is free to slide up and down, while the bottom plate is fixed. Thus, the core is subjected to a triaxial pressure while allowing the effluent to exit at atmospheric pressure. Distributor plates are Teflon coated on all surfaces exposed to the core or leachate.

Brine was pumped into the core from an accumulator, which was a simple cylinder and piston sealed at both ends. Double, high pressure, liquid chromatography syringe pumps drive water into one end of the accumulator, which forces brine out the other. The accumulator prevented contamination and fouling of the pumps, while the double pump configuration allowed automatic filling of the syringe pumps and continuous operation. Effluent was collected with a fraction collector operating in time mode set to provide approximately 5 ml per sample. Due to the actinides used, the columns were operated within a large glove box to provide secondary containment.

Actinide isotope selection was critical to the testing. Column tests require an isotope with a moderate half-life, roughly greater than one day and less than a few hundred years. Obviously, measurable amounts of a tracer must remain at the end of a test to have any hope of measuring it in the column effluent, thus very short-lived isotopes are impractical. The maximum half-life is dictated by the need to have measurable activity at molar concentrations below solubility limits. Radioassay methods, gamma ray spectrometry (γ Spec) and liquid scintillation counting (LSC), were used to measure effluent molar concentration. Those techniques measure isotope decays, not molar mass as chemical methods do. At a constant molar concentration, a shorter-lived isotope is easier to detect than a longer life isotope of the same element. Since actinide solubility is generally low, measurable activities cannot be achieved with solutions of isotopes with half-lives greater than a few hundred years.

Isotope decay emission is important, since radioassays were used to quantify the effluent concentrations. Of the two methods used, γ Spec is preferable, since it does not require sample preparation and can easily distinguish different isotopes. Sample tubes can be directly loaded into the instrument and all gamma-emitting isotopes measured simultaneously. LSC can quantify

alpha and beta emissions, but requires the sample to be mixed with scintillation cocktail. It has poor energy resolution to distinguish between isotopes and requires knowledge of what isotopes are present in the sample. LSC does have one advantage over γ Spec in that its detection limit is generally an order of magnitude lower. The total mix of isotope and emissions had to be considered to minimize interference in radioassays of the various tracers including accounting for any short-lived daughter products. Since daughters in-grow with their own half-lives, a short-lived daughter will soon equal the activity of the parent in any solution. Finally, the isotope had to be available at economical prices. This implies that the isotope could either be obtained from commercial suppliers, or in the case of shorter-lived isotopes, separated from a stock of a long-life parent. Isotopes obtainable from dedicated reactor operations were investigated but found too costly and operationally impractical. Table 3 presents the isotopes used, their primary emission, and the minimum detection activity, (MDA) for γ Spec and LSC.

Injection spikes were prepared and assayed by Newton et al. (1995). They dispensed the desired isotope activity into Teflon bottles and then added brine to bring the total spike volume between 10 and 20 ml. These procedures produce a spike of known isotope activity with an ionic strength slightly less than the brine itself.

During the planning phase for these experiments, several reviewers expressed concern that actinide spikes would plate out in the injection apparatus and never reach the core. Thus, a procedure was developed to insure the tracer materials reached the core at the desired activity and in soluble form. Before each core was mounted, a small reservoir, approximately 5 cm in diameter and 1 cm deep with a 20 ml volume was milled into its inlet end. When a spike was ready for injection, a Teflon tube, attached to a plastic syringe, was inserted into the core holder and used to empty the inlet reservoir. The syringe was then used to directly inject the spike into

the reservoir, and the pumps restarted within 15 minutes. Spike subsamples taken from the syringe and post-test destructive analysis (Perkins and Lucero, 1998) proved the actinides reached the core. While the temporary flow interruption and inlet reservoir are undesirable, their effects are small compared to the total test time and core size.

Some experiments with Cores A and B used 500 or 2000 ml slugs of tracer to provide a constant concentration boundary condition. For those tests, a dedicated "hot" accumulator was placed inside the glove box. Tracer was dispensed into it along with the appropriate brine volume.

Test spike activity, spike volume, flow rate and brine used for each experiment are listed in Table 4. Twenty-six individual tests were run on the five cores, most of which had multiple isotopes in the injection spike. In total, there were five ^{3}H spikes, three spikes with ^{241}Pu and ^{241}Am, four ^{228}Th spikes, ten spikes of ^{239}Np and ^{232}U, and twenty-two spikes of ^{22}Na. ^{22}Na was used repeatedly to quantify and monitor the core hydraulics. Two tests, C5 and C7, were carried out with ERDA 6 brine to quantify the impact of brine type on transport. Most tests were carried out at a total flow rate of 0.1 ml/min, which corresponds to a volume flux of 9.8×10^{-6} cm/s (3.2 m/yr). That flow is at the upper end of the estimated natural conditions (Ramsey et al., 1996). Tests B5 to B8 and D6 were performed at different flow rates to explore flow rate dependencies.

An important feature of these tests is the multiple spike injection in the same core. This strategy has two specific benefits. First, the multiple spikes allow direct comparison in the same core of different isotopes while minimizing interference in the radioassays. Second and most importantly, the multiple spikes with continuous analysis make very long tests practical. Once an isotope has been injected in a core, it is analyzed for in all later effluent, which is significant in the quantification of noneluting actinides. As an example, while Test C3 was nominally carried

out for two liters, all column effluent after that time, (over 62 liters) has been assayed for both ^{241}Am and ^{241}Pu. Thus, minimum *R* analysis on those two isotopes may confidently be based on an eluted volume of 250 pore volumes.

Solubility of Am, Th, and Np were computed by Craft and Siegel (1998). Values corresponding to solutions both supersaturated with calcite and in equilibrium with dolomite are listed. Plutonium solubility was obtained from measurements made by Nitsche et al. (1994). Uranium solubility during the tests is clearly demonstrated by its elution from the cores with moderate retardation, as shown in the results. Plutonium, Np and Th spike activities were well below the solubility limit. Unfortunately, Am concentrations used were greater than the solubility determined later. Therefore, to be conservative, it was assumed that the injected americium concentration was equal to the solubility.

Effluent activity was measured with a Canberra γ Spec, equipped with a large area germanium detector (Canberra Model GL2020R) and multichannel analyzer. It was calibrated with a multiple energy source standard with the same geometry as the sample tubes. Approximately every fifth sample was analyzed by LSC for alpha and beta radiation on a Canberra model 2550 TR/AB. Minimum detection activities (MDA) for each isotope with no interference are listed in Table 3 for both γ Spec and LSC. The only major interference for the isotopes in these experiments occurs with the LSC analysis of ^{3}H and ^{241}Pu. The LSC cannot distinguish between those isotopes, thus ^{3}H use was limited to the initial hydraulic test of each core. ^{228}Th daughters produce some interference in both the γ Spec and LSC analysis. When they are present, the analysis was delayed for up to 45 days until they decayed below interference levels.

^{232}U is analyzed by both γ Spec and LSC since it emits a weak, but measurable gamma ray (57 keV with 0.02% yield) and a strong alpha (5.32 MeV with 68.6% yield). The sensitivity by LSC is much better for this isotope and LSC results were used for all parameter fitting. The γ Spec provides proof that the LSC is measuring ^{232}U. ^{241}Am may also be measured by both γ Spec and LSC. LSC has a much lower MDA but interference from ^{232}U obscures its analysis when uranium is present in the effluent, but the strong ^{241}Am γ ray emission stills provides a reasonable detection limit in those cases.

PARAMETER FITTING TO RESULTS

Effluent curves were analyzed using COLUMN Version 1.4 (Brown et al., 1997). That code provides parameter fits to the data for two different models. The first is a homogeneous single porosity medium, with advective and dispersive transport, based on the analytical solution of Parker and van Genuchten (1984). The second is a dual porosity, fractured-matrix numerical model similar to the Performance Assessment transport model, SECO-TP (WIPP Performance Assessment, 1992-1993).

The single porosity model assumes a homogeneous porous media with single valued porosity, ϕ, dispersion, D and retardation, R. Flux weighted concentrations were used, as recommended by Parker and van Genuchten (1984). COLUMN is able to find optimal fits to the single porosity model in a few seconds of computing time using a dual-Pentium 166-processor PC under the Windows NT 4.0 environment. The dual porosity model divides the rock into two portions: a system of fractures or mobile porosity, in which transport is dominated by advection, and a surrounding rock matrix in which advection is negligible, but into which molecular diffusion can take place. The hydrological parameters include the fracture and matrix porosity, ϕ_f

and ϕ_m; the fracture and matrix dispersions, D_f and D_m; and the fracture spacing, B. Chemical sorption is characterized by the fracture and matrix retardation coefficients, R_f and R_m. Using the same PC above, the dual porosity model can take up to a day to fit experimental data.

When fitting retarded solute breakthrough, two cases were evaluated to distinguish where solute adsorption occurred. In the first case, the fracture retardation was set to one and the matrix porosity had to provide all adsorption, while the second case fitted the fracture retardation along with the matrix retardation.

A major difficulty when fitting data is the lumped parameter nature of the dual porosity model. The functional form of the transport equations makes the individual parameter definitions ambiguous. For the data available from the column experiments, it is difficult to distinguish fits using very different parameter values. For example, a decrease in D_m can be almost exactly offset by a decrease in B. Therefore four parameters values were fixed. Observations of cores indicated most fractures and large pore features were relatively straight, thus the fracture tortuosity was set to one. Matrix porosity was fixed at 0.11, which corresponds to roughly the lower 33 percentile of measured porosity in the Culebra Cores (Kelley and Saulnier, 1990). That lower fraction is assumed to consist of cores with only primary porosity. Matrix toruosity was set to 0.067 to represent a highly tortuous diffusion path.

Matrix diffusion was set to 1.5×10^{-5}, 3×10^{-6}, 2.2×10^{-6} cm^2/sec for Na, U, and Np, respectively. This leaves the fracture spacing, B, as the single parameter describing the effects of dual porosity. The matrix dispersion values are the free-solution diffusion coefficients for the respective ions, and is the average of the probable oxidation states for the actinides (Brush, 1998a).

Determination of actinide retardation in the column experiments is problematic for isotopes that do not appear in the effluent. Actual retardation coefficients cannot be computed, since lack of detection means only that the test may not have been run long enough, or that the solute eluted from the column at a concentration lower than the analysis detection limits. Nevertheless, minimum values can be estimated based on the known hydraulics of flow and instrument MDA. Two cases that limit estimates of retardation coefficients are shown in Figure 3. The figure presents possible breakthrough curves, only one of which will apply in a given test. Curve **A** is for a solute that eluted during the sampling, but whose maximum activity concentration at the outlet was below the MDA of the analysis instrument. In that case, the estimated minimum R will be that value that produces a peak equal to the MDA. Curve **B** is for a solute that would elute at activities higher than the MDA if the test was run longer. Solute may be in the effluent, but at activities below the MDA. In that case, minimum R is defined by the smallest retardation value that does not produce an activity greater than the MDA before the last sample. The limiting case, **A** or **B** is a function of the spike activity, dispersion, radioactive decay, total sampling volume and the MDA.

Minimum R and the limiting case was estimated by trial and error runs of the single porosity model using the last sample volume assuming constant values for flow rate, dispersion, porosity and MDA. Flow rate, porosity and dispersion were equated to the fitted values from the ^{22}Na breakthrough for the same test, while MDA was to the value in Table 3.

RESULTS

Typical measured and fitted breakthrough curves for eluting species are shown in Figures 4 to 7. In general, the curves have the shape expected for advective-dispersive transport. ^{3}H, ^{22}Na, ^{232}U and ^{239}Np eluted in that general order. There was little difference between ^{3}H and

^{22}Na, indicating sodium is a conservative species in this NaCl rich system. Figure 4 shows their similarity in Test C1 once the activities are scaled to the maximum. Not all tests yielded useful results due to experimental difficulties. Problems included pump interruptions, liner failures and defective solute spikes.

The results of the parameter fitting are summarized in Tables 5 and 6 for the conservative and retarded species respectively. Generally the lower porosity values shown in Table 5, compared to Table 1, is due to non-mobile porosity. Also listed are values of the root mean squared error (*RMS*), between the measured and fitted effluent concentrations. *RMS* provides a method to compare the goodness-of-fit of the two models to a single breakthrough curve. The smaller the *RMS*, the better the fit. However, *RMS* is a function of the effluent activity, which varies with injection activity and test conditions. Thus, it should not be used to compare the fit between tests. Column 1.4 was unable to fit some effluent curves with the dual porosity model, as noted in the tables.

Table 7 lists the limiting case and minimum R for the noneluted species. Minimum R values were 520 to 25,000 for ^{241}Am based on an injection concentration equal to the solubility. Minimum R values were 9.1 to 47 for ^{228}Th, and 800 to 20,000 for ^{241}Pu.

DISCUSSION

It is possible to compare the applicability of the two porosity models by two steps. First, comparison of the fitted parameter values of ϕ and ϕ_f for the conservative solutes show that the dual porosity model provides ϕ_f values only slightly less than the single porosity model. This indicates that the "fracture porosity" of the dual porosity model is largely the same void space as the porosity of the single porosity model. Second, two Student t, paired two-sample for means

tests were performed to determine if there is significant difference between the *RMS* of the single and dual porosity models. The two data sets tested were,

$$E_R = RMS_{single} - RMS_{dual} \quad (1)$$

and

$$E_N = (RMS_{single} - RMS_{dual}) / Injected\ Activity \quad (2)$$

where E_R is the raw difference between the fits and E_N is the difference normalized by the injection activity. Tests on both E_R and E_N failed to reject a hypothesis that the fittings were equivalent. It is apparent the dual porosity model is providing essentially a single porosity fit to the data.

In the dual porosity fitting of the eluted but retarded U and Np, good fits could be obtained only if the fracture, (or advective) porosity is allowed to retard the solute. As shown in Figures 6 and 7, without fracture retardation the solutes would break through earlier than measured. Fitting with retardation produces good fits to the measured data, but again are very similar to the single porosity fits. The time and space dimensions of these experiments place them at the lower end of the expected spectrum of Damkohler numbers (Holt, 1997). The Damkohler number, *DaI* is a dimensionless ratio of the advective travel and diffusion times. For a layered dual porosity system it is given by,

$$DaI = \left(\frac{\pi}{2B}\right)^2 \left(1 + \frac{R_m \phi_m}{R_f \phi_f}\right) \frac{D_m L R_f}{v}, \quad (3)$$

where L is the travel distance and v is the seepage velocity. Using a more complete analysis with multiple pore structures, Holt (1997) estimated for the column experiments that $DaI << 1$ and diffusion times were three orders of magnitude greater than advective travel time. Thus, the evidence of preferential flow is to be expected. Since only a portion of the pore space was accessed by the solute during the experiment, R values measured here are almost certainly

smaller than the core's full retardation potential. Better estimates of the Culebra's full potential for actinide retardation with column experiments will require much slower advective velocities, or different testing strategies to increase the effective Damkohler number.

No clear trend can be seen in relation to flow rate over the limited set of relatively high flow velocities used. Porosity estimates in B core are similar in B4, B5 and B8 that span an order of magnitude in flow rate. Similarly, D6 and D5 have equivalent porosity fittings. In regards to uranium retardation, in B core, the high flow Test B7 had the lowest R value, while in D core the lower flow rate Test D6 had the lower R. If flow rate dependencies are present at these flows, they are within the parameter fitting errors. This insensitivity is consistent with the previous discussion of the Damkohler number. The higher flow rate reduced DaI to even smaller values, while the lowest flow rate only increased DaI by a factor of two.

Brine type had no impact on core porosity estimates. Test C5 and C7 had similar porosity fittings as the other Core C tests. Comparing Tests C2 and C7 indicates that uranium retardation was reduced by a factor of four in the higher ionic-strength brine. However, comparing Tests C6 and C7 shows Np retardation appears to be unaffected by the change in ionic strength. Considering that all the R values are near the range displayed by other experiments, no definite conclusion is possible.

Minimum R values are very large except for ^{228}Th. The range of the minimum R values is a function of the individual test conditions and does not indicate data uncertainty. The lower values are provided by the shorter duration tests. The small minimum R estimated for ^{228}Th is due to its MDA that is 20 to 200 times greater than the other isotopes. Perkins et al. (1998) using in-situ emission tomography have been able to greatly increase that estimate to the same magnitude as the other non-eluting actinides.

CONCLUSIONS

The core column experiments successfully demonstrate actinide transport and retardation in the Culebra Dolomite. The procedures used were able to address the concerns for lab safety, low actinide solubility and analysis of multiple concurrent tracers, while obtaining a reasonable number of experimental results.

Two actinides (U and Np) eluted from the columns. Retardation is lower for uranium, with R values of 2 to 18. Neptunium shows greater retardation and has R values of 30 to 78. Three actinides (Pu, Am and Th) did not elute from the columns. Theoretical analysis indicates that retardation is very high for plutonium and americium. Thorium is not yet well constrained by these tests, due to a MDA that is 20 to 200 times greater than the other isotopes. Minimum R values were 520 to 25,000 for Am, 9.1 to 47 for Th, and 800 to 20,000 for Pu. The range of these minimum R values is a function of the individual test conditions and does not indicate data uncertainty or measurement error. No clear trend is apparent with regard to flow rate dependencies at the high flows tested. Use of the Salado brine, ERDA 6, did not produce a significant change in actinide retardation.

Significant evidence of preferential flow was found. Since only a portion of the pore space was accessed by the solute during the experiment, R values measured here are probably smaller than the core's full potential. Better estimates of the Culebra's full potential for actinide retardation will require much slower advective velocities, or different testing strategies.

REFERENCES

Bertram-Howery, S.G., M.G. Marietta, R.P. Rechard, P.N. Swift, D.R. Anderson, B.L. Baker, J.E. Bean, Jr., W. Beyeler, K.F. Brinster, R.V. Guzowski, J.C. Helton, R.D. McCurley, D.K. Rudeen, J.D. Schreiber, and P. Vaughn. 1990. *Preliminary Comparison with 40 CFR Part 191, Subpart B for the Waste Isolation Pilot Plant, December 1990.* SAND90-2347. Albuquerque, NM: Sandia National Laboratories.

Brown, G.O., H-T. Hsieh, and Y-W. Lin. 1997. "Column: A Computer Program for Fitting Model Parameters to Column Flow Breakthrough Curves." Version 1.4 for Windows 95/NT3.51/NT4.0. June 13, 1997. Software Documentation Submitted to Sandia National Laboratories. Stillwater, OK: Oklahoma State University, Biosystems and Agricultural Engineering. (Copy on file in the Sandia WIPP Central Files, Sandia National Laboratories, Albuquerque, NM as WPO#46281.)

Brush, L.H.. 1998a. "Revised Free-Solution Tracer Diffusion Coefficients (D_{sol}s) for Dissolved Pu, Am, U, Th, Np, Cm, and Ra in Boreholes and the Culebra for Use in PA Calculations to Support the WIPP CCA," *Laboratory Column Experiments for Radionuclide Adsorption Studies of the Culebra Dolomite Member of the Rustler Formation.* D.A. Lucero, G.O. Brown, and C.E. Heath. SAND97-1763. Albuquerque, NM: Sandia National Laboratories. D-5 through D-9. (Memorandum to M.S. Tierney, Dated May 11, 1996.)

Brush, L.H.. 1998b. "Ranges and Probability Distributions of K_ds for Dissolved Pu, Am, U, Th, and Np in the Culebra for the PA Calculations to Support the WIPP CCA," *Laboratory Column Experiments for Radionuclide Adsorption Studies of the Culebra Dolomite Member of the Rustler Formation.* D.A. Lucero, G.O. Brown, and C.E. Heath. SAND97-1763. Albuquerque, NM: Sandia National Laboratories. D-11 through D-108. (Memorandum to M.S. Tierney, Dated June 10, 1996.)

Casas, I., D. Casabona, L. Duro, and J. de Pablo.. 1994. "The Influence of Hematite on the Sorption of Uranium(VI) onto Granite Filling Fractures," *Chemical Geology.* Vol. 113, no. ¾, 319-326.

Craft, C.C., and M.D. Siegel. 1998. "Additional Calculations of Solubility-Limited Concentrations of Actinides for Injection Spikes Used in WIPP Core Column Experiments at Sandia National Laboratories," *Laboratory Column Experiments for Radionuclide Adsorption Studies of the Culebra Dolomite Member of the Rustler Formation.* D.A. Lucero, G.O. Brown, and C.E. Heath. SAND97-1763. Albuquerque, NM: Sandia National Laboratories. D-109 through D-115. (Memorandum to D.A. Lucero, Dated June 9, 1997.)

Helton, J.C., J.W. Garner, R.D. McCurley, and D.K. Rudeen. 1991. *Sensitivity Analysis Techniques and Results for Performance Assessment at the Waste Isolation Pilot Plant.* SAND90-7103. Albuquerque, NM: Sandia National Laboratories.

Helton, J.C., J.W. Garner, R.P. Rechard, D.K. Rudeen, and P.N. Swift. 1992. *Preliminary Comparison with 40 CFR Part 191, Subpart B for the Waste Isolation Pilot Plant, December 1991. Volume 4: Uncertainty and Sensitivity Analysis Results*. SAND91-0893/4. Albuquerque, NM: Sandia National Laboratories.

Holt, R.M. 1997. *Conceptual Model for Transport Processes in the Culebra Dolomite Member, Rustler Formation*. SAND97-0194. Albuquerque, NM: Sandia National Laboratories.

Hölttä, P., H. Hakanen, and A. Hautojärvi. 1991. "Migration of Radionuclides in Fracture Columns," *Scientific Basis for Nuclear Waste Management XIV, Materials Research Society Symposium Proceedings, Boston, MA, November 26-29, 1990*. Eds. T.A. Abrajano, Jr. and L.H. Johnson. Pittsburgh, PA: Materials Research Society. Vol. 212, 669-676.

Kelley, V.A., and G.J. Saulnier, Jr., *Core Analysis for Selected Samples from the Culebra Dolomite at the Waste Isolation Pilot Plant Site*, Contractor Report SAND90-7011, Sandia National Laboratories, Albuquerque, New Mexico, 1990.

Lucero, D.A., Y.K. Behl, G.O. Brown, K.G. Budge, M. Dunn, A.J. Francis, J.B. Gillow, and H.W. Papenguth. 1998. *Laboratory Evaluation of Colloid Transport Under Simulated Subsurface Conditions at the Waste Isolation Pilot Plant (WIPP): 2. Large-Scale-Intact-Core Column Flow Experiments. Experimental & Modeling Studies of Radionculide Speciation in Real Systems*. Eds. D.T. Reed, S. Clark, and L. Rao. New York, NY: Plenum Pub. Corp.

Lucero, D.A., G.O. Brown, and C.E. Heath. 1998. *Laboratory Column Experiments for Radionuclide Adsorption Studies of the Culebra Dolomite Member of the Rustler Formation*. SAND97-1763. Albuquerque, NM: Sandia National Laboratories.

Lynch, A.W. 1979. "Migration of Cesium in Dolomite from the Rustler Formation in the Los Medanos Area in Southeastern New Mexico," *Scientific Basis for Nuclear Waste Management, Proceedings of the Symposium on "Science Underlying Radioactive Waste Management," Boston, MA, November 28-December 1, 1978*. Ed. G.J. McCarthy. New York, NY: Plenum Press. Vol. 1, 399-402.

Newton, G.J., W.E. Bechton, and K.R. Ahlert. 1995. "Preparation and Transfer of Samples for Brine Penetration Studies." ITRI SOP 1037. Albuquerque, NM: Inhalation Toxicology Research Institute. (Copy on file in the Sandia WIPP Central Files, Sandia National Laboratories, Albuquerque, NM in records package WPO#40975.)

Nitsche, H., K. Roberts, R. Xi, T. Prussin, K. Becraft, I. Al Mahamid, H.B. Silber, S.A. Carpenter, R.C. Gatti, and C.F. Novak. 1994. "Long Term Plutonium Solubility and Speciation Studies in a Synthetic Brine," *Radiochimica Acta*. Vol. 66/67, 3-8.

Parker, J.C., and M.Th. van Genuchten. 1984. *Determining Transport Parameters from Laboratory and Field Tracer Experiments*. Virginia Agricultural Experimental Station Bulletin 84-3. Blacksburg, VA: Virginia Agricultural Experiment Station, Virginia Polytechnic Institute and State University. (Copy on file in the Sandia WIPP Central Files, Sandia National Laboratories, Sandia National Laboratories, Albuquerque, NM as WPO#44584.)

Perkins, W.G., and D.A. Lucero. 1998. *Interpretation of Data Obtained from Non-Destructive and Destructive Post-Test Analyses of an Intact-Core Column of Culebra Dolomite*. SAND98-0878. Albuquerque, NM: Sandia National Laboratories.

Perkins, W.G., D.A. Lucero, and G.O. Brown, 1998. *Column Experiments for Radionuclide Adsorption Studies of the Culebra Dolomite: Retardation Parameter Estimation for Non-Eluted Actinide Species*. SAND98-1005. Albuquerque, NM: Sandia National Laboratories.

Public Law 96-164. 1979. *Department of Energy National Security and Military Applications of Nuclear Energy Authorization Act of 1980*. (93 Stat. 1259).

Ramsey, J.L., M.G. Wallace, and H-N. Jow. 1996. "Analysis Package for the Culebra Flow and Transport Calculations (Task 3) of the Performance Assessment Calculations Supporting the Compliance Certification Application (CCA), AP-019." Albuquerque, NM: Sandia National Laboratories. (Copy on file in the Sandia WIPP Central Files, Sandia National Laboratories, Albuquerque, NM as WPO#40516.)

Sims, R., T.A. Lawless, J.L. Alexander, D.G. Bennett, and D. Read. 1996. "Uranium Migration Through Intact Sandstone: Effect of Pollutant Concentration and the Reversibility of Uptake," *Journal of Contaminant Hydrology*. Vol. 21, no. 1-4, 215-228.

Toulhoat, P. 1986. "Experimentation and Modelling of U, Th and Lanthanides Transport in Fissured Rocks: Influence of Complexation," *Scientific Basis for Nuclear Waste Management IX, Materials Research Society Symposium Proceedings, Stockholm, Sweden, September 9-11, 1985*. Ed. L.O. Werme. Pittsburgh, PA: Materials Research Society. Vol. 50, 755-762.

U.S. DOE (Department of Energy). 1996. *Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant*. DOE/CAO-1996-2184. Carlsbad, MN: United States Deparment of Energy, Waste Isolation Pilot Plant, Carlsbad Area Office.

U.S. EPA (Environmental Protection Agency). 1993. "40 CFR Part 191 Environmental Radiation Protection Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes; Final Rule," *Federal Register*. Vol. 58, no. 242, 66,398-66,416.

Vandergraaf, T.T., D.J. Drew, D. Archambault, and K.V. Ticknor. 1997. "Transport of Radionuclides in Natural Fractures: Some Aspects of Laboratory Migration Experiments," *Journal of Contaminant Hydrology*. Vol. 26, no. 1-4, 83-95.

WIPP Performance Assessment Department. 1992-1993. *Preliminary Performance Assessment for the Waste Isolation Pilot Plant, December 1992.* SAND92-0700/1-5. Albuquerque, NM: Sandia National Laboratories. Volumes 1-5.

Table 1. Test sample cores.

Series	A	B	C	D	E
Core: VPX	28-6B	26-11A	28-6C	25-8A	27-7A
Cut core measures					
Length (cm)	40.6	50.9	10.2	10.8	10.2
Diameter (cm)	14.5	14.5	14.5	14.5	14.5
Wet weight (gm)	16582	20900	4146	4401	4102
Estimated Properties					
Dry bulk density (gm/cm^3)	2.38	2.40	2.40	2.40	2.38
Porosity	0.15	0.14	0.14	0.14	0.15

Table 2. Brine composition.

Brine	VPX 25	VPX 26	VPX 27	VPX 28	ERDA 6
Ions (gm/L)					
Boron	0.0258	0.0263	0.0266	0.0274	0.68
Bromine	0.054	0.0226	0.0243	0.0217	0.88
Calcium	0.8750	0.832	0.8580	0.8350	0.49
Carbon, inorganic	0.0113	0.0121	0.017	0.0120	0.19
Chloride	18.9	19.3	19.2	19.4	170
Magnesium	0.4540	0.4190	0.4500	0.4230	1.04
Potassium	0.3220	0.3330	0.3220	0.3170	3.79
Sodium	13.1	13.8	13.3	14.2	112
Sulfate	6.65	7.25	6.94	7.41	16.3
Borehole pH	7.65	7.69	8.10	8.09	6.17

Table 3. Properties of isotopes used in testing.

Isotope	Half Life	Principal Emissions	Moles per Curie	Solubility (Molar)	MDA[3]	
					γ Spec (nCi/ml)	LSC (pCi/ml)
^{3}H	12.28 y	beta	3.43×10^{-5}			1.5
^{22}Na	2.602 y	γ	7.28×10^{-6}			
^{241}Am	432.2 y	γ & alpha	1.21×10^{-3}	6.46×10^{-9} [1]	0.06	0.1
^{239}Np	2.355 d	γ	1.80×10^{-8}	4.17×10^{-5} [1]	0.62	
^{228}Th	1.913 y	γ	5.35×10^{-6}	1.90×10^{-7} [1]	3.8	
^{232}U	72 y	γ & alpha	2.0×10^{-4}		1.2	0.1
^{241}Pu	14.4 y	beta	4.03×10^{-5}	3.0×10^{-8} [2]		1.5

[1] Calculated solubility in a air-intake shaft brine without dolomite equilibrium.
[2] Lower limit of measured solubility in a air-intake shaft brine.
[3] MDA based on 15 minute counts.

Table 4. Test conditions.

Test	Injected Isotopes	Spike (ml)	Flow Rate (ml/m)	Vol. (L)	Time (days)
A-1	0.641 μCi ^{3}H	20	0.5	2	2.8
A-3	0.22 μCi ^{3}H	20	0.1	2	13
A-4	23 μCi ^{22}Na 156 μCi ^{239}Np	20	0.1	2	13
B-1	0.246 μCi ^{3}H	13	0.1	0.5	
B-2	8.69 μCi ^{22}Na 375 μCi ^{239}Np	18	0.1	2	13
B-3	8.23 μCi ^{22}Na 70.7 μCi ^{232}U 70.7 μCi ^{228}Th	13.7	0.1	2	13
B-4	300 μCi ^{22}Na	2000	0.1	4	30
B-5	274 μCi ^{22}Na	2000	0.05	2	60
B-6	4.22 μCi ^{22}Na 5.94μCi ^{232}U	17	0.05	2	60
B-7	9.0 μCi ^{22}Na 4.28 μCi ^{232}U	18	0.5	4	
B-8	220 μCi ^{22}Na	2000	0.5	4	
C-1	1μCi ^{22}Na 10μCi ^{3}H	20	0.1	2	13.3
C-2	3.7μCi ^{22}Na 10μCi ^{232}U 10μCi ^{228}Th	20	0.1	2	21
C-3	3.3μCi ^{22}Na 20μCi ^{241}Pu 5.6μCi ^{241}Am	20	0.1	2	16
C-4	11.5μCi ^{22}Na 78.3μCi ^{239}Np	10	0.1	2	49
C-5	3.4μCi ^{22}Na 26.8μCi ^{239}Np 4.8μCi ^{232}U 4.8μCi ^{228Th}	10	0.1	2	13
C-6	5.3μCi ^{22}Na 175μCi ^{239}Np	8.5	0.1	2	13
C-7	6.83μCi ^{22}Na 327μCi ^{239}Np 50μCi ^{232}U	10	0.1	2	13
D-1	0.35μCi ^{3}H	18	0.1	0.5	4.0
D-2	3.4μCi ^{22}Na 4.8μCi ^{232}U 4.8μCi ^{228}Th 26.8μCi ^{239}Np	10	0.1	2	12
D-3	3.1μCi ^{22}Na16.1μCi ^{241}Pu 4μCi-^{241}Am	10	0.1	2	13
D-4	5.3μCi ^{22}Na 175μCi ^{239}Np	8.5	0.1	2	13
D-5	3.97μCi ^{22}Na 43.2μCi ^{232}U	10	0.1	2	13
D-6	3.4μCi ^{22}Na 53μCi ^{232}U	20	0.05	2	60
E-1	3.17μCi ^{22}Na 40 μCi ^{232}U 156μCi ^{239}Np	20	0.1	2	12
E-2	3.07μCi ^{22}Na 20μCi ^{241}Pu 20μCi ^{241}Am	18.5	0.1	2	13

Table 5. Parameter fitting for conservative solutes.

Test	Isotope	Single Porosity			Dual Porosity			
		ϕ %	D cm^2/s	RMS nCi/ml	ϕ_f %	D_f cm^2/s	B cm	RMS nCi/ml
A1	^3H	4.4	0.00372	0.20	3.2	0.00147	0.89	0.04
A3	^3H	1.9	0.00489	0.07	1.5	0.00465	6.00	0.06
A4	^{22}Na	2.1	0.00288	6.58	2.2	0.0025	13.5	11.4
B1	^3H	19.9	0.00134	0.03	7.9	0.00092	1.27	0.02
B2	^{22}Na	9.2	0.00118	1.01	6.0	0.00081	1.74	0.39
B3	^{22}Na	9.2	0.00142	0.69	4.9	0.00010	1.50	0.38
B4	^{22}Na	7.9	0.00207	6.90	8.0	0.002	12.0	8.34
B5	^{22}Na	7.9	0.00103	6.54	8.0	0.002	12.0	8.55
B7	^{22}Na	13.0	0.00870	0.45	5.6	0.00656	0.58	0.12
B8	^{22}Na	8.3	0.00675	2.94	*Unable*	*to*	*fit*	
C1	^3H	3.2	0.00057	7.42	2.2	0.00030	1.21	6.08
C1	^{22}Na	2.5	0.00038	0.02	2.6	0.00038	8.33	0.03
C2	^{22}Na	8.5	0.00266	2.37	3.7	0.00439	2.70	1.45
C3	^{22}Na	3.3	0.00204	2.44	*Unable*	*to*	*fit*	
C4	^{22}Na	4.8	0.00133	4.65	1.3	0.00033	0.57	1.89
C5	^{22}Na	4.3	0.00250	1.19	1.6	0.00206	1.14	0.92
C6	^{22}Na	5.9	0.00170	2.63	1.5	0.00096	0.79	1.33
C7	^{22}Na	2.0	0.00155	2.63	1.9	0.00151	8.50	2.62
D1	^3H	14.3	0.00055	0.07	7.3	0.00047	0.78	0.04
D2	^{22}Na	8.0	0.00058	0.43	5.2	0.00046	1.05	0.21
D3	^{22}Na	8.9	0.00053	0.44	5.4	0.00042	0.88	0.42
D4	^{22}Na	9.7	0.00054	1.60	3.5	0.00035	0.67	0.81
D5	^{22}Na	9.7	0.00054	0.35	5.6	0.00034	0.76	0.31
D6	^{22}Na	9.6	0.00045	0.59	5.4	0.00020	0.73	0.60
E1	^{22}Na	18.3	0.00024	0.23	15.5	0.00022	1.46	0.15
E2	^{22}Na	23.8	0.00029	0.36	15.0	0.00025	0.88	0.37

Table 6. Parameter fitting for U and Np retardation.

Test	Isotope	Single Porosity		Dual Porosity				
				Rf = 1		*Rf > 1*		
		R	RMS nCi/ml	R_m	RMS nCi/ml	R_f	R_m	RMS nCi/ml
B3	U	4.50	1.36	68.8	4.99	1.14	65.4	4.95
B6	U	6.40	1.24	*Unable*	*to fit*	*Unable*	*to*	*fit*
B7	U	3.70	0.30	63.6	2.19	4.35	1.00	0.48
C2	U	13.9	1.69	4577	3.52	16.2	4287	3.09
C7	U	3.23	2.28	2975	5.32	2.64	486	2.11
D5	U	18.1	0.78	1500	2.22	12.6	675	0.54
D6	U	10.1	1.42	332	7.22	9.77	71.5	2.08
E1	U	1.80	1.30	236	3.27	1.84	29.3	1.14
C6	Np	77.5	0.37	5667	2.01	56.2	700	0.26
C7	Np	75.1	2.28	*Unable*	*to fit*	8.90	17421	1.71
D2	Np	29.7	0.04	*Unable*	*to fit*	18.3	10395	0.04
D4	Np	37.0	0.25	5921	0.58	25.6	1095	0.07

Table 7. Lower Bounds on Retardation for Noneluting Species.

Test	Element	Effluent Volume (L)	Limiting Case	Lower Limit of *R*
C3	Am	71.7	B	25,000
D3	Am	48.2	B	2,800
E2	Am	15.0	B	520
C3	Pu	71.7	B	20,000
D3	Pu	48.2	B	3,700
E2	Pu	15.0	B	800
B3	Th	18	A	23
C2	Th	71.1	A	47
C5	Th	68.1	A	27
D2	Th	46	A	9.1

LIST OF FIGURES

Figure 1. Borehole locations.

Figure 2. Schematic of test apparatus.

Figure 3. Possible breakthrough curves for non-eluting solutes.

Figure 4. Comparison of ^{3}H and ^{22}Na effluent breakthrough in Test C1.

Figure 5. Test B4 measured and fitted ^{22}Na effluent activities.

Figure 6. Test D5 measured and fitted ^{232}U effluent activities.

Figure 7. Test C6 measured and fitted ^{239}Np effluent activities.