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A Transport Code for Radiocolloid Migration: With an
Assessment of an Actual Low-Level Waste Site

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ABSTRACT

Recently, there is increase concern that radiocolloids may act as a rapid transport mechanism for the release of radionuclides from high-level waste repositories. The role of colloids is, however, controversial because the necessary data and assessment methodology have been limited. Evidence is accumulating to indicate that colloids are an important consideration in the geological disposal of nuclear waste. To quantitatively assess the role of colloids, the TRACR3D transport code has been enhanced by the addition of the population balance equations. This new version of the code can simulate the migration of colloids through combinations of porous/fractured, unsaturated/saturated, geologic media.

The code was tested against the experimental laboratory column data of Avogadro et al. in order to compare the code results to both experimental data and an analytical solution. Next a low-level radioactive waste site was investigated to explore whether colloid migration could account for the unusually rapid and long transport of plutonium and americium observed at a low level waste site. Both plutonium and americium migrated 30 meters through unsaturated volcanic tuff. The nature and modeling of radiocolloids are discussed along with site simulation results from the TRACR3D code.

INTRODUCTION

The disposal of radioactive waste is a long-term problem for mankind with few historical cases to serve as guiding examples. Outside of the natural reactor Oklo [1], the man made low level nuclear waste sites located at Los Alamos National Laboratory are our oldest geological disposal analogs. In 1943, Los Alamos National Laboratory constructed four adsorption beds filled with gravel and cobble at Area T in the DP West site [2]. The plan and cross-sectional views of the adsorption beds illustrated in Fig. 1 show the bed size and construction details. From 1945 to about 1967, these beds received liquid radioactive wastes from the plutonium purification plant. Since 1945, these adsorption beds at Area T have received frequent periodic investigation [2-7]. Nyhan et al. [7] discusses and summarizes findings from the earlier studies. To date, the four beds contain approximately 10 ci of plutonium of which 98% was discharged between 1945-1952.

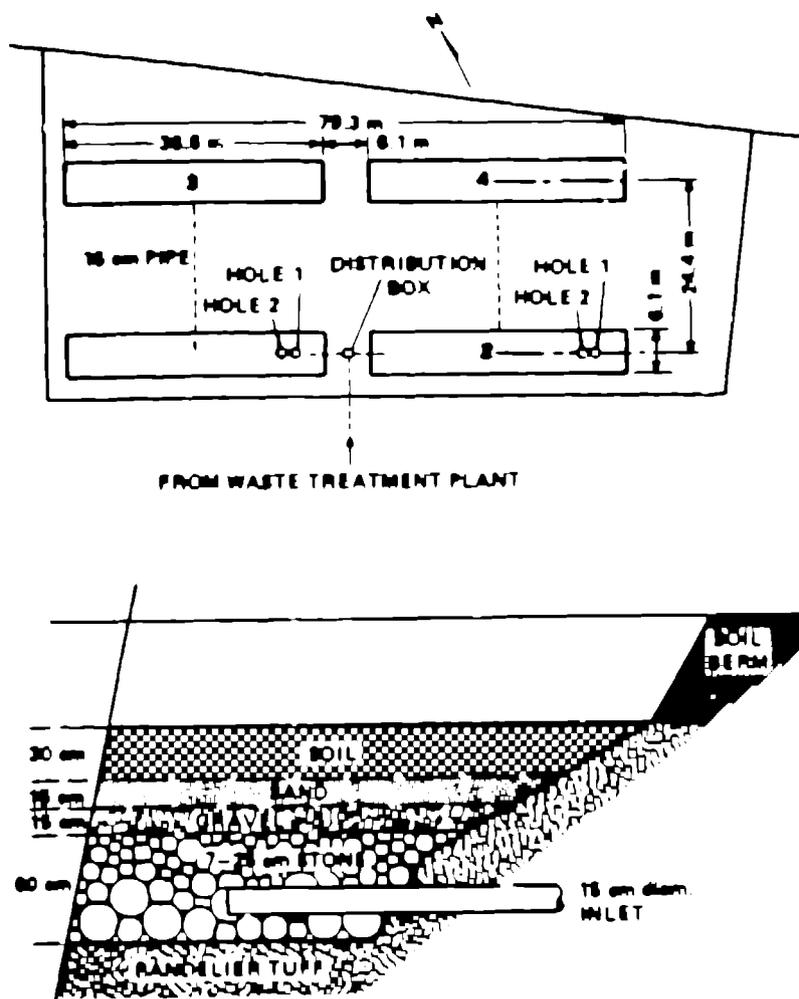


Fig. 1. Plan and cross-sectional views of the Los Alamos National Laboratory DP West plutonium adsorption beds. These beds began operation in 1945 and received radioactive liquid wastes until 1967.

Two factors are of interest at this time. First, the geological setting of the site is in volcanic tuff with properties that appear similar to those of the Yucca Mountain site. The MTS Yucca Mountain site located in Nevada is being considered for the geological storage of high-level nuclear waste. Secondly, Nyhan et al. have found from core samples taken in 1978 that both plutonium and americium had migrated vertically downward to a distance of over 30 m. The reason for this surprisingly long migration distance is unknown. Fried et al. [6] in 1975, suggested as a result of their experimental studies with tuff and solutions of plutonium that colloidal forms of plutonium may account for this rapid migration. The assumed polymeric form of the plutonium was observed to travel ten times faster than the ionic form. In experiments on large blocks of tuff, they clearly observed two peaks in the measured plutonium concentration profile; one peak corresponded to the ionic form and the other to the colloid/hydrolysed form.

Although laboratory experiments strongly indicate the likelihood of rapid colloid migration, the unanswered question is whether colloidal forms of plutonium and americium can account for the measured rapid and long migration of radioactive waste at the DP West Site. To address this question a numerical simulation of the site was performed. A comprehensive numerical code called TRAC3D [8] developed at Los Alamos National Laboratory was used to simulate the unsaturated site hydrology and the postulated transport of radiocolloids. The 1978 field study by Myhan et al. [2] provided moisture content versus depth data and radionuclide concentrations versus depth curves for plutonium and americium. In this paper we simulated the site hydrology and radionuclide transport to determine if colloid migration could account for the rapid and long migrations measured in the field study by Myhan et al.

Background on Colloids

Colloids are a class of extremely small particles which were first studied early in the nineteenth century by Michael Faraday and other scientists [10]. They are characterized as particles containing several hundred to several thousand atoms, ions, or molecules and having diameters ranging from ten to one thousand angstroms.

Particles in the colloidal state scatter light in a phenomenon known as the Tyndall effect. They also exhibit Brownian movement in a dispersing medium. They exhibit a very slow rate of settling in a dispersing medium giving rise to stable colloidal dispersions. Colloids may be separated by the process of electrophoresis due to their surface charge characteristics. Matter in the colloidal state has a large surface area (300 square meters per gram), thus it is not surprising that the most important properties of colloids are those which are dependent on surface interactions such as adsorption.

Drever [11] discusses the nature and geochemistry of colloids with emphasis on the charge surrounding colloids and its effect on suspension stability. In most natural colloids other than smectites (e.g. oxides of Si, Al, Fe and colloidal organic matter), the surface charge results from ionization or adsorption of ions on the surface of the solid. In strongly acidic solutions the surface will gain a proton and become positively charged while the opposite occurs in strongly alkaline solutions. Surrounding colloids is a double layer of ions. The Stern layer is more or less attached to the solid surface and outside is the Gouy layer in which the ions are free to move. The structure of the double layer is of great interest and mathematical models are available to describe the distribution of ions within it. The stability of a colloid suspension depends on the thickness of the Gouy layer, which depends on the potential at the outside of the fixed layer, and on the ionic strength of the solution. Colloids also exhibit ion exchange behavior as measured quantitatively in soil sciences by the cation-exchange capacity (CEC).

Olofsson et al. [12-14] classify radiocolloids as true colloids and pseudocolloids depending on their formation process. True colloids are formed by condensation of the molecules or ions as a result of hydrolytic or precipitation

processes. They consist mostly of hydroxides or polymers formed by hydrolysis. They have a very rapid formation rate and are favored at high pH values. Pseudocolloids, on the other hand, are formed as a result of adsorption on impurities in the solution and tend to be much larger than true colloids (up to 5000 angstroms). Pseudocolloids can be of two types, reversible and irreversible. The former are produced by reversible surface adsorption. In this case, the adsorbate may easily pass back into solution. In the irreversible case, the element is either incorporated into the interior of the foreign particle or irreversibly adsorbed on it. The formation rate of pseudocolloids is basically determined by the sorption rate on colloidal impurities [12].

Radiocolloids are colloids containing radionuclides. They possess all the properties of normal colloids but in addition are radioactive. They may migrate in the ground matrix by virtue of groundwater and may also be captured by existing colloids. Radiocolloids are believed to be a significant vector for the transport of radionuclides from failed waste repositories, and might actually accelerate this transport [15,16].

Radiocolloids may arise from a variety of sources. Leaching of the waste form with groundwater may lead to the isotope itself producing colloids. Champ, et al. [17] have demonstrated experimentally the existence and rapid transport of plutonium colloids using core samples and groundwater.

Olofsson, et al. [12,13,14] showed the formation and rapid nonadsorbing migration of americium colloids over a wide range of pH. Corrosion of canister material can lead to the formation of adsorbant colloids. Olofsson, et al. suggest that the elements which are most likely to form colloid species would be hydrolyzable elements like the actinides and possibly Sr, Pb, and Cu representing the encapsulation material in the Swedish program. Degradation of engineered backfills at the end of a repository's active life may lead to colloid formation. Also at other geological sites, naturally occurring colloids from clays (smectites, vermiculites, illites, kaolinite and chlorite) present in groundwater may adsorb radionuclides.

MODELING APPROACH

Several researchers have prepared models for the transport of radiocolloids with varying degrees of success. Apps, et al. [19] carried out preliminary modeling employing many simplifying assumptions which could be very important to repository assessment. A particular shortcoming is the very limited treatment of particle size effects. Chiang and Tien [20] modeled the capture of colloids within a porous medium but did not treat radioactive decay, particle size effects, the migration of individual nuclides or radiocolloids specifically. Their model is complete though for the treatment of colloid capture by the ground matrix. Avogadro, et al. [16] prepared a one-dimensional filtration model employing the population balance to treat colloid transport and a sink term to treat colloid capture. They claim that the predominating mechanisms affecting the migration of radiocolloids are filtration and solubilization.

TRACR3D Computer Code

The TRACR3D numerical computer code [8] was developed at Los Alamos National Laboratory to solve general porous/fractured media transport problems. The code uses an implicit finite difference scheme to solve simultaneously the mass and chemical species conservation equations, a reduced form of the momenta equations, and an equation of state plus several constitutive relations. The code also treats unsaturated flow problems and the transport of monodispersed colloids. Future versions of TRACR3D will treat polydispersed and reactive colloids; however, the current version was quite suitable for simulating colloid and radionuclide transport at the DP West disposal site as described in the following section.

Colloids are a discontinuous phase of discrete particles and are modeled using the population balance equations in the form derived by Randolph [20]. Muttall [9] applied the population balance to radiocolloids and showed that, in general, the dissolved species mass balance and population balance equations are coupled through the migration of radionuclides onto natural colloids or through the precipitation of species to form true colloids. The model equations [9] are summarized below and include the mass balance, the true and natural colloid population balance, and the reduced 1-D monodispersed form of the population balance equation.

DISSOLVED SPECIES MASS BALANCE

$$\frac{\partial C_i}{\partial t} + \vec{v} \cdot \nabla C_i = D \nabla^2 C_i - \lambda_i C_i - \text{sink} \quad (1)$$

where

- C_i = concentration of species 'i'
- D^i = effective diffusivity
- sink = transfer of species to the colloids and rock matrix
- t = time
- \vec{v} = fluid velocity
- λ = radioactive decay constant for species 'i'

TRUE COLLOID POPULATION BALANCE

$$\frac{\partial \phi_{t1}}{\partial t} + \nabla \cdot (\vec{v} \phi_{t1}) - D_b \nabla^2 \phi_{t1} + \sum_{j=1}^m \frac{\partial}{\partial t_j} (v_j \phi_{t1}) + D_1 - B_1 = 0 \quad (2)$$

NATURAL GROUNDWATER COLLOID POPULATION BALANCE

$$\frac{\partial \phi_{nk}}{\partial t} + \nabla \cdot (\vec{v} \phi_{nk}) - D_b \nabla^2 \phi_{nk} + \sum_{j=1}^m \frac{\partial}{\partial t_j} (v_j \phi_{nk}) + D_k - B_k = 0 \quad (3)$$

SIMPLIFIED VERSION OF THE POPULATION BALANCE

$$(4) \quad \frac{\partial \phi}{\partial t} + \vec{v} \cdot \nabla \phi - D_b \nabla^2 \phi + \sum_{j=1}^n \frac{\partial}{\partial \xi_j} (v_j \phi) = -D$$

where

B = colloid birth function
D = colloid death function
D_b = Brownian diffusion
fluid/colloid velocity vector
time growth rate and

Greek
φ = population density
function
ξ = property axis
v = property rate \vec{v} =
function (includes t =
concentration change)

Subscripts

i = index for different types of true colloids
j = property axis type (growth/size, concentrations)
k = index for different types of natural/pseudo colloids
n = natural/pseudo colloids
t = true colloids.

The TRACR3D code was used to study colloid transport in both a laboratory column experiment and at a low level nuclear waste disposal field site.

SIMULATION OF RADIOCOLLOID TRANSPORT IN A LABORATORY COLUMN EXPERIMENT

To test the code and better understand colloid transport in porous media, Avogadro's [16] experimental laboratory column data and analytical model results were compared to simulations using TRACR3D. Avogadro, et al. [16] showed that the total concentration of colloids in a 1-D column experiment can be modeled as

$$C = \int_0^{\infty} C^0 f(\lambda) \exp(-\lambda x) d\lambda \quad (5)$$

$$c = \int_0^{\infty} \lambda C^0 f(\lambda) \exp(-\lambda x) (t - \pi \omega/U) d\lambda \quad (6)$$

where

C = concentration of colloids in the liquid phase, expressed as volume of colloids per unit volume of liquid.

$f(\lambda)$ = distribution of λ , assumed to be log normal in our paper.

U = Darcy's velocity in the medium.

λ = filtration coefficient.

ω = kinematic porosity.

σ = concentration of colloids retained by filtration in the medium, expressed as volume of colloids per unit volume of porous medium.

Avogadro et al. showed that their data could be fit using Equation (6) and assuming a log-normal distribution for the filtration coefficient, λ . Fig. 2 is a plot of Avogadro's column profile data and the results from Equation (6) for various mean values of λ and sigma deviations in the log-normal distribution. They reported that λ ranged from 0.2 to 10 cm^{-1} . When the width of the distribution is small or a single value of λ is used the concentration versus position is a straight line. In our TRACR3D simulations, we assumed a discrete size distribution and were able to fit the experimental data as shown in Fig. 2.

COLUMN EXPERIMENT

Radiocolloid Concentration

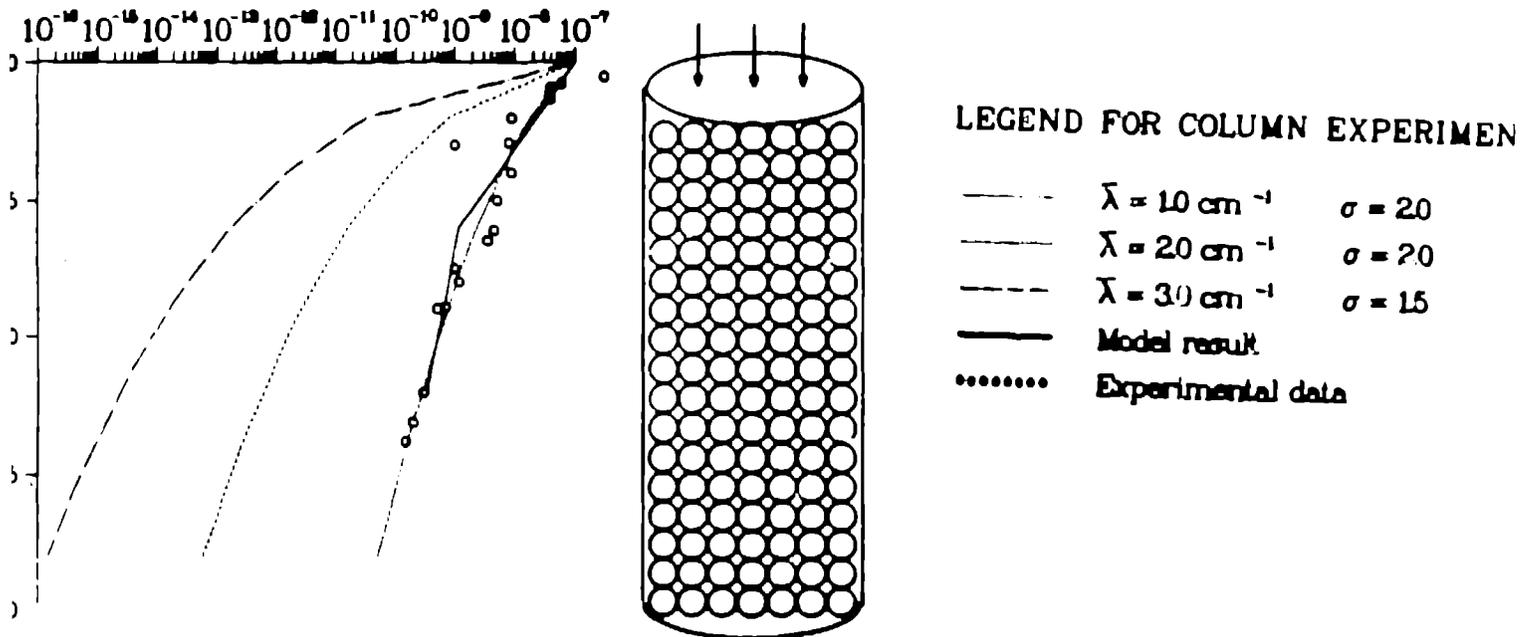


Fig. 2. Modeling studies of americium colloid laboratory column data [17]. Results from two models are shown: an analytical model assuming a lognormal distribution of colloid sizes and the TRACR3D numerical code.

The TRAC3D code with its advanced hydrology and transport capabilities was used to assess the likelihood of colloid migration in the volcanic tuff below the Los Alamos DP West low-level waste disposal site. Field measurements showed that plutonium and americium migrated 30 meters in unsaturated Bandelier tuff over a 33 year period. The DP West site geological setting is in volcanic tuff which exhibits some properties similar to those at the proposed Yucca Mountain high-level nuclear waste disposal site.

The calculations modeled one-dimensional, vertical liquid flow and tracer transport over the 33 year period from 1945 to 1978. Three scenarios were studied two assuming ion migration with different adsorptions and a third assuming colloid migration. All cases were calculated assuming the same hydrology and the same dynamic liquid input flux. The stratigraphy was modeled assuming 30 m of tuff (density = 1.5 gm/cc and void fraction = 0.38) with a 1 m clay layer at a depth of 10 m. Results were compared with the measured plutonium concentration profile take from the field study by Nyhan, et al. [2]. The calculated profiles and field data are compared in Fig. 3.

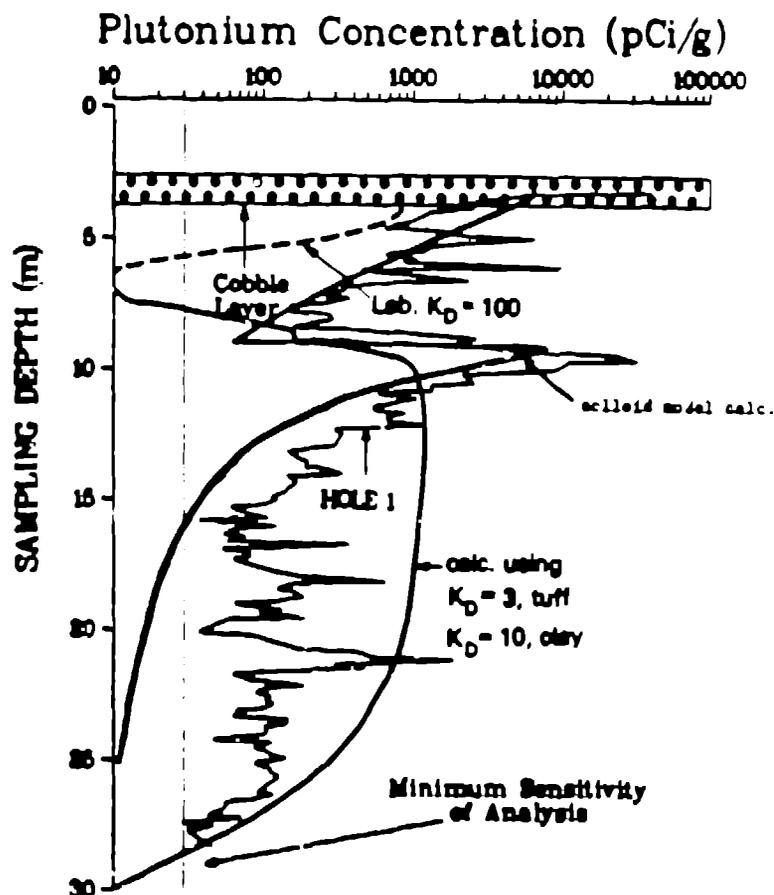


Fig. 3. The measured and simulated plutonium concentration profiles for the region below bed #1 at the DP West disposal site.

Case 1 was calculated using a constant adsorption coefficient, $K_d = 100$, which is the lowest value suggested by laboratory experiments. In this case, the radionuclides migrated only a few meters during the 33 year period which is much less than the measured 30 m migration. Case 2 was calculated using $K_d = 3$ for tuff and $K_d = 10$ for the clay layer. In this case, the tracer reached observed depths but the shape of the concentration profiles did not match the measured profiles. In addition, the low K_d values may be difficult to justify. Case 3 was calculated using the colloid population balance equations that were added to TRAC3D. As shown in Fig. 3, calculated concentration profiles matched field data much better than the two previous cases and indicate that colloid transport was a likely mechanism for radionuclide migration at the DP West disposal site.

SUMMARY

The calculations strongly suggest the presence and rapid migration of plutonium and americium radiocolloids. Both laboratory column experiments and the DP West disposal site data were analyzed using the population balance methodology. This approach is useful in treating particulate transport in porous media. Our analysis of DP West Site using the comprehensive TRACR3D code also indicated the presence of a rapidly migrating form of plutonium and americium which we assume is a radiocolloid form.

The following conclusions summarize our findings.

The population balance methodology was applied successfully to the modeling and analysis of radiocolloid migration.

Both laboratory column data and field data were analyzed using the population balance equations as implemented in the TRACR3D numerical code.

Numerical simulations of the DP West Site hydrology indicated that the region below the beds became saturated during the high input period from 1945 to 1952. This is consistent with reports that the beds would not accept further discharge in 1952 and a waste treatment plant was constructed at this time to reduce the waste discharge.

Calculations indicated the presence of colloid migration as was found by Fried et al. [6] in their 1975 laboratory studies. They observed, in their column experiments on Bandelier tuff, a fast migration form of plutonium.

REFERENCES

1. Douglas G. Brookins, Geochemical Aspects of Radioactive Waste Disposal, (Springer-Verlag, 1984), pp. 212-216.
2. J. W. Nyhan, et al. Distribution of Radionuclides and Water in Bandelier Tuff Beneath a Former Los Alamos Liquid Waste Disposal Site After 33 Years, Submitted to Journal of Environmental Quality, 1984.
3. W. V. Abee, M. L. Wheeler, and B. W. Burton, Geohydrology of Bandelier Tuff, Los Alamos National Laboratory, LA-8962-MS, October, 1981.
4. M. A. Rogers, History and Environmental Setting of LASL Near-Surface Land Disposal Facilities for Radioactive Wastes (Areas A, B, C, D, E, F, G, and T), Los Alamos National Laboratory, LA-6848-MS, Vol. 1 and Vol. II June, 1977.
5. C. W. Christenson and R. G. Thomas, Movement of Plutonium through Los Alamos Tuff," in "Second Ground Disposal of Radioactive Wastes Conference," Technical Services, US Department of Commerce report TID-7628(1962), pp. 249-282.
6. S. M. Fried, A. M. Friedman, J. J. Hines, and L. A. Quarterman, "Annual Report on DWMT Project ANO115A, FY 1975, Argonne National Laboratory report ANL-75-64(1975).
7. S. M. Fried, A. M. Friedman, J. J. Hines, R. W. Atcher, L. A. Quarterman, and A. Volesky, "Annual Report for FY 1976 on Project ANO115A: The Migration of Plutonium and Americium in the Lithosphere," Argonne National Laboratory report ANL-76-127(1976).
8. B. J. Travis, TRACR3D: A Model of Flow and Transport in Porous/Fractured Media, Los Alamos National Laboratory, LA-9667-MS, May, 1984.
9. H. E. Nuttall, Radioactive Colloids, Report prepared for Sandia National Laboratory; Waste Management System Division, December, 1983.
10. Encyclopedia Americana International Edition, (1975).
11. James I. Drever, The Geochemistry of Natural Water (COLLOID PROPERTIES), (Prentice Hall, 1982) pp. 78-89.
12. U. Olofsson, B. Allard, K. Andersson, and B. Torstenfelt, "Formation and Properties of Radiocolloids in Aqueous Solution-A Literature Survey," Programradet for Radioaktivt Avfall, National Council for Radioactive Waste, Report Proav 4.25, Department of Nuclear Chemistry, Chalmers University of Technology, Goteborg, Sweden, 1981.
13. U. Olofsson, B. Allard, K. Andersson, and B. Torstenfelt, "Formation and Properties of Americium colloids in Aqueous Systems," Scientific Basis for Nuclear Waste Management, Vol. 4, S. Topp, Ed., (1982).
14. U. Olofsson, B. Allard, B. Torstenfelt and K. Andersson, "Properties and Mobilities of Actinide Colloids in Geologic Systems," Scientific Basis for Nuclear Waste Management, Vol. 5, Werner Lutze, Ed., pp. 755-764 (1982).
15. A. Avogadro, and P. Lanza, "Relationship between Glass Leaching Mechanism and Geochemical Transport of Radionuclides," Scientific Basis for Nuclear Waste Management, Vol. 5, Werner Lutze, Ed., pp. 103-112 (1982).
16. A. Avogadro, and G. De Marsily, "The Role of Colloids in Nuclear Waste Disposal," Scientific Basis for Nuclear Waste Management, Gary L. McVay, Ed., pp. 493-505, (1983).

17. D. R. Champ, W. F. Merritt, and J. L. Young, "Potential for the rapid Transport of Plutonium in Groundwater as Demonstrated by Core Column Studies," Scientific Basis for Nuclear Waste Management, Vol. 5, Werner Lutze (Ed), pp. 745-754, (1982).
18. J. A. Apps, C. L. Carnahan, P. C. Lichtner, M. C. Michel, D. Perry, R. J. Silva, O. Weres, and A. F. White, Status of Geochemical Problems Relating to the Burial of High-Level Radioactive Waste, NUREG/CR-3062, LBL-15103, Prepared for the Nuclear Regulatory Commission, 1983.
19. Hsu-wen Chiang and Chi Tien, Deposition of Brownian Particles in Packed Beds, Chemical Engineering Science, 17, (8), 1159(1982).
20. A. D. Randolph, A Population Balance for Countable Entities, Can. J. Chem. Eng., 42, 280(1962).