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POPULATION BALANCE MODEL FOR COLLOID TRANSPORT

NNWSI REPORT/MILESTONE

by

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ABSTRACT

Recently, there is increased concern that radiocolloids may act as a rapid transport mechanism for the early 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. In this report the population balance methodology is presented and developed as a method for quantifying the role of colloids in ground water transport problems. The population balance is a number continuity equation which has been applied successfully to crystallization, aerosols, and biological processes. The equations are developed and applied to the treatment of polydispersed radiocolloid transport and to colloid migration data from column experiments. The population balance approach provides a sound basis for analyzing the impact of colloids on nuclear waste repositories.

I. INTRODUCTION

The behavior and transport of colloids is becoming an important consideration in understanding hydrogeological systems. The migration of suspended matter impacts on many environmental groundwater problems, for example, the disposal of nuclear waste, the movement of heavy metals, and the migration of toxic organic compounds. In natural systems clay particles are believed to migrate and in some cases transport and concentrate silica and iron as chemical deposits [Pettijohn, 1949]. A more recent [McDowell-Boyer et al., 1985] study has shown that clay colloids provide ideal adsorption sites for microbes and that bacteria and viruses carried presumably by clay colloids have been found to migrate through aquifers up to distances of 400-800 meters. The migration of sediments from streams, to lakes, to rivers, and eventually into oceans is a topic of considerable interest and active investigation. Suspended particulate matter also plays a vital role in ocean chemistry. In the biosphere, studies have shown that atmospheric plutonium attaches to colloids which subsequently migrate down streams and rivers to the oceans where they agglomerate with organic matter and finally settle to the ocean floor [Yariv and Cross, 1979].

There have been many general articles addressing problems associated with the assessment of geological disposal of nuclear waste [Gonzales, 1982; Klingsberg and Duguid, 1982; Pigford, 1982; Technical Report, 1983; Siegel, 1985]. Recently, radiocolloids have been identified as a potential hazard in the disposal of nuclear waste. Radionuclides in a colloidal or particulate form could conceivably migrate farther and faster than they would in a dissolved form [Apps et al., 1983]. McDowell-Boyer et al. [1985] recently expressed concern over the possibility of colloid transport in nuclear repository sites. "One aspect of radionuclide migration in subsurface flows that casts further doubt on the distribution coefffficient approach is the possibility that colloidal matter and small particles to which radionuclides adsorb are mobile. Particles of sizes less than a few micrometers are much smaller than inter-granular pores or fracture sizes and could migrate considerable distances with flowing fluid. Colloid migration becomes significant in predicting contaminant migration because small particles have high surface areas per unit mass and represent available sites for adsorption." The 1984 Beijer report [Parker et al., 1984] made many references to the importance of colloids in nuclear waste disposal and to the currently unresolved problems in assessing nuclear waste repositories because we do not fully understand the role of colloid transport. In this report Parker et al. [1984] suggested that in fractures colloids may not be retarded.

Unfortunately, previous studies have not provided sufficient information concerning these complicated processes to quantify colloid transport in groundwater [Stumm and Morgan, 1981]. As stated in the conclusions of report by Apps et al. [1983] "nothing is known about the migration behavior of colloids." By contrast there is great interest and many studies which address the basic chemical and physical nature of colloids [Matijevic, 1973; Adamczyk et al., 1983; Allard et al., 1980; Avogadro and Lanza, 1982; Avogadro and Marsily, 1983; Drever, 1982; James and Parks, 1982; Means and Wijayaratne, 1982; Olofsson et al.; 1981, 1982a, 1982b]. Colloid science is a mature and well developed field. The classical colloid science book by Alexander and Johnson [1949] summarized the historical development of this subject and initiated the term COLLOID SCIENCE. In recent years many models have been presented to characterize the behavior of colloids [James and Parks, 1982] in batch systems but there has been no unified approach to colloid transport modeling.

To address the problem of modeling colloid transport, we present, in this paper, a general colloid transport model which can treat the complex problems of colloid migration in geological media. The physical and chemical nature of ground water colloids are reviewed. The potential role of colloids in various nuclear waste repository scenarios is presented. The population balance equations are developed and applied to the analysis of colloid column data. The population balance transport model is solved numerically and results compared to column data. The important population balance submodels for nuclear waste disposal are identified and developed. The filtration type capture submodel is used within the population balance code to represent removal of colloids by porous media.

This new modeling and assessment approach provides a solid basis for analyzing the impact of colloids on nuclear waste repositories.

A. Colloids--Background

Colloids were initially studied by Michael Faraday and other scientists early in the 19th century. The name colloid was given to these extremely small particles by the Scottish chemist Thomas Graham in 1861 [Encyclopedia Americana International, 1975]. By definition colloids are very small particles ranging in size from 1 to 1000 nm. In geological systems natural colloids are chemically the hydrated aluminum silicates (clay minerals), hydrated iron, manganese, aluminum oxides and certain types of organic matter [Berry and Mason, 1959]. Particles smaller than 1 nm (10 Å) do not exist as a discrete phase, and any system containing them is not considered heterogeneous [van Olphen, 1977; Apps et al., 1983]. Soil scientists regard the upper particle diameter for the definition of colloids as 2 or 3 μm [Apps et al., 1983].

There are two classes of colloids: lyophobic and lyophilic. Lyophobic colloids are the type generally found in geological systems and associated with nuclear waste disposal systems. They are considered metastable because they are prevented from agglomerating by their electrokinetic double-layer. Ground water colloids can form from the build-up of particles by precipitation or from the chemical and physical decomposition of bulk matter into colloid-size particles. Geologists refer to the formation of clays as a result of a diagenesis process, i.e., changes of various kinds occurring in sediments between the time of deposition and the time at which complete lithification takes place [Berry and Mason, 1959].

Perhaps the most important property of colloids is the double-layer of ions that surrounds each particle. The Stern layer is closest to the particle's surface followed by the outer region of ions called the Gouy layer. James and Parks [1982] developed a unified model to predict surface charge and potential. In acidic solutions the colloid gains a proton and becomes positively charged while the opposite occurs in basic solutions. The stability of colloid solutions depends on the thickness of the Gouy layer. As the ionic strength of the solution increases, the Gouy layer becomes compressed and the particles tend to agglomerate, held together by the short range van der Waals attractive force. Very stable colloid solutions can be formed which will remain for hundreds of years as in the case of India ink, which is a rather stable colloid solution of lampblack.

B. Radiocolloids

The Beijer Report [Parker et al., 1984] suggests that in nuclear waste disposal environments, radiocolloids may be formed by the following processes:

1. The elements may naturally assume a colloidal form at system temperatures, pressures, pHs and Ehs.
2. The element may attach itself to colloids naturally present in the ground water.
3. The element may attach itself to colloids produced from the high level waste (HLW) matrix during leaching, e.g., colloidal silica from borosilicate glass.
4. The element may attach itself to the small clay particles which can act as colloids

Pseudocolloids are defined [Apps et al., 1983] as natural ground water colloids that have adsorbed radionuclides, and true colloids are defined as precipitates of various radionuclides. These definitions will be used in this report.

C. Modeling

Previous colloid studies did not provide a unified nor comprehensive colloid transport model, but rather modeled individual subsets of the problem. Apps et al. [1983] recently reviewed colloid and particulate transport in the geologic storage of nuclear waste. They provided numerous references suggesting that colloid formation is strongly evident in natural systems but they did not quantitatively assess the potential formation and convective migration rates of nuclear colloids in repository environments. They presented a continuum model for diffusive transport of uncharged colloidal particles in spherical geometry and calculated fluxes relative to fluxes of dissolved species in a nonsorbing environment. Colloid size distribution, chemical retardation, colloid electrical charge, and production of radionuclides from decay of possible ancestors were not included in this model. McDowell-Boyer et al. [1985] discussed the classical filtration model and used filtration theory in a parameter sensitivity study to investigate various capture mechanisms as a function of particle size. They used the filtration coefficient model presented by Tien and Payatakes [1979]. This model only describes the filter coefficient which includes the sum of three terms: one representing capture by Brownian motion, the second representing interception collision, and finally a term for gravitational sedimentation. Their resulting empirical model also assumed no electrostatic repulsion between particles and the media surfaces. Hence, this model would not be applicable to many radiocolloid applications and would most likely over predict the colloid capture rate.

Saltelli et al. [1984] performed a series of column experiments and applied a modified version of the filtration equations to describe the measured capture profiles. They attempted to included colloid size effects by assuming a distribution for the filtration coefficient. More recently, Travis and Nuttall [1985] modeled colloid migration using the population balance method. They showed that the population balance model accurately described the colloid column capture data of Saltelli et al. [1984] and that the filtration coefficient in this study was a simple linear function of the colloid size.

Chiang and Tien [1982] have modeled in some detail the capture of colloids within a porous medium; however they did not specifically treat radioactive colloids. They stated that when Brownian diffusion is the dominant force the common trajectory calculation approach is no longer possible. It is believed at this time that Brownian diffusion will be the dominant capture mechanism because of the very small size of radiocolloids (<0.1 µm). Although the authors include most of the attractive and repulsive forces in their rather complete mathematical description, they neither include particle size effects nor do they consider radioactive decay and the migration of individual nuclides. Their work has limited applicability to the modeling of colloid capture in a porous medium. It will be shown later in this report that the capture model is actually a submodel and will appear as a death term in the population balance which is presented in the next section. Guzy et al. [1983], Adamczyk et al. [1983], Spielman et al. [1977, 1970a, 1970b, 1970c], Fitzpatrick et al. [1973, 1974] and Chiang et al. [1982] as well as many other researchers have modeled the capture of particles/colloids.

With the exception of the modeling by Apps et al. [1983] and Saltelli et al. [1984] the literature on radioactive colloids has been experimental in nature, showing the readily apparent formation of radiocolloids but essentially nothing on the quantitative modeling of colloid transport. The absence of colloid models and the lack of quantitative assessment clearly points to the need for such modeling information.

In the following section we will develop the generalized approach to colloid transport in ground water by using the now well established population balance methodology. The population balance methodology results in an additional transport equation which was derived in the early 1960s [Randolph, 1962; Hulburt and Katz, 1964] to model particulate processes such as crystallization; but the approach has subsequently been used successfully in many fields to model particulate systems [Randolph and Larson, 1971; Fredrickson and Tsuchiya, 1963; Kiparissides and Ponnuswamy, 198[illegible]] These are just a few of the numerous references to the population balance

Application of the population balance approach to modeling colloid transport, though new, is a straightforward extension of this well established modeling technique. The population balance methodology and its applications are discussed in the following section.

II. POPULATION BALANCE MODEL

A. Background

Randolph [1962] and Hulburt and Katz [1964] derived the general form of the population balance equation. These very formal and complete derivations of the population balance equation in the early 1960s set the foundation for the subsequent mathematical analysis of many particulate system studies ranging in fields from engineering to biology. The population balance is a well established transport equation which is commonly used to model systems of countable entities. The equation is similar to the mass balance equation except rather than conserving mass it conserves the number of particles/colloids--thus the name population balance equation. The resulting dependent variable of the population equation is number density. Randolph and Larson [1971] make reference to the diverse and numerous applications of the population balance equation. Included are processes such as crystallization, grinding, air pollution, and biological systems just to name a few. The population balance equation is an important addition to the mass and energy transport equations.

Using a size distribution, the population balance equation permits a full treatment of the colloid problem from the birth of colloids to their capture on the surrounding matrix, as well as modeling the gradual effects of colloid growth or dissolution. Radioactive decay of specific nuclides within the colloids is treated by assigning a concentration property axis within the population balance to each species we wish to track. The addition of these property axes allows correct treatment of the decay chain problem with full accounting of the daughter product concentrations. Also, the adsorption of multiple nuclides on the same colloid (heterogeneous colloids) can be modeled.

Randolph and Larson [1971] discuss in detail an example of using the concentration property axis within the population balance equation. For each nuclide there is a separate concentration property axis which defines the number of colloids at a point in time/space/size that have a particular concentration. Integrating over the concentration property axis and the size axis gives the amount of colloidal plutonium at a point in time/space.

The important factor at this stage is that the general population balance equation permits a correct mathematical accounting and quantitative assessment of the nuclear colloid problem. Of course, the soluble species mass transport and energy balance equations must also be included as well as the appropriate system geometry to complete an overall repository assessment model. Also it is common to measure colloid size distributions in terms of weight rather than number density functions. The complete relationship between the number density function and the corresponding weight distribution is discussed in the section on Analysis of Experimental Column Data. The level of model complexity, however, is set by the desired results with the option of using simplified models and submodels to perform conservative repository assessment calculations.

Application of the population balance equation is further enhanced by the wealth of information and experience provided by over 20 years of frequent use in many scientific fields [Nuttall, 1971; Cise, 1971; Griffiths et al., 1982; Gupta et al., 1982; Herbst and Fuerstenau, 1980; Barone et al., 1980; Bhatia and Perlmutter, 1979; Pasiuk-Bronikowska and Rudzihski, 1980; Randolph, 1962, 1969, 1971, 1977]. Therefore, the solution methods and the nature of the various terms have often been studied by previous researchers and their results can now be applied directly to the nuclear colloid problem without the delays of extensive research and development. To further clarify the use of the population balance equation as developed here, it will be applied with a detailed description in the section on Model Development.

The birth, growth, and death rates of micro-organisms in biochemical processes are also commonly modeled with the aid of the population balance equation. The work by Fredrickson and Tsuchiya [1963] is a good example of the interdisciplinary applications of the population balance equation. Randolph and Larson [1971] in their book on the Theory of Particulate Processes also give many interdisciplinary examples and applications of the population balance. Several recent studies using the population balance range in topics from modeling gas bubbles to mineral grinding models.

B. Application to Nuclear Waste Repository Assessment

In applying the population balance equation to repository assessment, two scenarios are considered and the descriptive mathematical models are developed. These scenarios do not represent a specific repository or site but rather are used to derive a quantitative description of colloid transport and release.

Scenario (A) represents perhaps a worst case, near-field problem in which the backfill surrounding a single canister fails, water penetrates the canister, and radioactive colloids are released through the fractured backfill and into the surrounding geological formation where groundwater carries the colloids away from the engineered barrier. Also, the dissolved species are in high enough concentrations to precipitate into additional colloids, and adsorption of dissolved species on natural groundwater colloids is occurring. This scenario is initiated during the thermal period and leads to the far-field transport of colloids. A schematic of the processes involved in the near-field region of scenario A is given in Figure 1.

The second scenario (B) represents the far-field problem in which dissolved nuclides have migrated beyond the repository and are available to bond with natural groundwater colloids and be transported through the fractured/porous geological formation. Colloids from the canister and/or natural colloids which have adsorbed radionuclides may also be present. A schematic of the far-field processes involved in scenario B is given in Figure 2.

The model for scenario (A) will require the energy, mass, and population balance transport equations. The distributed energy balance models the fluid temperature as a function of spatial position and time [Bird et al., 1962]

Energy Balance:

$$\rho C_p \left(\frac{DT}{Dt} + \vec{v}\cdot\nabla T\right) = k \nabla^2 T \qquad (1)$$

Next the mass transport equations describe the migration of dissolved species. One equation is needed for each species, thus the equation is written for the general species 'i'.

Mass Transport Equations:

$$\frac{\partial C_i}{\partial t} + \vec{v}\cdot\nabla C_i = D\nabla^2 C_i - \lambda_i C_i - S_i \qquad (2)$$

A sink term, S_i, is required in the mass balance to represent the dynamic transfer of dissolved species to either the true or natural colloids.

Next, the additional population balance equations are required to model the formation and migration of radioactive colloids. A few assumptions are necessary at this point to clarify the number and type of population balance equations needed. These assumptions can be relaxed or changed as the descriptive scenario may require. First, only one type of natural colloid is assumed to exist, but the colloid may adsorb various nuclides. If more than one type of natural colloid should exist we would simply use an additional population balance equation to describe each one. Second, we will need a set of population balance equations to describe each true colloid (Pu, Am, etc.). True colloids, as opposed to natural colloids, are formed by precipitation of a specific radionuclide and will contain only that nuclide plus daughter products. Applying these assumptions, two types of population balances will be required, one describing natural colloids and the other modeling the true colloids.

The general form of the population balance allows for any arbitrary number of continuous property axes where particle size is just one such axis [Randolph, 1962; Randolph and Larson, 1971]. In the case of nuclear waste modeling, a concentration level property axis is required for each nuclide that is adsorbed on natural colloids, and in the case of true colloids, one is required for each daughter product.

In this way the population balance can track the adsorption and decay of each nuclide of interest. Of course, if it is not necessary to track each nuclide then the problem can be simplified. The population balance equation for true and natural colloids is given below.

True Colloid Population Balances:

$$\frac{\partial \psi_{ti}}{\partial t} + \nabla \cdot (\vec{v} \psi_{ti}) - D_b \nabla^2 \psi_{ti} + \sum_{j=1}^{m} \frac{\partial (v_i \psi_{ti})}{\partial \xi_j} + D_i - B_i = 0 \qquad (3)$$

Natural Groundwater Colloid Population Balances:

$$\frac{\partial \psi_{nk}}{\partial t} + \nabla \cdot (\vec{v} \psi_{nk}) - D_b \nabla^2 \psi_{nk} + \sum_{j=1}^{m} \frac{\partial (v_i \psi_{ti})}{\partial \xi_j} + D_k - B_k = 0 \qquad (4)$$

The energy, mass, and population balance equations together describe mathematically the near-field process where many physical and chemical processes are occurring simultaneously. To complete the above model, the system geometry, boundary conditions, and specific terms within the equations must be defined. Submodels or kinetic expressions are required to represent the certain terms in the population balance equation. The extensive population balance and colloid modeling literature provides the general forms for these submodels [Randolph and Larson, 1971; Clontz and McCabe, 1971; Nielson, 1964; Volmer and Weber, 1926; Treybal, 1980; Waldie and Wilkinson, 1983; and McDowell-Boyer et al., 1985]. Key terms in Equations 3 and 4 which require special consideration are the following:

1. D_{ik}. This term represents the rate of particle number disappearance from a particular particle size category per unit solution volume. Death is caused by colloid capture on the rock matrix, agglomeration, and dissolution.

2. B_{ik}. In a similar fashion, this term represents the rate of appearance of particles into a size category per unit solution volume. Births result from nucleation, agglomeration, and release of captured or new colloids from the rock matrix.

3. v_i, is the growth rate or dissolution rate on a molecular scale for colloids. This term accounts for the gradual increase or decrease of particle size due to mass addition or subtraction from colloids

4. $\sum_{j=1}^{m} \frac{\partial(v_j \psi_{ti})}{\partial \xi_j}$, is the rate of population density change along a property axis, for example, colloid growth along the particle size axis. Also, it represents and accounts for the concentration of radionuclides on the colloids.

5. $\frac{\partial\psi_{nk}}{\partial t} + \nabla\cdot(\vec{v}\psi_{nk}) - D_b\nabla^2\psi_{nk}$. These three terms represent respectively, the accumulation in the number of colloids of a particular size per unit solution volume, the convective transport of particles, and the dispersive transport of particles in the fluid stream.

Parameters within the submodels can in many cases be assigned conservative values or may require estimates from experimental data. Many investigators in numerous fields have used the population balance model and this information can aid in developing and evaluating the necessary submodels.

Submodels. Mathematical submodels are required to describe the following phenomena:

Birth (heterogeneous and homogeneous nucleation) rate
Release rate of colloids from the rock matrix
Death rate
Growth rate
Agglomeration rate
De-agglomeration rate
Adsorption/Desorption of radionuclides
Decay of Nuclei within or on a colloid

These submodels are generally site specific incorporating the appropriate geochemisty, reaction kinetics, and transport processes for a potential waste disposal site. The more important submodels will be discussed in the following sections. Future studies will be required to define these submodels for the NNWSI site; however, the technical literature does provide structural guides for the various submodels.

The second scenario (B) is the far-field problem in which the thermal period has passed and nuclides have migrated out from the repository into the groundwater of the surrounding geological formation. Natural groundwater colloids of Si, Fe, and Al may be present to adsorb dissolved nuclides and thus provide a mechanism for rapid transport along cracks or faults. Here, as in the previous case, true colloids originating within the repository may also be present and have migrated into the far field. The overall assessment model consists of the dissolved nuclide mass balances, a set of true colloid population balances (one for each nuclide), and the natural colloid population balance. If there is more than one type of natural colloid, then one population balance equation is required for each type.

The population balance methodology establishes an overall structure for modeling colloid transport. However, to describe site specific physical systems, the various terms in the equation must be correctly evaluated and the appropriate submodels supplied. The submodels are sometimes developed through general rules which can be applied to many systems, but more often the submodels and/or parameters within the submodels must be defined for specific systems. Each of the required submodels in the population balance will be discussed separately. The problem of defining submodels is open ended and models will evolve as new physics and chemistry for a specific system are identified.

Submodels for colloid transport include: birth, capture, agglomeration, and growth. For more complex applications of the population balance model where the concentration of chemical species on individual colloids is required, submodels are needed to describe the adsorption/desorption and other appropriate chemical reactions.

1. Birth/Nucleation. The birth/nucleation term treats the formation of new colloids caused by a phase change in the form of nucleation (precipitation), by the introduction of new colloids into the system from the surrounding rock matrix or by the agglomeration of smaller colloids

The introduction of colloids can be caused by evaporation and cooling of the solution, by addition or removal of a reagent which changes the system solubility, and in some cases by heating the solution [van Nostrand's Scientific Encyclopedia, 1958.

Randolph and Larson [1971] state that new crystal formation can result from homogeneous nucleation, heterogeneous nucleation, secondary nucleation, and attrition. In practice, Miers nucleation model has been successful for describing many inorganic systems. The Miers nucleation model is written as

$$B^{0} = k(C - C_{m})^{i} \qquad (5)$$

Often C_m is very close to the saturation concentration C_s, therefore C_s is used in most crystallization studies. Therefore, nucleation rate, B^0, is a function of the degree of super saturation.

In geological systems clay minerals will most likely constitute the natural colloids because of their very fine particle size. H. van Olphen [1977] points out that clay minerals may be formed in nature either by alteration (diagenesis) of mica minerals or by synthesis from oxides (genesis). Clay minerals exhibit a crystal structure and belong to the phyllosilicates. The main building elements are the two-dimensional arrays of silicon-oxygen tetrahedra and two-dimensional arrays of aluminum- or magnesium-oxygen-hydroxyl octahedra. Though clays have been formed in the laboratory, birth rate models for the appearance of clays in natural systems are not available. Further work and site specific studies are needed in this regard.

Other types of colloids may also be present in the geological system for disposal of nuclear waste. The proposed glass and iron waste canisters react under geological conditions to produce iron silicate colloids ($FeSiO_3$) [Jantzen and Bibler, 1985]. Birth models or colloid canister release models are needed in the assessment modeling. Waste package studies should be required to provide this type of information.

2. <u>Capture Models</u>. The capture rate for colloids is very important in determining colloid transport. Mechanistically the colloids are removed

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from solution by simply attaching to the rock matrix. However, on close examination of this process the picture is more complex. McDowell-Boyer et al., [1985] indicate three general types of particle removal: filter caking, straining, and Physical-Chemical removal. There are five mechanisms for the capture of colloids in the Physical-Chemical removal scheme: Brownian motion, inertia, interception, hydrodynamic, and sedimentation [Ives, 1970]. For very small particles less than 1 μm, the particles are captured by Brownian motion. To model capture phenomena, most researchers begin with the basic filtration equation empirically proposed by [Iwasaki, 1937]. The equations are:

Liquid

$$\frac{dC}{dx} = -\lambda C \qquad (6)$$

Solid

$$\frac{d\sigma}{dx} = \varepsilon v \lambda C \qquad (7)$$

The simple filtration model is a useful starting point in providing a capture submodel to the population balance. This submodel will be developed further and applied to the treatment of experimental column data in a later section of this report.

3. Agglomeration. Agglomeration, the grouping of colloids to form clusters, is a very important consideration affecting the net migration of colloids through natural media. Because colloid science appears in many fields, agglomeration is referred to as flocculation, aggregation, precipitation, and coagulation. The stability of colloid solutions is a subject of considerable study among colloid scientists. Clay colloids are negatively charged and tend to repulse other colloids in solutions of weak ion strength. Here the electric double-layer is sufficiently far reaching to act as a shield to approaching colloids or clusters of colloids. Both

the chemical nature of the colloids and that of the solution affect colloid stability, i.e., the tendency to coagulate.

The birth and death terms in the population balance are well suited to treating the problem of agglomeration. Smoluchowski [1917] was first to develop a diffusion limited agglomeration model for monodispersed particles. More recently Hidy and Brock [1971] reviewed the work by Smoluchowski and the extensions by Swift and Friedlander [1964] to polydisperse size distributions of agglomerating particles. Most recent work by Hurd [1986] has included charge effects in a Witten-Sander model and has shown that the resulting fractal like particle has a fractal dimension of 2. The two dimensional fractal studies by Hurd [1986] produce interestingly shaped particle clusters but at present the amount of calculations are prohibitive for inclusion of this type of model in the population balance.

The birth term for agglomeration can be written in terms of particle volumes v_p and u_p as:

$$B = \int_0^{v_p} K(u_p, v_p - u_p) P(u_p, t)(v_p - u_p, t)\, du_p \tag{8}$$

and the death term as:

$$D = P(v_p, t) \int_0^{\infty} K(u_p, v_p) P(u_p, t)\, du_p \tag{9}$$

[illegible] Birth and Death are functions of the rate of colloid agglomeration. [illegible] $K(u_p, v_p)$ is defined by the type of agglomeration. In the case of [illegible], agglomeration will be by Brownian diffusion and the kernel is written as

$$K(u_p, v_p) = \frac{2kT}{3\mu} [u_p^{1/3} + v_p^{1/3}]\, [u_p^{-1/3} + v_p^{-1/3}] \tag{10}$$

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Here Birth and Death are functions of the rate of colloid agglomeration. The kernel $K(u_p, v_p)$ is defined by the type of agglomeration. In the case of small colloids, agglomeration will be by Brownian diffusion and the kernel is written as

$$K(u_p, v_p) = \frac{2kT}{3\mu} [u_p^{1/3} + v_p^{1/3}] [u_p^{-1/3} + v_p^{-1/3}] \qquad (10)$$

Particle disruption models are also available but disruption of small colloid clusters seems rather unlikely.

Growth rate submodels are also available from the literature but it doesn't appear likely that ground water colloids will be growing or dissolving; however, if needed the population balance can adequately model this phenomenon.

III. ANALYSIS OF EXPERIMENTAL COLUMN DATA

A. Background

In this section the population balance methodology is developed and applied to the transport and capture of polydispersed colloids in packed columns. Model simulations are compared to experimental data. The transient model developed earlier includes particle growth, capture, convective transport, and dispersion. In this application the dynamic accumulation of captured colloids on the solids is coupled to the population balance for the liquid phase.

The packed column experiments by Saltelli et al. [1984] were re-analyzed incorporating the experimentally reported size distribution of the colloid feed material. Colloid capture was modeled using a linear size dependent filtration function. The effects of a colloid size dependent filtration factor on colloid migration and capture were investigated. Also, we modeled the changing colloid size distribution as a function of position in the column.

Modeling results from the analysis of these laboratory studies were used to interpret the likelihood of colloid migration at the candidate NTS Yucca Mountain waste disposal site.

To date both laboratory [Saltelli et al., 1984; Fried et al., 1976] and site studies [Champ et al., 1982; Travis and Nuttall, 1985] have demonstrated the existence and in some cases the accelerated transport of colloids. Travis and Nuttall [1986] developed a theory for colloid transport using the population balance concept. Travis and Nuttall [1985] applied the population balance theory and the TRACR3D computer code to study the hydrology and transport of radicolliods at the Los Alamos DP West low-level waste disposal site. Saltelli et al. [1984] derived and tested a one-dimensional filtration model. They modeled transient column profile data obtained by injecting ^{241}Am contaminated waste-glass colloids into a 26 mm [illegible] mm sand packed column. They measured the size distribution of feed colloids and attempted to model the effects of the polydispersed colloids on the capture profile by assuming a distribution for the filtration factor. This approach did not yield a fundamental understanding of the effect of colloid size, but they did show that one must consider the size distribution in treating the experimental data.

In the following analysis of colloid transport, we used the multidimensional form of the population balance equation to analyze directly the effects of polydispersed colloids. The theory is developed to model the transport of polydispersed colloids through a one-dimensional porous region. The problems of converting from a weight distribution to the corresponding number density function and back to a weight distribution after solution in the population balance equation are treated. We used the model to investigate the effects of the various size distributions and to compare the effects of a constant versus size dependent filtration type colloid capture model.

B. Applied Population Balance Theory

In this study, we apply the dynamic microscopic form of the population balance model with convective transport in one spatial dimension and particle growth along a colloid size axis to the problem of polydispersed radiocolloid transport in nuclear waste disposal.

The colloid population density function, P(t,z,L), is dependent on time, space and the colloid characteristic size which we assume to be the colloid diameter. P(t,z,L) is the number of colloids of a particular size at a point in space and time per unit volume of solution such that when P is integrated over the colloid size range, we have the total number of colloids per unit volume. In general, colloid charge or any other useful colloidal properties could be modeled by simply adding the appropriate property axes. The population balance also includes a birth/death term f(P,t,z,L) which again accounts for the birth of new colloids as well as the adsorption and release of colloids by the rock matrix. The adsorption and release function treats colloids of arbitrary size. In this study we do not treat the adsorption of radionuclides on the colloids nor are we investigating the growth of colloids. To model colloids of the same size but with differing amounts of radionuclides would require an additional property axis for concentration. Under these assumptions the population balance is:

$$\frac{\partial P}{\partial t} + v\frac{\partial P}{\partial z} - D_e\frac{\partial^2 P}{\partial z^2} + u\frac{\partial P}{\partial L} = f \qquad (11)$$

It is desirable to work with a dimensionless form of the population balance. Carrying out the transformation of Eq. (11) using the dimensionless variables defined in the notation section leads to:

$$\frac{\partial \phi}{\partial \tau} + \theta \frac{\partial \phi}{\partial \zeta} - \frac{D_e}{\bar{z}\,\bar{v}} \frac{\partial^2 \phi}{\partial \zeta^2} + \upsilon \frac{\partial \phi}{\partial \rho} = \frac{\bar{z}}{P_i \bar{v}} f(\phi,\tau,\zeta,\rho) \qquad (12)$$

Adsorption of colloids on the surrounding solids is assumed to follow the filtration model where the rate of mass accumulation is proportional to the concentration of solids in the solutions. In our model the solids concentration in solution must be expressed in terms of the population distribution function. The mass filtration term is

$$f_{mass} = \lambda(L)\, v\, c \qquad (13)$$

Where c is the mass concentration of colloids and is expressed in terms of the population density distribution as

$$c = \int \lambda(L)\, P(L)\, L^3\, dL \qquad (14)$$

$$m(L) = \rho_p K_v P(L) L^3 \qquad (15)$$

The rate of mass build up on the matrix at a point in space for each colloid size is

$$\text{[illegible]} = \epsilon\, \lambda(L)\, v\, m(L) \qquad (16)$$

The [illegible] Rate of mass accumulation for all colloid sizes is equal to the integral of Eq. (16) over the colloid size range.

$$\frac{d\sigma}{dt} = \epsilon\, \rho\, v\, k_v \int_0^{L_m} \lambda(L)\, P(t,z,L)\, L^3\, dL \qquad (17)$$

In the general case $\lambda(L)$ will be an unknown function of colloid size. However, if $\lambda(L)$ is size independent, i.e., equal to a constant, then the filtration follows the conventional form showing a straight line profile for the concentration of colloids captured on the sand packing when plotted on semilog paper.

To treat experimental data, it is often necessary to convert between weight distributions and number distributions. In terms of the number density function the distributed weight function is [Randolph and Larson, 1971]:

$$w(L) = \rho k_v L^3 P(L)/M_T \tag{18}$$

Randolph and Larson [1971] also showed that the number distribution was related to the weight distribution, Eq. (18), by

$$P(L) = M_T\, w(L)/(\rho k_v L^3) \tag{19}$$

By dividing by the total mass of sample, M_T, the number of colloids per unit mass of sample is given. The equation is

$$P(L)/M_T = w(L)/(\rho k_v L^3) \tag{20}$$

k_v = volumetric shape factor, ($\pi/6$ for a sphere)

Note: The length units on ρ, $w(L)$, and L^3 must be the same, microns. Also, the mass units on ρ and M_T must be the same.

The number of colloids at any size per unit volume of solution can be found by multiplying Eq. 20 by the total mass concentration of colloids. The population balance, Eq. 12, was solved numerically by an improved method of characteristics technique presented by Douglas and Russell [1982]. The buildup of colloids on the porous matrix is described by Eq. 17 which was coupled to the population balance and solved as a series of ODEs using the 4th order Runge-Kutta method. Note that σ is a function of column position, z, and time.

In our studies we tested both a gamma and a log-normal distribution to model the initial weight distribution of radiocolloids. The log-normal distribution gave a better fit to the measured feed distribution. The cumulative and distributed forms for the log-normal distribution are respectively [Randolph and Larson, 1971]:

$$W(L) = 0.5 + 0.5\,\mathrm{erf}(z) \tag{21}$$

where

$$z = [\ln(L/\bar{L}')]/2^{1/2} \ln \sigma'$$

where $\bar{L}'$ = size parameter, geometric mean size, μm
σ' = width parameter, geometric STD

and the cumulative form of the log-normal function is

$$w(\ln(L)) = \frac{1}{(2\pi)^{1/2} \ln \sigma'} \exp\left[\frac{-\ln^2(L/\bar{L}')}{2\ln^2 \sigma'}\right] \tag{22}$$

C. Packed Column Simulations

Saltelli et al. [1984] investigated the migration of polydispersed ^{241}Am colloids through a packed column of glauconitic sand. Colloidal ^{241}Am, leached from a simulated waste glass, was injected into a column. Three experiments of 28, 80, and 170 day duration were run. At the end of each test the column was dismantled, sectioned, and the ^{241}Am profile analyzed. The size distribution of the colloid feed was measured by filtration and represented in our analysis by a log-normal distribution. The authors analyzed their data using the filtration capture model and found that the column profiles could not be matched using the conventional constant parameter filtration model. To fit the profile curves, they assumed that the colloid feed exhibited a distribution of filtration coefficients. In this way they hoped to approximate the affects of size dependent filtration and by adjusting the filtration distribution parameters they did fit the shape profile curves. Their model also included a Langmuir isotherm model to treat the observed early adsorption of ^{241}Am which occurred throughout the length of the column. This rapid adsorption of ^{241}Am on the porous matrix was at a very low concentration level and the mechanism for this phenomenon has not been directly investigated; therefore, we did not choose to include this mechanism in our model. To match the experimental data, we simply assumed an initial solids ^{241}Am concentration of 10^{-10} moles/liter.

The measured ^{241}Am colloid distribution along with our curve-fitted distributed and cumulative log-normal distributions are illustrated in Fig. 3. The measured range of the feed colloids was from approximately .05 μm to a maximum of 10 μm. Our curve-fit parameters for the log-normal distribution were $\bar{L}' = 0.45$ μm and $\sigma' = 7.39$.

The upper colloid size was experimentally controlled by passing the feed solution through a 10 μm filter prior to entering the column. The experimental conditions are give in Table I.

The population balance model for the above conditions was solved using the log-normal distribution to represent the colloid feed. The resulting concentration profile for ^{241}Am on the porous matrix is compared with the experimentally measured profile after 170 days of continuous column operation and is shown in Fig. 4 . The strong curvature in the calculated profile is created by the linear size dependent filtration function, $\lambda = 2L$. The asymptotic level of concentration at 10^{-10} shown on the far right of the curve was modeled by arbitrarily setting this level of concentration as an initial condition in the column. The mechanism for this initial low level of concentration is still speculative and can be modeled in several ways; however, the true physical mechanism has not been identified.

The numerical solution of the population balance also provides some insight into the change in the colloid size distribution in the fluid phase as a function of position down the vertical column. Fig. 5 illustrates in

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three dimensions the varying colloidal weight distribution in the liquid as a function of position . The surface shows both the rapid decrease in the mass of colloids in solution and the shift in the mode of the distribution to small sizes. Because of the size dependent filtration coefficient, the larger colloids are preferentially removed early at the top of the column, leaving the smaller particles to transport downward through the porous medium. In the case of a constant filtration factor, λ, the nature of the colloid size distribution has no effect on the solid concentration profile since each particle has the same capture probability independent of size.

D. Results

The population balance methodology which operates on a number continuity approach is well suited for describing the complex phenomena of colloid transport. In the present study the problem of polydispersed colloid transport in a porous medium was successfully modeled and very good agreement was found between model results and data. The advantages of this methodology are that it provides a comprehensive and fundamental structure for analyzing the complex mechanisms of colloid migration. The approach requires conversion back and forth between the weight and number distributions; however, this conversion is a straightforward process. In this study, the colloid size distribution had a significant effect on the migration and capture process when a size dependent filtration capture model was used. In the case of size dependent filtration, the larger colloids were rapidly captured while the smaller ones are less likely to be captured and therefore the smaller ones migrate much further through the porous medium. Both a constant and a linear size dependent filtration type capture model were tested. The size dependent model was required to match the measured column profile data. The linear filtration model was of the form λ = [illegible] where the function is simply proportional to the particle size; hence, implying that the larger colloids are preferentially captured. This model was verified by the shape of the experimental concentration profile curves. The experimental data were modeled successfully with only one adjustable parameter, s, the slope of the filtration coefficient function. If λ, the filtration factor, is constant then the colloid size distribution has no effect on transport or capture.

A limited study of parameter sensitivity showed that the width of the colloid feed distribution influenced the curvature on a semilog plot of the solid phase concentration profile with narrowing of the distribution converging to the monodispersed mode, and producing a linear concentration profile on a semilog plot.

In light of our findings, we made a preliminary review of the colloid transport characteristics for the candidate NTS nuclear waste disposal site. We found that many of the geological factors were favorable for retarding colloid migration. However, the potential for very small colloids to migrate in fractures with episodic flow characteristics may be significant and therefore requires further study and analysis.

IV. NTS YUCCA MOUNTAIN SITE

Colloids may originate from several sources: by the corrosion of the waste glass and canister, by degradation of the engineered backfills, and by erosion from naturally occurring clays. Hence, there is a reasonable likelihood that colloids will exist. If colloids migrate, there is a strong likelihood that they will increase radionuclide migration. Hence, the important consideration is whether the geological medium is conducive to colloid transport or whether colloid migration and capture will retard their transport. The semiarid candidate NTS waste disposal site has many advantageous geological characteristics which should impede the migration of radiocolloids. Colloid transport depends on at least four factors: filtration, pH of the solution, water velocity, and diffusion.

At Yucca Mountain, filtration will be an effective barrier in the tuff matrix. Pore size is an important element in filtration. Pseudocolloids will obviously not flow through pores that are smaller than the pseudocolloids themselves. Pore size distributions have been measured for several Yucca Mountain tuff samples. Mercury porosimetry data, measured by Quantachrome [illegible] on a sample of Topopah Spring tuff showed that most of the pores are [illegible] than [illegible] µm and approximately 50% are smaller than 0.1 µm. Even though a small percentage of pores are larger than [illegible] µm, these large pores will not transport colloids because they will be dry. In the Topopah Spring formation at NTS, the saturation is less than 90% and large pores are the last to become saturated. In another NTS site formation, Calico Hills, approximately 50% of the pores are smaller than [illegible] µm.

Hence colloids must be on the order of 0.1 um in diameter or less to pass through the NTS tuff.

Pore water velocities, assuming matrix flow, are estimated at less than 2.0 mm/yr. These low velocities are on the order of molecular diffusion rates; thus, greatly limiting the migration of colloids within the tuff matrix. Transport of colloids through fractures is possible; however, for the measured fracture apertures of 50 to 250 μm at Topopah Spring tuff, the water flow rate would only be about 2 m/yr or still the order of molecular diffusion transfer rates. If fracture flow were episodic, corresponding to a few intense rainfalls per year, flow rates in fractures might be much larger but for only very short times.

Colloids greater than 0.1 μm in diameter will likely be removed by gravitational settling [Apps et al., 1983]. The transporting ability of very small colloids may be diminished by diffusion of radionuclides out of the particles and subsequent adsorption of the nuclides on the tuff matrix. Migration of small true colloids may be possible in a fracture flow regime. Work is continuing on understanding the migration mechanisms of the very small colloids.

V. CONCLUSIONS

Radiocolloids must be considered in the assessment of a nuclear waste repository. The mathematical approach to colloid assessment was presented and tested using experimental column data for Americium/glass colloids. Certain key submodels and supporting data are needed to assess the NNWSI candidate waste repository site. The following conclusions summarize the current findings.

A. Presence of Natural Colloids

Geological studies of Yucca Mountain have shown the widely distributed presence of the colloid producing clay, montmorillonite (smectite).

Recent studies on J-13 well water have not conclusively identified the chemical composition of the colloid material. [illegible] of material in J-13 water measured about 30 ppb. This is a very [illegible] concentration of groundwater.

B. Adsorption Capacity of Natural Clay Colloids

Clays (montmorillonite) have a high ion adsorption capacity (80-100 meq/100g) [van Olphen, 1977].

C. Migration in Porous Geological Media

Clays do migrate in geological formations. Clays adsorb microbes and have been shown to migrate.

D. Colloid Size Considerations

The upper and lower sizes of colloids is limited. In porous media (not large fractures), particles greater than 1 micron should readily be captured (inertia and gravitational forces are both active on these larger colloids). Solutions of very fine colloids have been shown to be unstable because the repulsive energy between small particles is smaller than that between large particles carrying an identical double layer because of the larger interaction surface of the latter. Hence very small colloids will have a strong tendency to aggregate, thus limiting the presence of small colloids.

E. Status of the Population Balance Approach

The population balance equation was successfully solved and applied to the analysis of experimental data. There was very good agreement in fitting the experimental colloid transport data using the population balance equation with a size dependent filtration type capture submodel.

This modeling approach is applicable to colloid transport assessment at the NNWSI site.

Future studies are needed in both the submodels and experimental verification areas. Submodel development is needed for the agglomeration, capture/release and bacterial colloid behavior. Submodels will require supporting experimental and eventually field verification data.

NOTATION

B	colloid birth function	
B^o	nucleation rate	
C	solute concentration	
C_s	saturation concentration	
c	colloid concentration	gm/cm^3
C_i	concentration of species 'i'	
D_e	hydrodynamic dispersion coefficient	cm^2/d
D	colloid death function	
D_b	Brownian diffusion	
f	birth/death rate function	#/cm^{3}μmd
f_{mass}	mass filtration term	#/cm^{3}μmd
k	nucleation rate constant	
Kv	colloid shape factor, π/6 for a sphere	
$K(u_p,v_p)$	agglomeration kernal	
L	colloid size dimension	μm
$\bar{L}'$:	size parameter, geometric mean size, cm	
M_T	Initial mass concentration of colloids	gm/cm^3
$m(L)$	mass concentration of size L colloids	gm/cm^3
P	population density function	#/cm^{3}μm
P_o	normalising factor	#/cm^{3}μm
P_i	population density function at z=0.0	#/cm^{3}μm
s	slope of filtration function	cm^{-2}
S_i	transfer of species to the colloids and rock matrix	
T	absolute temperature	
t	time	d
u	growth rate along the size axis	μm/d
u_p	colloid volume	

v	Darcy water velocity	cm/d
v_p	colloid volume	
w	weight distribution function	gm/cm³μm
W	cumulative weight distribution	gm/cm³
z	space dimension	cm

Greek Symbols

ψ	population density function (P/P_i)	dimensionless
ϕ	velocity ($v/\bar{v}$)	dimensionless
ν	growth rate ($u\bar{z}/\bar{v}\bar{L}$) or property rate	dimensionless
ε	space ($z/\bar{z}$)	dimensionless
ρ	colloid size ($L/\bar{L}$)	dimensionless
ρ_p	colloid density	gm/cm³
λ	filtration coefficient	cm^{-1}
λ_i	radioactive decay constant for species 'i'	
σ	mass concentration of colloids on the solid	gm/cm³
σ_i	mass concentration of colloids at size L	gm/cm³μm
σ'	width parameter in log-normal distribution	
τ	time ($t\bar{v}/\bar{z}$)	dimensionless,
$-$	average properties or limiting properties	
ξ	property axis	
κ	Boltzmann's constant	
μ	fluid viscosity	

Subscripts

i = index for nuclides which form true colloids

j = property axis type (size and concentrations)

k = index for type of natural colloid (Si, Fe, Al, etc.)

m = number of property axes

n = natural colloids

t = true colloids

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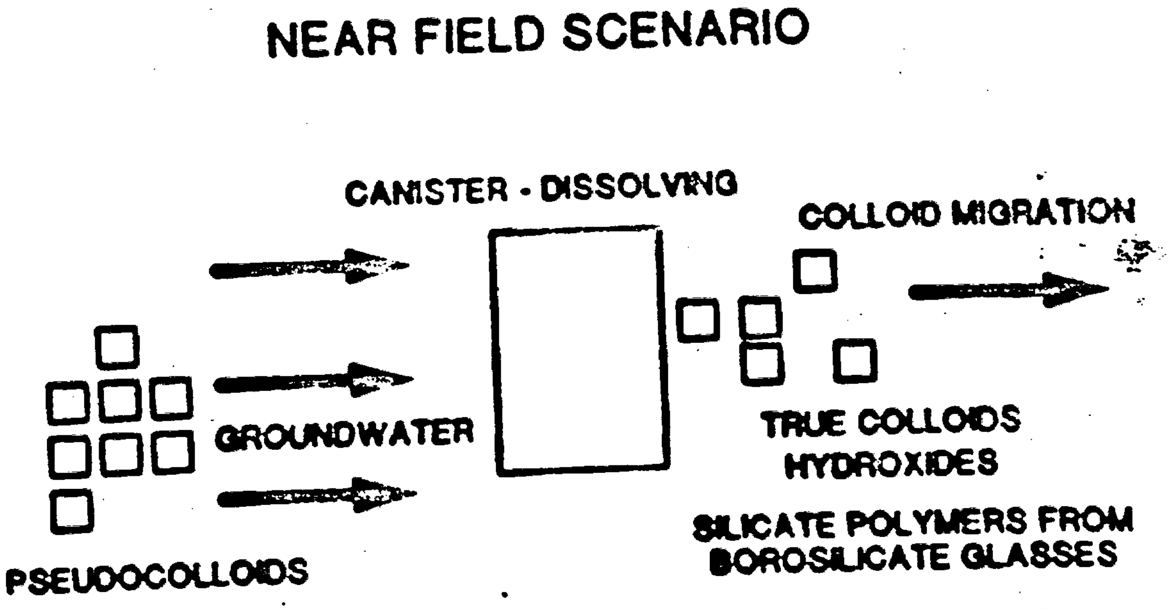

Figure 1. Near-Field Nuclear Waste Scenario (A)

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FAR FIELD SCENARIO

FRACTURED/POROUS MEDIUM

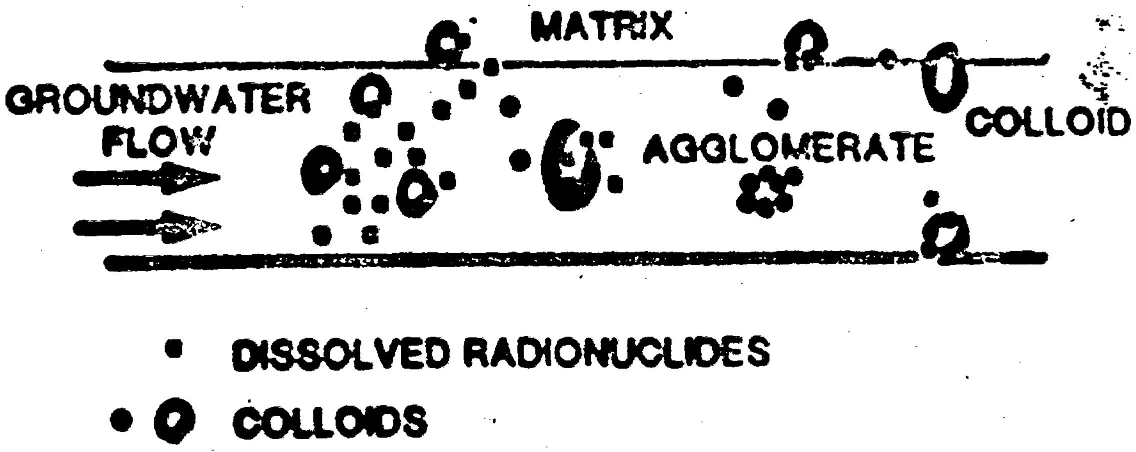
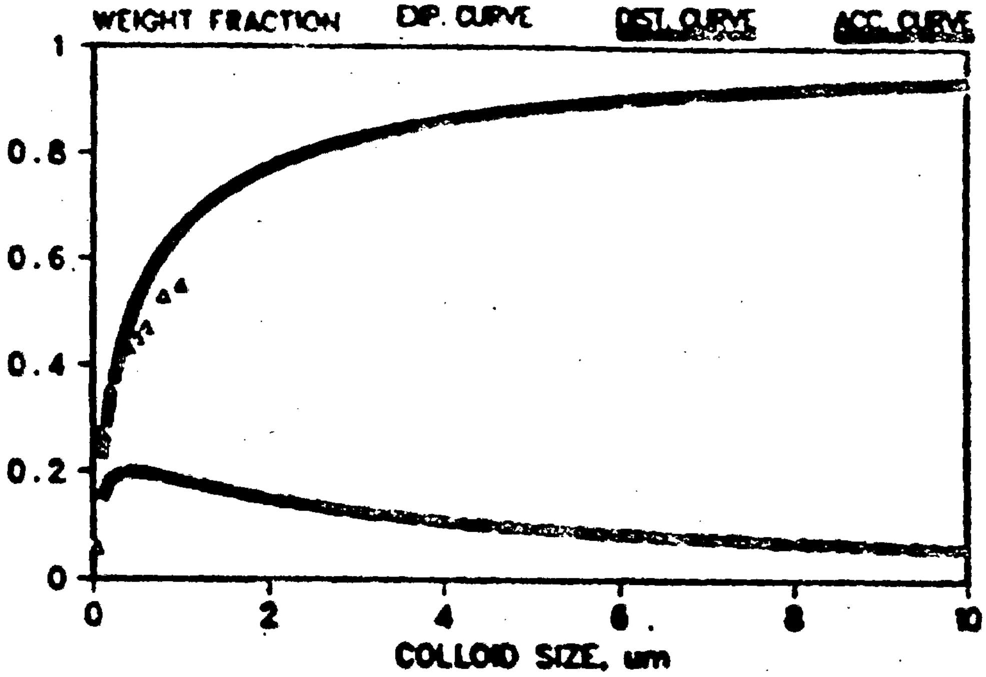
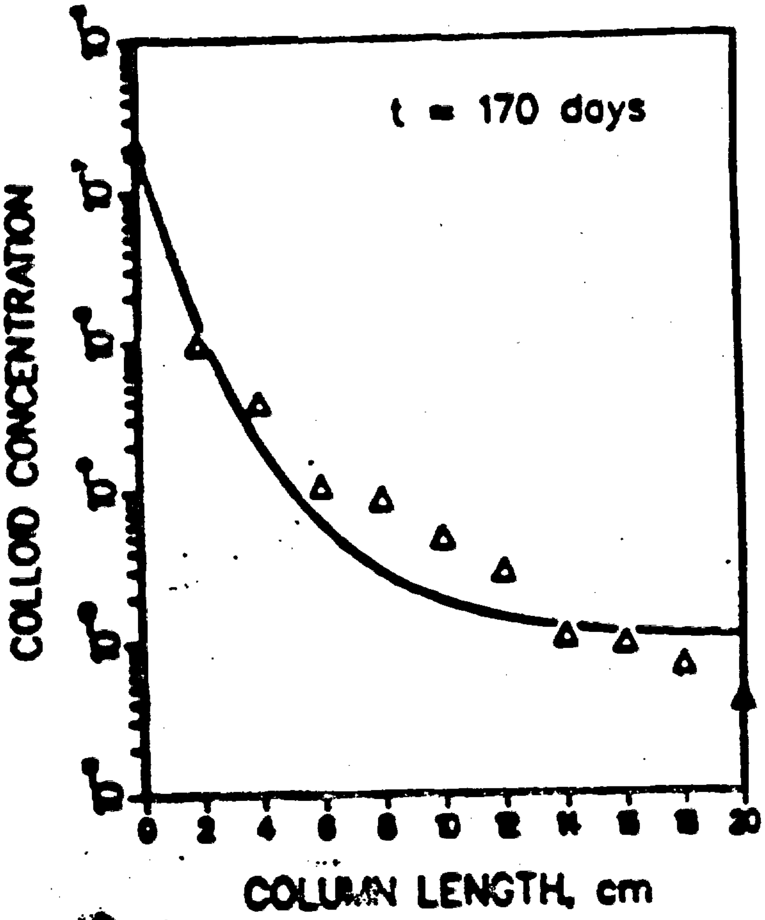


Figure 2. Far-Field Nuclear Waste Scenario (B)



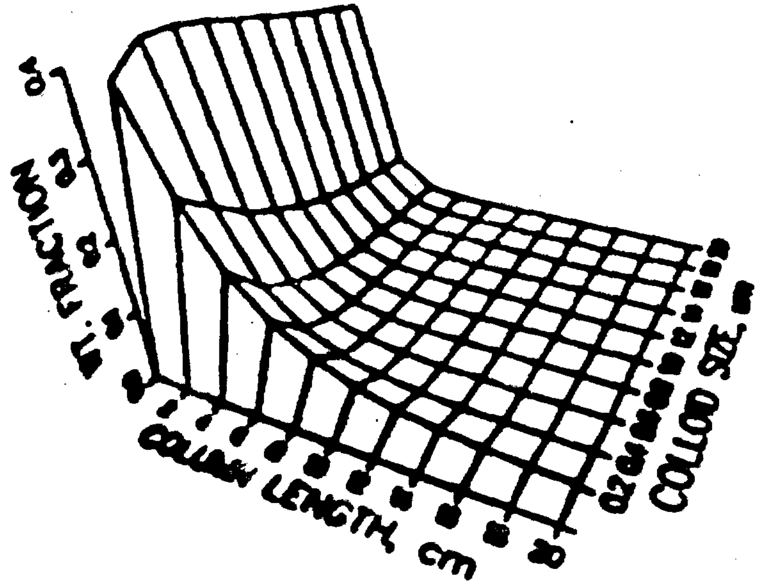
Colloid Feed Size Distribution.

Figure 3. Colloid Feed Size Distribution.



Measured and Calculated Solid Concentration Profile for ^{241}Am. (Concentration, moles/liter of Column.)

Figure 4. Measured and Calculated Solid Concentration Profile for ^{241}Am. (Concentration, moles/liter of Column.)



Liquid Phase Colloid Weight Distribution Versus Position Along Column.

Figure 4 Liquid Phase Colloid Weight Distribution Versus Position Along Column

TABLE I - Experimental Parameters

Column Dimensions:	18 cm by 1.25 cm
Porosity:	0.38
Dispersion Coefficient:	62.6 cm^2/d
Darcy Velocity:	20.9 cm/d
Inlet Concentration:	3.8×10^{-10} M
Exit Concentration:	$3.5\text{-}6.5 \times 10^{-13}$ M
Feed Concentration Correction at 170 d:	0.242
Column Packing	Sand with 20% clay