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AN APPLICATION OF THE POPULATION BALANCE TO THE ASSESSMENT OF THE IMPORTANCE OF RADIOACTIVE COLLOIDS IN HIGH-LEVEL WASTE MANAGEMENT

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1.0 INTRODUCTION AND LITERATURE REVIEW

There are many recent papers on the geological disposal of waste and repository assessment but they have not quantitatively addressed the impact of colloid formation and transport [A1-A5]. Since about 1979 the question of colloid formation and migration has increased in importance and is now a topic of major interest in the scientific community. To date several experimental studies have shown the presence of radioactive colloids under waste disposal conditions. Their impact on repository assessment, however, has not been addressed because the existing mathematical models developed to model geologic waste disposal cannot treat this problem. Additional theory and equations are required to mathematically describe colloid formation and migration. The population balance equations and submodels can be added to the existing radionuclide transport theory and codes to accomplish this goal. Through the correct use of the population balance equations coupled with the existing theory, problems of colloid formation and migration can be assessed quantitatively. The well established theory of the population balance can be applied to the difficult radioactive colloid problem with the same success as it has been used to treat many physical and biological particulate problems over the past 20 years.

In this report the key experimental research on radioactive colloids is reviewed, and the population balance is developed. Its application to waste assessment is illustrated by modeling two postulated repository scenarios: 1. a near-field study in which the backfill is breeched and waste leakage occurs during the thermal period and 2. next a far-field problem involving colloids from both the repository and from natural sources.

1.1 Literature

The reference section of this report is divided into the following key topics:

A. Repository Assessment
B. Colloid Studies
C. Population Balance
D. Transport Models for Fractured Media
E. Transport Modeling and Particulate System Modeling
F. Fractured Media Flow Studies.

In this section the key colloid and population balance references are discussed and their application to the nuclear colloids highlighted.

1.1.1 Colloids

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 [B1]. This class of very fine particles ranges in size, by definition, from 1 to 1000 nm. A single ounce of colloids may have 100,000 square feet of surface (300 sq meters per gram). Approximately 1 out of every 100 of a colloidal particle's atoms or ions either is exposed to the surrounding medium or is close enough to the surface of the particle to be subjected to forces arising from interaction with the medium [B1].

Colloids have many interesting properties. For example they can change size with the larger particles growing at the expense of the smaller ones and the particles can either coagulate or be repelled. Very stable colloid solutions can be formed which will remain for hundreds of years. India ink is an example of a rather stable colloid solution of lampblack.

There is an increasing number of references to nuclear colloids and their role in nuclear waste management. Drever [B7] 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, Mn; colloidal organic matter), the surface charge results from ionization of or adsorption on the surface of the solid. In strongly acid solutions, the surface will gain a proton and be positively charged while the opposite occurs in strongly alkaline solutions. A double layer of ions surrounds colloids. The Stern layer is attached to the solid surface and is surrounded by 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. For example as the ionic strength increases, the Gouy layer becomes compressed close to the particle. When this occurs to a large enough degree, the double layer electrokinetic force is negligible and the van der Waals attractive force will pull the particles together; thus rendering the suspension unstable.

The ion exchange behavior of colloids [B7] is measured quantitatively in soil sciences by the cation-exchange capacity (CEC). Cation-exchange capacity is often measured by uptake and release of ammonium ions from a 1 M ammonium acetate solution at pH 7.0. Some typical cation-exchange capacities (meq/100 g) for clay minerals are:

Smectites	80-150
Vermiculities	120-200
Illites	10-40
Kaolinite	1-10
Chlorite	<10 .

It is often pointed out that CEC values for colloidal oxyhydroxides must be interpreted with caution because the surface charge, and hence CEC, of these materials can be strongly dependent on pH. Drever [B7] suggests that the common distribution coefficient Kd can be used to represent the exchange equilibrium between the concentration of trace species on the colloid and in the solution; however, he cautions that Kd may be a function of the other ions in solution so that a distribution coefficient measured for a particular ion on a particular clay in particular solution cannot be used for calculations involving other solutions or other types of colloids.

1.1.2 Colloids in Nuclear Waste

Radioactive colloid experimental studies in recent literature have illustrated the strong likelihood of the occurrence of nuclear colloids in the geological storage of nuclear waste [B3-B6, B8]. Apps, et al. [B2] recently reviewed colloid and particulate transport associated with nuclear waste disposal. They provided numerous references suggesting that colloid formation is strongly evident in natural systems. Olofsson, et al. [B3, B4, B9] in their literature review of this subject suggest that the elements, present in spent nuclear fuel, which are most likely to form colloid species would be hydrolyzable elements. These include the actinides, possibly Sr, as well as Pb and Cu representing the encapsulation material in the Swedish program. The definition of true and pseudocolloids is presented in this work. 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 of an ion formed by hydrolysis of the radioelements. On the other hand, pseudocolloids are formed as a result of adsorption of the radionuclide on impurities in the solution. These pseudocolloids are also referred to in our report as natural colloids. Pseudocolloids are usually much larger than true colloids (up to 500 nm). These are two types of pseudocolloids: reversible and irreversible. The former are produced by reversible surface adsorption in which the radionuclide can easily pass back into the solution. In the irreversible case, the element is either incorporated into the interior of the foreign particle or irreversibly sorbed onto it. A special case is the formation of pseudocolloids through interaction of nuclides with organic colloids. Such organic colloids, for example humus substances, are present in natural waters.

The formation rates of true and pseudocolloids are quite different. True colloids form rapidly while the rate of pseudocolloid formation basically is determined by the sorption rate of nuclides onto colloidal impurities. In their review article, Olofsson, et al. [B3] state that many data are available on pseudocolloid formation rates. For example, they point out that an equilibrium distribution of tetravalent plutonium between colloidal impurities, the vessel surface, and solution is achieved wtihin 3-5 hours. Olofsson, et al. [B3] also point out that colloids age, i.e. grow in size (also coagulate) and can change properties through recrystallization of microcrystals. Data on colloids for actinides and some other elements of interest are presented in Appendix J. These data show the pH region where more than 10% of the radioelement is present in colloidal form (under laboratory conditions).

Champ, et al. [B5] have demonstrated experimentally the existence and rapid transport of colloids containing plutonium. This carefully executed set of experiments, using core samples and ground water, provides added insight and confirmation into colloid formation and rapid migration rates. The experimental work by Olofsson, et al. [B4] showed the formation and rapid nonadsorbing migration of colloids containing americium over a wide range of pH. In their more recent study [B9] they measured the diffusion rate of Am and Pu as well as studied the effects of pH on the colloid formation of Am, Pu, and Np. True colloids tended to form at the higher pH values. True colloids of Am and Np formed at pH values above 12 and 10, respectively, while Pu colloid formation occurred at values above 8. Olofsson, et al. [B9] also point out that colloid particles have a much slower diffusion rate than ions and molecules.

Means and Wijayaratne [B5] discuss the role of natural colloids in the transport of heavy metals and show experimentally the very strong adsorptive strength of colloids for organic contaminants. Allard, et al. [B8] provide experimental data for the expected species of uranium, neptunium and plutionium in neutral aqueous solutions. Their work demonstrates the effect of pH on species concentrations. They point out that at low pH (below 4-5) the trivalent state is predominant and that the hydroxide form is dominant at pH above 11-12. In the intermediate pH region a mixture of different species exists.

Avogadro, et al. [B10, B11] discuss the role of nuclear colloids in waste disposal. They claim that the dominant mechanisms affecting the migration of nuclear colloids are filtration and solubilization. In their most recent paper [B11], reference was made to laboratory column experiments in which they showed that colloidal filtration is a major retention mechanism governing colloid transport through porous geological media.

1.1.3 Colloid Modeling

Apps, et al. [B2] attempted to qualitatively assess the potential formation and migration rates of nuclear colloids through a back fill barrier. The modeling was rather preliminary and made use of many simplifying assumptions which could be very important to a repository assessment. Perhaps the most obvious shortcoming was the very limited treatment of particle sizes and the size effects.

Avogadro, et al. [B-11] present a 1-D filtration model to represent their column data. This model has two deficiencies: 1. it was limited to the treatment of a monodispersed (single particle size) distribution, and 2. a very simplified capture submodel was used to describe the removal of colloids from the solution. Avogadro, et al. suggested that the filtration capture submodel could be modified to treat a distribution of colloid sizes, however, this suggestion was not developed in detail by the authors. As discussed previously, the colloidal size range spans three orders of magnitude. Thus, a polydispersed size distribution must be considered in any adequate description of colloid transport in natural systems. In addition, by including all particle-particle-solute-solution-matrix interactions in a single filtration coefficient, Avogadro, et al. [B11] ignored possible changes in processes that may be important under natural conditions.

Eichholz, et al. [B12] have performed column experiments to investigate the migration of radioactive clay particles. The columns were packed with various types of host rocks (sand, crushed basalt, limestone and shale). Then results showed that particle capture was influenced by the ionic strength of the solution and the degree of host rock conditioning (cleaning by acid solution). The suspended clay particles were very effective in absorbing the dissolved ions. Both particle retention profiles and effluent concentration histories were reported. These experiments can be applied to the modeling of pseudocolloids.

Chiang and Tien [E10] have modeled in some detail the capture of colloids within a porous medium but did not treat radioactive colloids specifically. They point out that when Brownian diffusion is the dominant force, the common trajectory calculation approach is no longer possible. Though 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. Rather their work is limited to modeling the processes of colloid capture in a porous medium. This work could be a very useful contribution to the population balance repository modeling by providing a colloid capture model. The capture model will

appear as a death term in the population balance as explained in Appendix D. Guzy, et al. [E2], Adamczyk, et al. [E3], Spielman, et al. [E4,E7-E9], and Fitzpatrick, et al. [E5,E6] as well as many other researchers have modeled the capture of particles/colloids. Several of these works are discussed further in Appendix D.

With the exception of the modeling by Apps, et al. [B2] and Avogadro, et al. [B11], the literature on radioactive colloids has been experimental. The absence of colloid models and the lack of quantitative assessment points clearly to the need for such modeling information. The population balance is an additional transport equation which was derived in the early 1960s [C1 & C2] to model particulate processes such as crystallization, and the approach has subsequently been used successfully in many fields to model particulate systems [C3-C23]. The application of the population balance to nuclear waste colloids, though new, is a straightforward extension of this well established modeling technique. The population balance and its applications are discussed in the following sections and Appendices.

2.0 POPULATION BALANCE

2.1 Background

In 1962 and 1964, Randolph [C1] and Hulburt and Katz [C2] derived the general form of the population balance. These very formal and complete derivations of the population balance in the early 1960's 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 [C1-C23]. Randolph and Larson [C4] in their book make reference to the diverse and numerous applications of the population balance. Included are processes such as crystallization, grinding, air pollution, and biological systems. For example, the birth, growth, and death rates of microorganisms in biochemical processes are commonly modeled with the aid of the population balance. The work by Fredrickson and Tsuchiya [C6] is a good example of the interdisciplinary applications of the population balance. Randolph and Larson [C4] in their book Theory of Particulate Processes also give many interdisciplinary examples and applications of the population balance. Several recent studies using the population balance [C15-C22] range in topics from modeling gas bubbles to mineral grinding models. The population balance, which is derived in Appendix A, is an important addition to the common mass transport and energy transport equations. Using a size distribution, the population balance 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 within the population balance a concentration property axis to each species we wish to track. This concept is discussed further in Appendix C. The addition of these property axes allows correct treatment of the decay chain problem with full accounting of the daughter product concentrations. The adsorption of multiple nuclides on the same colloid (heterogeneous colloids) can also be modeled. Randolph and Larson [C4] discuss in detail an example of using the concentration property axis within the population balance. 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 size axes gives the amount of nuclide present as a colloid at a point in time/space. This concept is discussed further in Appendix D.

The general population balance permits a correct mathematical

accounting and quantitative assessment of the nuclear colloid problem. The soluble species mass transport and energy balance equations and the appropriate system geometry must also be included to complete an overall repository assessment model. The level of model complexity 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 is further enhanced by the wealth of information and experience provided by over 20 years of frequent use in many scientific fields. This means that the solution methods and the nature of the various terms have often been studied by previous researchers and their results can now be applied rather directly to the nuclear colloid problem without the delays of extensive research and development.

2.2 Application to Nuclear Waste Repository Assessment-Scenarios

In applying the population balance for repository assessment, two sample 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 examples of 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 into the surrounding geological formation. Ground water carries the colloids away from the engineered barrier to the accessible environment. The dissolved species are in high enough concentrations to precipitate into additional colloids and adsorption of dissolved species on natural ground-water colloids occurs. This scenario is initiated during the repository thermal period and leads to the far-field transport of colloids. The second scenario (B) represents a far-field problem in which dissolved nuclides have migrated beyond the repository and are available to bond with natural ground-water 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. The descriptive equations for each scenario are developed below.

The model for scenario (A) requires the energy, mass, and population balance transport equations. The distributed energy balance models the fluid temperature as a function a spatial position and time [D1].

Energy Balance:

$$\rho C_p\left(\frac{\partial T}{\partial t} + v_x\frac{\partial T}{\partial x} + v_y\frac{\partial T}{\partial y} + v_z\frac{\partial T}{\partial z}\right) = K\nabla^2 T \qquad (1)$$

This equation is coupled to the mass transport and population balance equations through temperature-dependent terms such as the diffusivity, growth and nucleation rates, solubility, etc.

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:

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

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

The 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 were to exist, an additional population balance equation could be used to describe each one. A second set of population balance equations is needed 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 [C1 & C4]. In the case of nuclear waste modeling, a concentration property level 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 approach described below is given only to show the comprehensiveness of the population balance model.

True Colloid Population Balances:

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

Natural Ground-water Colloid Population Balances:

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

where

- B = colloid birth function
- D = colloid death function
- D_b = Brownian diffusion
- $\vec{v}$ = fluid or colloid velocity vector
- t = time

Greek

- ψ = population density function
- ξ = property axis
- ν = property rate function (includes growth rate and concentrate change)

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.

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.

The second scenario (B) is a far-field problem in which the thermal period has passed and nuclides have migrated out from the repository into the ground water of the surrounding geological formation. Natural ground-water 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 is required for each.

The mass conservation and population balance equations are essentially the same as shown previously but of course with different initial and boundary conditions. The problem of convective transport through fractured media should be considered in this scenario thus requiring equations for the fracture and for the porous medium.

Submodels or kinetic expressions are used to represent the various terms in the population balance for both scenarios. The extensive population balance and colloid modeling literature [C1-C23,E2-E10] provides the general forms for these submodels as discussed in the Appendices. Parameters within the submodels can in many cases be estimated on a conservative approach method or may require estimates from experimental data. Many experiments in numerous fields have used the population balance model and this information can aid in modeling radioactive colloids. The types and nature of submodels are discussed in the Appendices with one Appendix corresponding to each term of the population balance.

3.0 CONCLUSIONS

The formation and transport of radioactive colloids is a potentially important pathway for the early release of radiation from a high-level waste repository. Previous studies on the properties of colloids have not examined these possible releases under geological conditions within the framework of an overall repository performance assessment model. The results of previous experimental studies are limited by the specific rock matrix, particle size, solution chemistry and the method used to introduce colloids into the system. The conclusions drawn from these experiments may be valid for the particular system studied, however, they may not be transferable to actual repository sites.

A quantitative assessment of the impact of colloid transport on nuclear waste disposal requires the coupling of the material balance for dissolved species with terms describing nucleation and growth, agglomeration, capture and particle dissolution. Such a coupling may be achieved by the addition of the population balance transport equations to existing mass and energy transport equations. The population balance approach has not been applied to the modeling of the transport of nuclear waste colloids but has been used successfully in many branches of science for over 20 years.

This report shows that the comprehensive model for colloid migration can be highly coupled, requiring the simultaneous solution of the coupled set of transport equations and involving a system of equations and submodels which describe the complex physical and chemical behavior of the colloids. Through the use of simplifying assumptions, however, it should be possible to develop reasonable assessment models which tell us a great deal about repository behavior. This approach should prove viable in modeling and in assessing the importance of radioactive colloids in the near future.

In the long term, the population balance approach could be used to formulate a more comprehensive and quantitative estimate of the transport of radioactive colloids, prioritize research objectives and provide a tool to the NRC to evaluate the results of field and experimental studies of colloid migration.

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APPENDIX A

GENERAL DERIVATION OF THE POPULATION BALANCE

The general population balance was derived by Randolph [C1] to solve a multitude of engineering and science problems involving dispersed phase particulate systems. The population balance is an additional conservation expression to the commonly used mass, momentum and energy equations. The derivation and concept of the population balance are analogous to these more familiar expressions.

Consider a distribution of particles, ψ, distributed in xyz space and through a region R' of property space, ξ. An example might be the size, age, and the internal heavy metal concentration distribution of fish in a lake. In nuclear waste management, the distribution of colloids in size, concentration of nuclides, and space (xyz) can be considered. From the solution of the population balance equation for the first example above, the number density function defines the number of fish at any time, at any point in the lake, for an arbitrary fish length and for any arbitrary concentration of heavy metal within the fish. In the case of radioactive colloids, the number density function would define the number of colloids at any point in time, space, colloid size, and nuclide concentration. In the population balance, a number density distribution is considered:

$$\psi = \psi(x, y, z, \xi_1, \xi_2 \ldots \xi_m, t) \tag{A-1}$$

where x, y, and z are the spatial coordinates, ξ_i, are the continuous property coordinates, and t is the time. Next consider the property rate of change functions which are given by the physical laws governing a process. For a change in particle size, the ν_i is a growth rate function. If the property axis were concentration of a specific actinide such as Pu, then the velocity of propagation along the Pu concentration axis is the rate of Pu addition or decay within a colloid. These property rate functions are defined in general as:

$$\nu_i = \frac{\partial \xi_i}{\partial t} \tag{A-2}$$

When the population balance is solved, these property rate functions must be defined in terms of the physical system. This concept is clarified in Appendices B and C. Additional terms to be considered are the birth and death functions which operate throughout spatial and property regions. These are point functions and governed by physical laws such as nucleation kinetics and coalescence rates. In colloid modeling the birth term could represent nucleation rates and the appearance of colloids released from the waste rock matrix or waste canisters. The death term could represent the capture of colloids onto the formation or coalescence of particles. If particles coalesce then there are both deaths and births occurring along the particle size axis. These terms represent discrete occurrences opposed to the continuous property velocities such as particle growth/dissolution and concentration changes.

Using the previous definitions, a continuity of numbers equation can be derived, i.e. stated simply that accumulation equals input minus output. Using the Lagrangian point of view the continuity equation is

$$\frac{d}{dt}\int_R \psi dR = \int_R (B - D) dR \qquad \text{(A-3)}$$

where

$$dR = dxdydzd\xi_1 d\xi_2 \ldots d\xi_m$$

Thus

$$\frac{d}{dt}\int_R \psi dR = \frac{d}{dt}\int_x\int_y\int_z\int_{\xi_1} \cdots \int_{\xi_m} d\xi_m \ldots d\xi_1 dzdydx$$

Equation (A-3) can be expanded to a useful form by repeatedly differentiating inside the integrals using the general rule of Leibnitz. As shown by Randolph [C1], Equation (A-3) transforms into the integral expression:

$$\int_R \left\{ \frac{\partial \psi}{\partial t} + \frac{\partial}{\partial x}(v_x \psi) + \frac{\partial}{\partial y}(v_y \psi) + \frac{\partial}{\partial z}(v_z \psi) + \sum_{i=1}^{m} \frac{\partial}{\partial \xi_i}(\nu_i \psi) + D - B \right\} dR = 0 \qquad \text{(A-4)}$$

As the region R was arbitrary, a necessary condition for Equation (A-4) to vanish identically is that

$$\frac{\partial \psi}{\partial t} + \nabla \cdot (\hat{v}\psi) + \sum_{i=1}^{m} \frac{\partial}{\partial \xi_i} (\nu_i \psi) + D - B = 0 \qquad \text{(A-5)}$$

Thus Equation (A-5) is the microscopic population balance which is the fundamental equation for modeling radioactive colloid migration.

It should be pointed out that in the modeling crystallizers, the microscopic population balance is integrated over the crystallizer volume giving what is often referred to as the macroscopic version of this equation. This integration simply removes the spatial variation in the number density function. Also in crystallizer modeling, the macroscopic population balance can be further simplified by forming the moment equations. The nth order moment is formed from integrating the product of particle diameter to the nth power times the number density function from zero to infinity. This integration reduces the dimensionality of the equation. The moment transformation can be applied to a multidimensional internal distribution, obtaining mixed moments; however, the mathematical difficulty in recovering a multivariate distribution from the set of mixed moments limits the utility of the moment transformation in the general modeling of colloids. For further details on moment transformation see Randolph and Larson [C4] and Hulbert and Katz [C2].

APPENDIX B

PROPERTY AXIS (SIZE)

As discussed in the general derivation of the population balance given in Appendix A, property axes are an important feature of the population balance. One of the property axes is colloid size and this axis accounts for the gradual growth or dissolution due to molecular diffusion processes. The concentration property axes are discussed in the following Appendix. These concentration axes model the changing nuclide concentration on natural or pseudocolloids.

Colloids range in size from 1 to 1000 nm. This wide variation in size can be compared to a grain of sand and a 1 meter diameter rock; hence, one would expect that size will play an important role in describing the migration and behavior of colloids. True colloids will grow in much the same manner as do crystals in saturated solutions. The mechanism requires that solute be transported to the crystal surface and then oriented into the crystal lattice. This two-step process consists of diffusion followed by surface reactions. In nonagitated systems such as colloid formation in nuclear repositories, the growth rate is limited by the rate of diffusion through a laminar film, thus the rate is diffusion controlled. The reverse process of dissolution may also occur in which the dissolving colliods will decrease in size. The population balance allows a full treatment of colloid size and positive or negative growth rates. Randolph and Larson [C4] provide a detailed discussion of growth rate theories and the corresponding mathematical models.

The starting equation to describe growth rate accounts for both diffusional effects and surface reaction. Assuming a linear dependence of the reaction rate on supersaturation gives [C4]

$$\frac{dm}{dt} = \frac{DA}{x + (D/k_r)} (C - C_s) \qquad \text{(B-1)}$$

where

A is the surface area of a colloid
C-Cs is the degree of supersaturation
D is the diffusion coefficient
k_r is the surface reaction rate constant
m is the mass of the colloid
X is the film thickness.

For colloids having size-invariant shape factors (i.e., colloids of different sizes are assumed to have the same geometric shape) the equation reduces to

$$dL/dt = G = ks \qquad \text{(B-2)}$$

where

L is the colloid size
G is the growth rate
s is C-Cs
k is $DK_a/K_v\ 3\rho[x+(D/K_v)]$!
k_a & k_v are size-invariant shape factors
ρ is the colloid density

Often when this equation is used it is assumed that growth rate (k) is independent of particle size. It has frequently been observed in crystallization systems that the growth rate is particle size dependent. Factors causing this size dependency are poorly understood but often are important when considering growth rate expressions. Hence a modified empirical two parameter growth rate expression which includes the size dependent growth effect is often used.

$$G = G_0(1 + aL)^b \quad b < 1 \qquad \text{(B-3)}$$

where

G_0 is the supersaturation-dependent growth rate at zero size

a & b are two adjustable empirical constants defining the size dependence of the growth rate

An alternate approach was suggested by Bhatia & Perlmutter [C9] who derived fundamental expressions for the growth rate that account for particle-size dependency. Growth rates can be measured in either bench scale flow or batch crystallizers. Cise [C11] describes in detail the required equipment and experimental methods commonly used to measure growth rates.

Natural Colloids

In general, natural colloids (pseudocolloids) are thought to come directly from the geological matrix or from the dissolving canister contents. In this case the number density distribution would not change in size but would change along the concentration property axes due to the adsorption of various nuclides.

The population balance can account for the nucleation and growth of natural colloids if this phenomenon is believed to occur. The mathematical formulation should follow directly from the discussion of true colloids. The adsorption of radionuclides onto natural colloids is discussed in Appendix C (Property Axes).

APPENDIX C

PROPERTY AXES (CONCENTRATION)

Randolph and Larson [C4] discuss an application of the population balance in which the concentration property axis is applied. This example of a fluid-fluid contacting operation involves a two phase system where one fluid is dispersed in the continuous phase in the form of droplets or bubbles. The droplets can be of various sizes and of different solute concentration. Coalescence of the drops is treated and a reaction of arbitrary order takes place involving reactant that is in the dispersed phase. The final expression given for particles of uniform size but including a reaction of arbitrary order "s" and coalescence is

$$\frac{\partial n}{\partial t} - k\frac{\partial(C^s n)}{\partial C} + \frac{n}{\Gamma} = \frac{n_o}{\Gamma} + \frac{2u}{U}\left[2\int_0^C n(C-\alpha)n(C+\alpha)d\alpha - n\right] \quad \text{(C-1)}$$

where

- α is the variable of integration
- k is a kinetic rate constant
- n is the number density function
- Γ is the residence time
- U is the total number of droplets in the dispersion
- u is the collision rate
- s is the reaction order
- C is the concentration of the reactant
- n_o is the number density function feeding into the system.

The moments of the number distribution generally have significance and in this case the first moment, m_1, is the average droplet concentration in the suspension.

$$m_1 = \int_0^\infty C n dC \quad \text{(C-2)}$$

In the above case the rate of concentration change was due to a chemical reaction and is presented as a kinetic expression; however, for radionuclides the change in concentration would result from several processes. First, radioactive decay and the sequence of daughter products could be considered as a change along the concentration property axis. Adsorption and desorption of nuclides from and to the solution will also contribute to this rate of concentration change. The physical laws of diffusion and adsorption/desorption will define this portion of the rate term.

APPENDIX D

DEATH TERM

The death term is a point function of the system and is specified by physical laws. It represents the capture of colloids onto the rock formation/backfill, agglomeration, and the mechanical breaking of particles (this is unlikely for colloids). This is a very important term in the population balance because once colloids are formed their retardation by the matrix becomes a key factor. There have been several recent studies which address the capture of colloids [E2-E10]. Hulburt and Katz [C2] treat the case of a plugflow agglomerator where the size distribution is a function of axial position and time. They assume that the proportionality factor for collision depends only on the environment and not on the particle size or shape. The rate of agglomeration of particles is proportional to the product of their number densities. The model is further simplified by the moment transformation which gives the population balance equation for the time and space variance of the total number of agglomerates, i.e., the total number of particles per unit volume at each point along the axis "x" and for all times.

$$\frac{\partial m_o}{\partial t} + U_x \frac{\partial m_o}{\partial x} = -\frac{1}{2} a m_o^2 \qquad \text{(D-1)}$$

where

- m_o is the zero moment or total number of particles
- a is the proportionality factor for collision
- x & t are the independent variables, position & time
- U_x is the fluid velocity

This treatment accounts for the disappearance (death) of particles from one size and the birth into a larger size. Colloid suspensions can become unstable and form agglomerates. The population balance model is well suited for treating this phenomenon.

Capture of colloids by the geological matrix is of major importance. Adamczyk, et al. [E3], in a recent article, compare and discuss several theories for predicting deposition rates of flowing colloidal particles onto various collector surfaces. Several experimental procedures for measuring deposition rates are presented, and experimental data are compared with theoretical predictions. They conclude that, in principle, successful theories must incorporate, besides hydrodynamic conditions in the vicinity of the collector and the energy of interaction between particles and the formation, a variety of other important factors affecting deposition such as particle detachment, aging of the particle-collector bond, masking, influence of the stability of the dispersion and surface heterogenity and roughness. They conclude that current theories are not complete and do not

represent the data very well. The authors suggest the addition of stochastic modeling to the existing theories as a means of more accurately describing the capture phenomenon.

Guzy, et al. [E2] use swarm theory to predict streamlines and particle trajectories and compare their results with hydrodynamic models to assess sensitivity of predicted efficiencies with respect to the type of flow model used. Brownian motion contribution to retention was also considered. This is another modeling approach that can be considered when describing the death term or capture of colloids by the matrix.

The work by Chiang and Tien [E10] presents a capture model which includes the double layer and van der Waal forces as well as the Brownian motion of the particles. The interesting aspect of this model is that the authors use the constricted tube porous media model developed by Payatakes, et al. [E11]. They found reasonably good agreement between the analysis and the available experimental data. However, none of the models described here are as comprehensive as Adamczyk, et al. [E3] suggested as necessary to accurately describe the capture phenomenon. Avogadro, et al. [B11] are currently using a simplified filtration model to represent colloid capture and are achieving some success. The question of which capture model is best and how much complexity is required can be answered only by further experimental results and analyses.

APPENDIX E

BIRTH TERM

In general, new particles can be formed from attrition, homogeneous nucleation, heterogeneous nucleation, and secondary nucleation. For true colloids, the most likely formation mechanism will be heterogeneous nucleation. Each of the mechanisms is discussed briefly, in this appendix.

Attrition is the mechanical degration of solid material in the system. An example, is the release of colloids from the canister or the release of natural colloids from the geological formation.

The starting point for nucleation deals with homogeneous nucleation but since real systems demonstrate combined homogeneous/heterogeneous nucleation the equations actually used in crystallization represent and model the combined phenomenon.

Homogeneous nucleation is the formation of new colloids as the result of only supersaturation. Heterogeneous nucleation results from the presence of foreign insoluble material.

The fundamental expression for the rate of homogeneous nucleation (in very clean systems) proposed by Volmer and Weber [C9] and presented in the book by Randolph and Larson [C4] is

$$B = C \exp(-\Delta G^{*}/kT) \qquad \text{(E-1)}$$

where

- ΔG^* is the free energy of formation of a nucleus
- k is Boltzmann's constant
- c is a proportionality constant
- T is the absolute temperature.

Though this rather fundamental equation has been tested and modified and retested many times, little success has been achieved in predicting experimental behavior. True homogeneous nucleation independent of heterogeneous nucleation seldom occurs and thus the failure of this more theoretical approach to nucleation kinetics.

Heterogeneous Nucleation

At a given temperature, Nielson [C10] notes that Eq. (E-1) can be approximated by a power-law function of supersaturation. Account-

ing for the fact that nucleation does not occur at very low supersaturations, Nielson's nucleation rate expression is

$$B = k(C - C_m)^i \qquad \text{(E-2)}$$

where C is the solute concentration, C_m is a concentration greater than the saturation concentration but below which nucleation does not occur. This equation is often referred to as the Miers nucleation model and in most inorganic systems, it appears that C_m is very close to C_s, the saturation concentration. It should be pointed out that k is assumed to be a function of system temperature while the exponent "i" is not. The Miers nucleation kinetics provide a good representation of experimental nucleation data.

Randolph and Larson [C4] consider secondary nucleation as crystals/colloids formed at and later washed by mechanical means from the surface sites of existing crystals in the system. Clontz and McCabe [C8], in a unique and informative experimental program, provided a clear example of secondary nucleation. In their experiment using a single suspended crystal in a flowing stream, the crystal was struck by a rod inflicting a known force. The nuclei released from the crystal surface were washed down stream and counted in a detector.

In commercial or laboratory crystallizers, the concentration of solid particles is often quite high and the agitation rate is strong. Under these conditions, secondary nucleation can be significant. To model the effects of secondary nucleation the mass concentration term is usually added to the Miers' nucleation model (E-2); however, in the modeling of colloidal systems secondary nucleation should not occur and thus this mass concentration term will not be required.

Both theoretical and laboratory studies are available to provide a guide for the values of the two parameters in the Miers nucleation kinetic model. This information can serve as a starting point in modeling the nucleation of true colloids. In a numerical simulation study of crystallizers, Nuttall [C3] showed that for a crystallizer to be stable the value of i must be less than 21. For a few systems experimental data have shown that the value of i can be slightly negative. Randolph and Larson, through many experiments, have verified Equation (E-2) and in their book [C4] list over forty references to nucleation-growth rate kinetic studies. For colloid modeling, this literature would provide reasonable starting values.

Bhatia and Perlmutter [C7] also discuss and present equations for homogeneous and heterogeneous nucleation. Their approach might also be considered in a colloid study.

The work by Cise [C11] gives both detailed experimental methods and extensive results on nucleation and growth rate kinetics for an inorganic crystallizer system. He also includes in his birth rate model an Arrhenius type term to correlate the temperature effects.

APPENDIX F

DISPERSION TERM (BROWNIAN & FLUID)

From experimental work, Randolph and White [C5] recognized that stochastic processes influence the number density function in the same manner as they affect the mass balance transport equations. The dispersion terms for both the fluid/Brownian effect and for the property axes were not included in Randolph's [C1] original derivation of the population balance but were later shown to be necessary and justifiable terms.

Specifically the microscopic population balance was modified by adding the fluid and property dispersion terms

$$\frac{\partial n}{\partial t} + v_z \frac{\partial n}{\partial z} + \frac{\partial (Gn)}{\partial L} = B - D + D_a \frac{\partial^2 n}{\partial z^2} + D_G \frac{\partial^2 n}{\partial L^2} \qquad \text{(F-1)}$$

where

- B-D are the birth and death terms
- D_a is the fluid dispersion coefficient
- D_G is the size axis dispersion coefficient
- G is the growth rate
- L is the particle size
- n is the population density function
- t is time
- v_z is the fluid velocity
- z is the position

Apps [B2] used the value (0.03 m^2/yr or 9.6E-6 cm^2/sec) for D_a for an ionic species modified by a tortuosity factor of 0.5. This value is similar in magnitude to the molecular diffusion of radionuclides. Chiang and Tien [E10] in their study on the deposition of colloids used a value of 8.0E-8 cm^2/sec.

Neither of these values can be considered to be representative of the dispersion coefficients of colloids under natural conditions. The dispersion coefficient is a function of the dispersivity, α and the diffusivity D.

$$D_a = D + \alpha v_z$$

The diffusivity varies with both particle size and temperature as

suggested by the Stokes-Einstein equation. This equation is fairly good for describing the diffusion of large spherical particles or large spherical molecules where the solvent appears as a continuum and can be used to estimate values of D_a for colloids under different conditions [E1].

$$D = \frac{kT}{6\pi R\mu} \qquad \text{(F-2)}$$

where

D is the diffusivity
k is the Boltzmann's constant
T is the absolute temperature
R is the colloid radius (or molecule radius)
u is the viscosity of the pure solvent.

In general, the dispersion coefficient should be measured under natural conditions in order to account for the tortuosity and constrictivity of the geologic medium.

APPENDIX G

DISPERSION TERM (PROPERTY AXES)

This term is similar in nature to the Brownian dispersion term described in Appendix F. Randolph and White [C5] added their dispersion terms to the population balance as a result of problems in matching experimental data. The theoretical basis for such a term is that stochastic processes occur not only in the fluid but also along the property axes (such as the size axis) as well. Randolph & White [C5] showed that the dispersion coefficient for the size axis is a linear function of growth rate. This result is analogous to mass dispersion in a porous medium where the dispersion is assumed proportional to the fluid velocity. It was also shown from experimental data that the size dispersion term is strongly dependent on the chemical system studied. Experimentally determined values ranged from 1.5 nm^2/min to 5,000 nm^2/min for aluminum trihydroxide and sugar repectively. This term may not be essential to the initial colloid modeling studies; however, it is important for completeness of the population balance to show this term.

APPENDIX H

ACCUMULATION

Since the population balance is a dynamic conservation equation, there can be increases or decreases in the number of particles at a point in space or property space as a function of time. The accumulation term $\partial n/\partial t$ accounts for this dynamic change.

APPENDIX I

CONVECTIVE TRANSPORT

This term represents the migration of colloids carried by the fluid. Because of their very small size, colloids are assumed to move with the fluid at the actual fluid velocity. This assumption should be satisfactory in nuclear colloid modeling at least for the initial studies.

APPRENDIX J

COLLOID DATA FOR SELECTED NUCLIDES [B3]

Nomenclature

PSC - pseudocolloids
TC - true colloids
NSC - presence of non-specified colloids proved
CF - centrifugation

This table shows conditions (pH, ionic strength, age of solution) under which 10% of a radioelement is present in colloidal form. In general, the ionic strength of these solutions was set by the concentration of $NaClO_4$ and ranged from 0.01M to 1.0M. The pH was adjusted by addition of NaOH or $HClO_4$. These solutions do not represent actual ground-water compositions. The purpose of these experiments was to determine the effects of pH and ionic strength on colloid formation. The ranges of pH and ionic strength bracket those encountered under natural conditions, however, effect of the particular ligands in the solution on colloid formation was not investigated.

TRACE ELEMENT	CONCENTRATION (M)	COMPOSITION AND AGE OF THE SOLUTION	EXISTENCE AND NATURE OF TRACE COLLOIDS
^{241}Am	10^{-9}	HNO_3-KOH	pH 4.5-11
^{241}Am	10^{-9}	HNO_3-KOH	pH 5-8 PSC pH 9-12 TC(?)
^{134}Cs	10^{-7}	HCl-NH_4OH	No evidence of colloids at pH 0-10
^{134}Cs	c.f.	0.5-1 M $NaNO_3$, 0.005-1 M sodium tetraphenylborate	TC of Cs tetraphenylborate
^{155}Eu	10^{-9}	HCl, NaOH, 0.001-1 M NaCl $NaNO_3$, Na_2SO_4, or $BaCl_2$	pH 4-11 NSC
^{155}Eu,	10^{-8}	HCl or NaOH	pH 5-11 NSC, probably TC at pH>7
^{155}Eu,	10^{-6}	HCl or NaOH	pH 5.5-11 NSC, probably TC at pH>7

Eu	$1.4 \cdot 10^{-7}$	HNO_3 or NH_4OH (NaOH)-CO_2-free	pH 5.8-11 PSC pH 12-13 TC
^{155}Eu	c.f.	HCl, NaOH, 0.01 M or 0.1 M NaCl	pH5-11 NSC
^{239}Np	c.f.	0.0001-0.021 M HNO_3, $8 \cdot 10^{-6}$-$8 \cdot 10^{-5}$ M La	No evidence of colloids
^{233}Pa	10^{-11}-10^{-13}	0-14 M HNO_3, NH_4OH or KOH	pH 2-7, 11-14 PSC pH 5-11 TC
^{233}Pa	$7 \cdot 10^{-1}$	0.015-0.5 M H_2SO_4, NH_4OH T = 0-13 d	pH 1.5-5 TC (hydrolytic polymers)
^{231}Pa	10^{-6}	0.015-0.15 M H_2SO_4 T = 0-13 d	0.015-0.05 M H_2SO_4 TC (hydrolytic polymers)
$^{212,210}Pb$	c.f. (-10^{-11})	HCl-NH_4OH or KOH	$\geq 10^{-3}$ M OH^- NSC
^{212}Pb	c.f.	HCl, satd.H_2S	pH 2-6 TC(PbS)
^{238}Pu	10^{-9}	0.0001-.021 M HNO_3, $8 \cdot 10^{-6}$-$8 \cdot 10^{-5}$ M La, various electrolytes	pH 2-4 PSC
Pu(IV)	$7 \cdot 10^{-8}$	HNO_3-KOH T = 0-10 d	pH 2.8-7.5 PSC, pH 7.5-12 TC

Pu(IV)	$(1-2)\cdot10^{-5}$	HNO_3-KOH	pH 1.4-12 TC
$^{239}Pu(IV)$	$5\cdot10^{-10}-10^{-8}$	HNO_3-NH_4OH T = 0-3 d	pH >2.8-3.6 TC(?)
$^{238,239}Pu(IV)$	$10^{-10}-10^{-8}$	HNO_3-NH_4OH T = 24 h	pH 2.5-6 PSC pH>3 TC(?)
$^{238,239}Pu(IV)$	$5\cdot10^{-7}-10^{-6}$	HNO_3-NH_4OH T = 24h	pH 3-6 PSC, pH 5.3-9(10) TC
$^{238}Pu(IV)$	10^{-11}	HNO_3-NaOH, I=0.01	pH 2-5 PSC
^{234}Th	$2.4\cdot10^{-8}$	$HClO_4$-NaOH, various electrolytes	Probably TC at pH>4
$^{228,234}Th$	c.f.	HCl-NH_4OH	pH 5-9.5 TC 0.03-1 M NH_4OH TC + PSC
$^{233}U(VI)$	10^{-8}	HCl-Na_2CO_3	pH 2-8 PSC
$^{233}U(VI)$	$4\cdot10^{-7}$	HCl-NH_4OH	pH 5-11 PSC
$^{233}U(VI)$	$10^{-6}-10^{-5}$	HCl($HClO_4$)-NH_4OH	pH 3-9 PSC(?) , pH>9 TC