MECHANISTIC MODELLING OF LONG-TERM LEACHING BEHAVIOR OF CEMENT-BASED RADIOACTIVE LOW-LEVEL WASTE FORMS

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ABSTRACT

The application of multi-concentration diffusion (MCD) group mathematical modelling to the long-term leaching behavior of cement-based radioactive waste forms is described. The modelling is illustrated by analyzing hypothetical cases using transport mechanisms such as molecular diffusion, ionic migration and convective flow for release of Sr-85 from a solidified waste form. The group parameters, which describe the transport mechanisms, are derived from the classical electrochemistry concept of ion transport in dilute electrolytic solutions. The numerical analysis is based on the Crank-Nicolson Implicit Method, which assures the stability of the equation at practical time intervals. The boundary conditions are based on the experimental results. The results show that, for a short time period of leaching in demineralized water, the leaching behavior follows the predominating diffusion mechanism. After this point, the role of other processes are apparent and continue until all radionuclides in the cement waste form are leached. When compared to the Semi-Infinite Diffusion model, which is based on a pure diffusion mechanism, the MCD model predicts higher leach rates.

INTRODUCTION

A solidified cement waste form has a complex, porous microstructure, the exact configuration of which is never defined. The semi-infinite mathematical model describing leaching behavior of a radionuclide from the waste form to the disposal environment is usually based on the diffusion process (1). Results of this model is typically expressed as the cumulative fraction release (CFR) of a radionuclide as a function of the square root of the leaching time.

Other processes have been added to this diffusion equation to describe the realistic behavior of radionuclide leaching, such as chemical dissolution, linear surface transfer and immobile-mobile source term (2,3). The characteristic parameters used to describe the mechanisms such as the diffusion coefficient and the reaction rate, are determined from experimental data and curve fitting to a particular mathematical model. This has lead to variations of their characteristic parameter.

For long-term prediction of the leaching behavior of a solidified radioactive waste form, a similitude law of leaching systems (4) was developed based on the diffusion process and radioactive decay of a particular radionuclide. The prediction is made with the assumption that the only prevailing mechanism is diffusion.

In this paper, the multi-concentration diffusion model is introduced as a basic mathematical guideline for predicting the long-term leaching behavior of a specific radionuclide from a solidified cement waste form.

LEACHING MECHANISMS

When radioactive waste is solidified with cement, the radionuclides are bound chemically by absorption or physically by adsorption within the massive or crystallized cement matrix structure. This is referred to as the SORPTION process.

In the leaching process, water permeates throughout the solid matrix until it becomes saturated and the static piezometric pressure of the water within the structure balances the pressure of the external water. The liquid involved in the leaching process consists of the aqueous solution, which is the water contained in the solid matrix structure, and the leachant, which is the water that surrounds the solid matrix.

When the solid waste form makes contact with the water, the radionuclides in the matrix begin to be released into the aqueous solution by the process referred to as DESORPTION. Desorption may occur by two processes; dissolution and ion exchange. Dissolution is a physico-chemical process which tends to

adjust the unbalanced electrostatic force between ions that are sorbed in the solid matrix structure and ions dissolved in the aqueous solution. Ion exchange is the process which tends to convert an immobilized nuclide in the solid matrix to a mobile form in aqueous solution. The desorption process acts to produce an equilibrium state between the dissolved and the sorbed radionuclides.

The transport of radionuclides begins when the concentration of nuclides of interest in the aqueous solution increases as a result of desorption and creates a driving force for a spontaneous change of the gradient of electro-chemical potential. A positive concentration gradient is formed, which results in the transport of radionuclides from within the solidified waste along the porous microstructure of the cement matrix to the waste form/leachant boundary by the molecular diffusion, ionic migration and fluid convection processes.

During transport, the radionuclides may be detained or lost along the way because of chemical/physical sorption, ion exchange, precipitation and radioactive decay. As the radionuclides are transported out of the solid matrix into the leachant, their concentration in the internal aqueous solution decreases. As a result, the desorption processes within the solid matrix are accelerated. This will result in a continuous transport of radionuclides, from the aqueous solution, to the leachant.

LEACHING EXPERIMENTS

Cylindrical specimens (7.30 cm in diameter x 8.83 cm in height) were fabricated using a mixture of cement and water based on precalculation of the minimum water/cement ratio for 100% hydration (5). A known concentration of Sr-85 was added to the cement mix and the waste forms were cured for 42 days prior to testing.

The leach test used for this study was a flow-through test. A flow rate of the leachant (~0.7 cc/min) was adjusted by a control pump to maintain the volume of the leachant in the leachate container as much as 10 times that of the surface area of the specimen. The leachant was collected daily for a period of three weeks and then once a week for the next twelve weeks. For each sampling, five aliquots (5 cc each), were counted in a Na-I counting system. The detector was calibrated at the energy peak of 0.514 MeV and counting time was 1000 seconds, with the dead time less than 1%. The incremental fraction release (IFR) and the cumulative fraction release (CFR) were calculated and used as the boundary condition in the mathematical model. The slow flow-through leaching system is illustrated in Fig. 1.

THE MATHEMATICAL APPROACH

The structure of a solidified cement waste form is assumed to be a uniform, porous medium with a solid phase and pore space which will be contact with the aqueous phase during the leaching process. It was stated earlier that radionuclides are leached from the solidified cement structure into the aqueous solution through the mechanism of desorption and rearrangement of ionic species within the solid-liquid system. Therefore, one can regard such a system as a solid-liquid electrolyte.

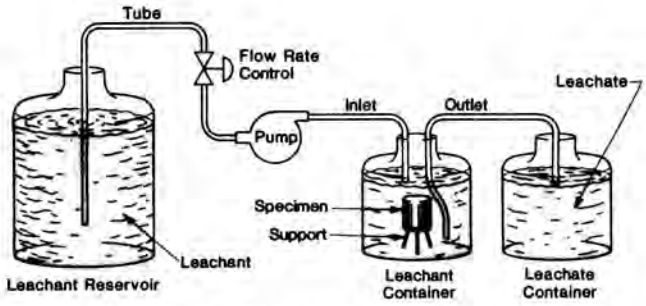

Fig. 1 Configuration of Leaching System.

The mathematics describing transport in an electrolytic solution, which include the effect of molecular diffusion, diffusion potential migration of different ionic species and leachant fluid flow convection (6) is given in Equation 1.

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i - z_i F u_i \dot{E}_{diff} \nabla C_i - \dot{W} C_i - f_i C_i + R_i C_i \quad (1)$$

diffusion migration covection

Two additional terms are added to Equation 1 to balance the system for a particular time; the production term (R_i) due to the desorption of nuclides from the solid matrix, and the "loss" term (f_i) due to the absorption, chemical reaction and decay of radionuclides.

THE MCD-MODEL APPROACH

The multi-concentration diffusion group is applied to the flow-through leaching experiment by using Sr-85 solidified in cement waste form. To demonstrate the MCD Model, a three-phase system with four concentration groups was chosen. Two of the concentration groups are in the solid-cement phase, one in the cement-leachant interface phase, and one in the water-leachant phase, as illustrated in Fig. 2.

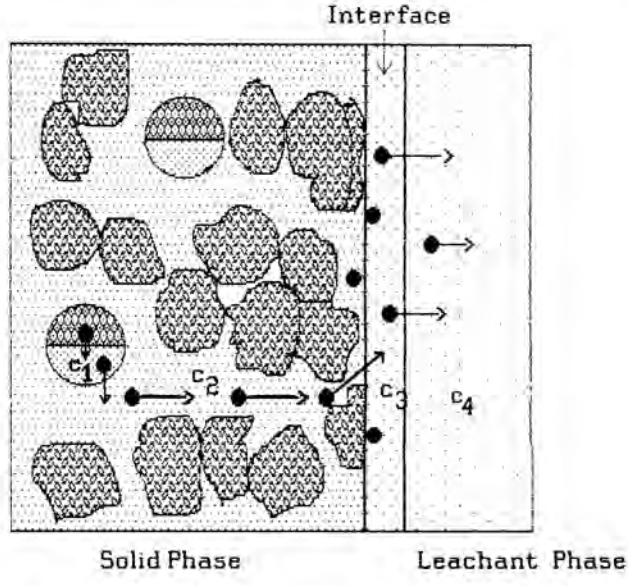

Fig. 2 The MCD-Mathematical Model Approach.

Solid-Cement Phase

Two concentration groups are applied in this phase. The Sr-85 radionuclides desorbed from cement matrix into aqueous solution occupies the pore space as the concentration of C_1, and the nuclides are transported through an irregular diffusion path of the cement matrix, as concentration C_2.

Concentration Group 1

In Figure 3, the initial concentration of Sr-85 is assumed to be uniform throughout the cement matrix, with a number N of discrete spheres per unit volume in a volume of radius R. Thus the volume fraction is V_1, and the assumed leaching mechanism of this group is the diffusion of Sr-85 nuclides from the sphere volume, characterized by the diffusion coefficient D_1. The effects of diffusion potential migration and the convection effects are neglected. The production rate is due to the desorption of Sr-85 from the cement matrix and is characterized by the desorption rate P_1 and the loss rate by radioactive decay, λ of Sr-85. The mathematic representation is

$$\frac{\partial C_1}{\partial t} = D_1 \left\{ \frac{\partial^2 C_1}{\partial r^2} + \frac{2}{r}\frac{\partial C_1}{\partial r} \right\} + (P_1 - \lambda)\, C_1 \qquad (2)$$

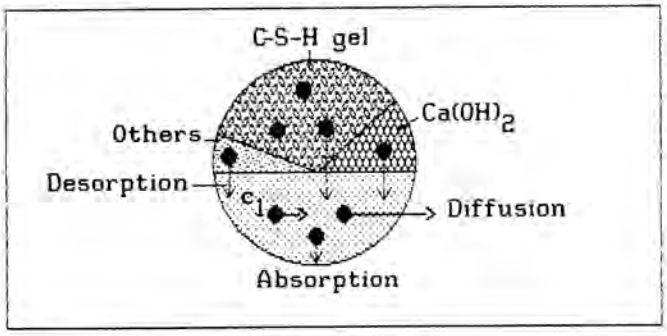

Fig. 3 Group One.

The production term is considered theoretically from the free energy changes when an ion interacts with solvent molecules according to the ion-quadrupole process. This free energy includes the work solvent molecules cavity information, dissociation, ion-quadrupole interaction, Born's charge, structure breaking and condensation of the remaining solvent molecule are given as (7).

$$\Delta G = 20 - \frac{N_A z_i^2 e_o^2}{2(r_i + 2r_w)} \cdot \left\{ 1 - \frac{1}{\varepsilon_w} \right\} - \frac{4 \cdot N_A z_i e_o \mu_w}{(r_i + r_w)^2} + \frac{4 \cdot N_A z_i e_o P_w}{2(r_i + r_w)^3} \qquad (3)$$

where r_i and r_w are the radius of ion molecule and water molecule respectively, μ_w is the dipole movement and P_w is the quadrupole moment of water molecule. Then, the rate of production may be considered by the rate process of the activation complex as

$$P_1 = \frac{kT}{h} \cdot e^{-\Delta G/RT} \qquad (4)$$

where h is the Plank's constant, k is the Boltzmann's constant and R is the Gas constant.

Concentration Group 2

The Sr-85 atoms travel through an irregular path in fissures of the cement matrix. The volume fraction of V_2 assumes that each sphere of Group 1 is completely surrounded by a layer of Group 2 that extends into the cement-leachant interface phase, as illustrated in Fig. 4.

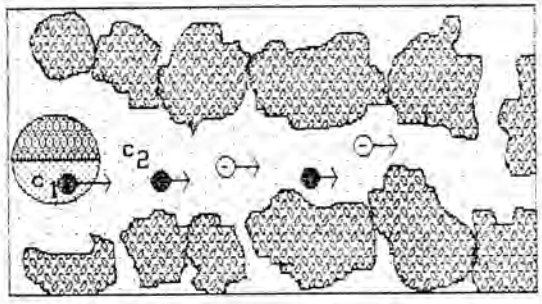

Fig. 4 Group Two

The leaching mechanism includes diffusion and the diffusion potential migration effect. Diffusion is characterized by D_2 and migration is characterized by u_{abs}. The diffusion coefficient also accounts for the diffusivity, Q, in the cement fissures. The leaching equation includes the transfer from the release of Sr-85 from each sphere of Group 1. The mathematical representation is

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2} + z_i u_{abs} \vec{FE}_{diff} \frac{\partial C_2}{\partial x} - \lambda C_2 + \frac{3V_1 D_1}{V_2 R} \left. \frac{\partial C_1}{\partial r} \right|_{r=R} \qquad (5)$$

where u_{abs} is the absolute mobility of an ion, F is Faraday's constant and $\vec{E}_{diff}$ is the electrical field due to diffusion potential.

Cement-Leachant Interface Phase (Group 3)

For a laminar flow over any plane parallel to the direction of the flow, a shear stress develops due to differences in velocity at successive points normal to the direction of flow, a diffusion layer is formed near the phase boundary.

The leaching mechanisms include diffusion, diffusion potential migration, and the effect of flow convection, which are characterized by D_3, u_{abs} and V_3, respectively. The production term in this phase accounts for the accumulation of the radionuclides due to the electrical double layer at the surface of the cement waste form and is characterized by accumulation rate of R_3 (Fig. 5), added to the release term from Group 2. The mathematical representation is

$$\frac{\partial C_3}{\partial} = \left\{ D_3 \frac{\partial^2 C_3}{\partial x^2} + z_i u_{abs} \vec{FE}_{diff} \frac{\partial C_3}{\partial x} - V_x \frac{\partial C_3}{\partial x} + (R_3 - \lambda) C_3 + \frac{S_2 D_2}{V_3} \cdot \frac{\partial C_2}{\partial x} \right|_{x=s} \qquad (6)$$

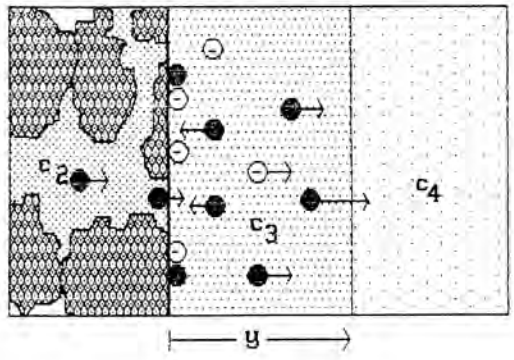

Fig. 5 Group Three.

The accumulation term due to the double layer formed at the surface of the waste form is derived from the Gouy-Chapman equation of free energy change at the surface (8).

$$\Delta G_{Gouy} = -\left\{\frac{8.kTN_A}{\chi} \cdot C_{sur}\right\} \cdot \left[\frac{ze_o}{2kt} \cdot \psi_{sur} - 1\right] \quad (7)$$

where C_{sur} and ψ_{sur} are the concentration and potential at the surface. Also, the rate of accumulation is considered by the activation complex theory as:

$$R_3 = \frac{kT}{h} \cdot e^{-\Delta G_{Gouy}/RT} \quad (8)$$

Water-Leachant Phase

For a low velocity flow system, the concentration of Sr-85 is characterized by C_4, as shown in Fig. 6. The leaching mechanism is dominated by the volumetric flow rate of the leachant, $\dot{m}$, and the release rate from Group 3. In this phase, one assumes that there is no chemical reaction or precipitation of Sr-85 nuclide. The mathematical representation is

$$\frac{\partial C_4}{\partial t} = \frac{S_3}{V_4} \times \bar{v}_x C_3 - \frac{\dot{m}}{V_4}[C_4(o) - C_4(t)] - \lambda C_4 \quad (9)$$

where $C_4(o)$ is the initial concentration of Sr-85 in the incoming leachant.

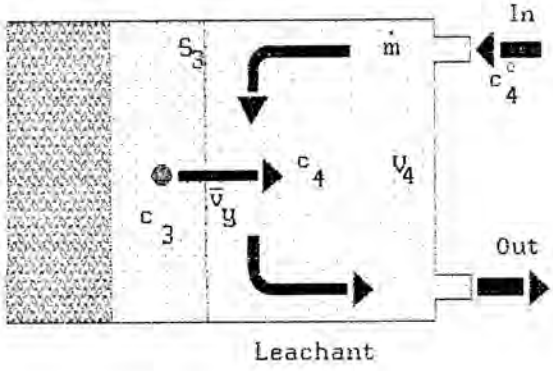

Fig. 6 Group Four.

Initial and Boundary Condition

The initial condition of the multi-concentration groups assumes that the Sr-85 in Group 1 is uniformly distributed throughout the waste form matrix, and the initial concentrations, of Groups 2, 3 and 4 are zero before the leaching occurs.

The boundary condition is assumed continuously across the boundary region between groups assuming that the rate at which the concentration of Sr-85 leaves one group is always equal to the concentration which enters the other group over the interface surface.

Numerical Analysis

The set of partial differential equations, given above for leaching mechanisms was solved by the Crank-Nicolson implicit method using the standard Gaussian elimination techniques. The computer flow chart of the MCD-method is illustrated in Fig. 7.

RESULTS AND DISCUSSION

The application of the multi-concentration diffusion group model describing the leaching of Sr-85 radionuclides from a solidified cement waste form, using a slow flow leach test, indicated good agreement with the experimental data. The results also indicated that, along with the diffusion process, mechanisms such as ionic migration, convection, desorption and accumulation at the surface of the waste form play an important role in the long-term leaching behavior of cement waste forms.

The calculated effective diffusion coefficients are 1.6×10^{-5}, 7.3×10^{-5}, and 3.4×10^{-6} cm^2/sec for D_1, D_2 and D_3, respectively. The flow of leachant is laminar and the convective velocity is 2.3×10^{-7} cm/sec. These coefficients are compared to 6.7×10^{-8} cm^2/sec as calculated by the semi-infinite diffusion model.

From Fig. 8, the MCD results indicate that the cumulative fraction release (CFR) increases sharply during the early stage of leaching due to the diffusion mechanism which predominates release. The CFR also has a lower value than the experiment data due to the assumption of desorption of Sr-85 from the solid matrix to the aqueous solution, which is the only initial source considered for leaching. Past this point, the role of other mechanisms such as migration and convection become apparent and continue at a slow leaching rate to the end of the prediction time. The multi-concentration diffusion group model indicates that the more Sr-85 will be leached from the cement waste form than is estimated by the semi-infinite diffusion model.

Further Investigation

The MCD method could be a basic mathematical model for using short-term experiment data to predict long-term behavior of radionuclide releases from solidified waste forms. The more accurate approaches can be applied in 2- or 3-dimensions depending on the purpose of use. Some other mechanisms such as chemical reaction, precipitation, erosion or biodegradation could be simply added to the model, if the parameters involved have been experimentally determined.

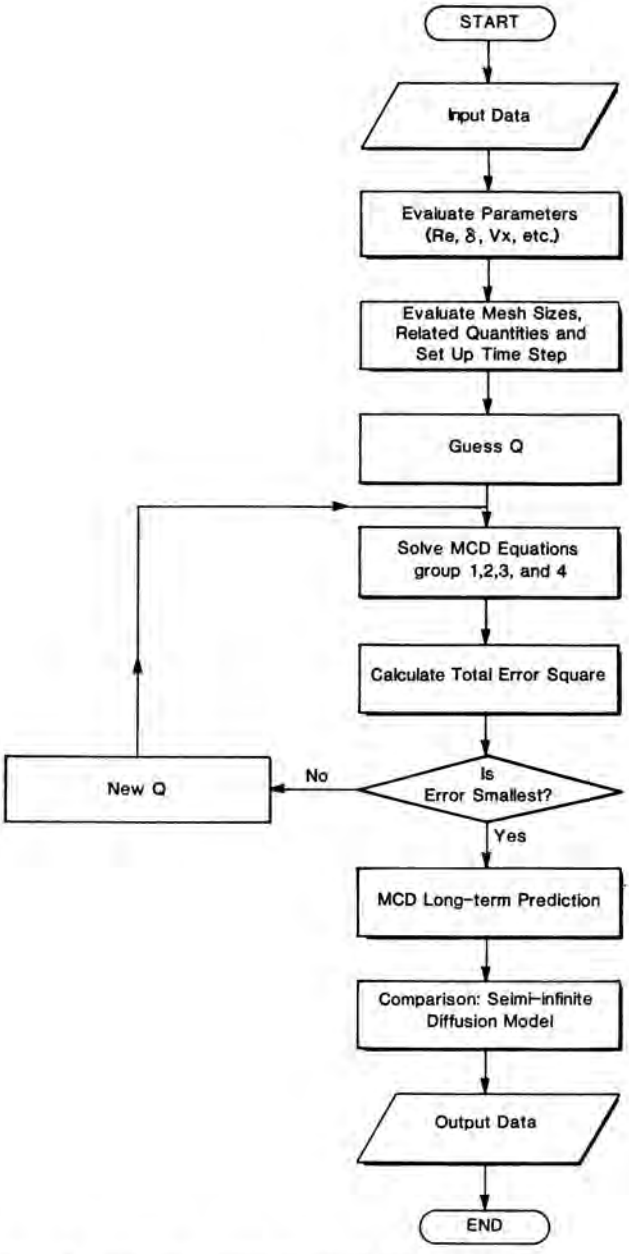

Fig. 7. Computer Flow Chart of the MCD-Method.

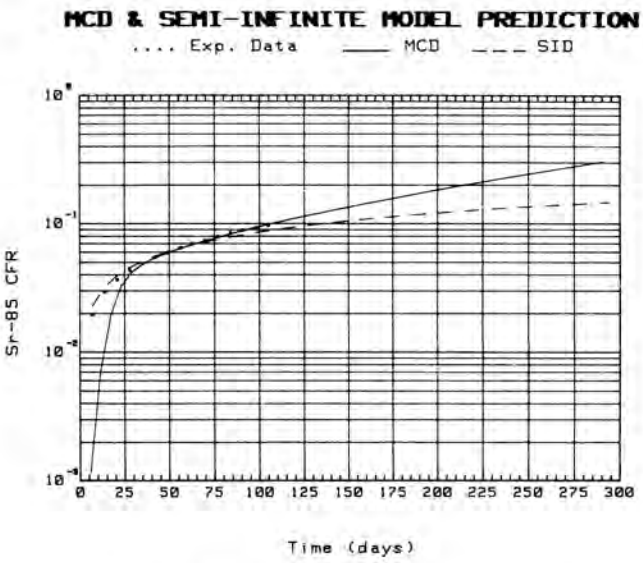

Fig. 8 MCD and Semi-Infinite Prediction.

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