Mathematical Modelling of Transport Phenomena in Radioactive Waste-Cement-Bentonite Matrix

Ilija Plecas, Uranija Kozmidis-Luburic and Radojica Pesic

Abstract—The leaching rate of $^{137}$Cs from spent mix bead (anion and cation) exchange resins in a cement-bentonite matrix has been studied. Transport phenomena involved in the leaching of a radioactive material from a cement-bentonite matrix are investigated using three methods based on theoretical equations. These are: the diffusion equation for a plane source an equation for diffusion coupled to a first-order equation and an empirical method employing a polynomial equation. The results presented in this paper are from a 25-year mortar and concrete testing project that will influence the design choices for radioactive waste packaging for a future Serbian radioactive waste disposal center.

Keywords—bentonite, cement, radioactive waste, composite, disposal, diffusion

I. INTRODUCTION

Radioactive waste is waste material containing radioactive chemical elements which does not have a practical purpose. It is often the product of a nuclear process, such as nuclear fission. Waste can also be generated from the processing of fuel for nuclear reactors or nuclear weapons. The main objective in managing and disposing of radioactive waste (or other) is to protect people and the environment. This means isolating or diluting the waste so that the rate or concentration of any radionuclides returned to the biosphere is negligible. Storage as the placement of waste in a nuclear facility where isolation, environmental protection and human control are provided with the intent that the waste will be retrieved at a later time. Disposal as the emplacement of waste in an approved, specified facility (e.g. near surface or geological repository) without the intention of retrieval. The processing of radioactive wastes may be done for economic reasons (e.g. to reduce the volume for storage or disposal, or to recover a "resource" from the waste), or safety reasons (e.g. converting the waste to a more "stable" form, such as one that will contain the radionuclide inventory for a long time). Typically processing involves reducing the volume of the waste (e.g. by incineration or compaction); solidifying non-solid wastes to make them physically stable, and packaging the waste to isolate it from the environment.

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II. THEORETICAL METHODS

Three methods are compared with respect to their applicability to experimental leaching data [2,3,4,5].

2.1 Method I: Diffusion equation based on a plane source model

In this model the fraction $f$ leached at time $t$ (d) is given by [1]

$$ f = \frac{\sum a_n}{A_o} = \frac{2S \sqrt{D_e t_n}}{V \sqrt{\pi}} \tag{1} $$

where $\Sigma a_n$ is the cumulative fraction leached of contaminant for each leaching period, $A_o$ is the initial amount of contaminant in the sample, $V$ is the volume of sample (cm$^3$), $S$ is the exposed
surface area of the sample (cm²), \( t_n \) the duration of leachant renewal period (d) and \( D_e \) is the diffusion coefficient (cm² d⁻¹).

The results may also be expressed by the cumulative fraction of the contaminant. Leach test results are plotted as the cumulative fraction of contaminant leached from the samples as a function of the square root of total leaching time:

\[
\frac{\sum \phi_i}{A_o} \text{ versus } \sqrt{\sum t_i} \quad (2)
\]

If the model is applicable a plot of \( \Sigma \phi_i/A_o \) versus \( \sqrt{\Sigma t_i} \) is a straight line and the diffusion coefficient \( D_e \) is given by:

\[
D_e = \frac{2}{m} \frac{V}{S} \quad (3)
\]

where \( m = (\Sigma \phi_i/A_o) (1/\Sigma t_i) \) is the slope of the straight line (d⁻¹/₂).

### 2.2 Method II: Rate equation for coupled diffusion and simultaneous first-order reaction

In this model, the rate equation is:

\[
\frac{\partial C}{\partial t} = D_e \left( \frac{\partial^2 C}{\partial x^2} \right) + g(C) \quad (4)
\]

Here, the special case where \( g(C) \) is directly proportional to the concentration \( C \), i.e. a first-order reaction was considered. The initial and boundary conditions are,

\[
t = 0, x > 0, C = C_0 \quad (5)
\]

\[
t = 0, x < 0, C = 0 \quad (6)
\]

\[
t > 0, x = 0, C = 0 \quad (7)
\]

From this, the fraction leached from a specimen having a surface area \( S \) (cm²) and volume \( V \) (cm³) is

\[
f = (S/V) \int_0^t D_e/k \left[ (kt+1/2) \text{erf} \left( \sqrt{kt} \right) + \sqrt{kt} \exp(-kt) \right] \quad (8)
\]

Where \( k \) is the rate constant of the first-order reaction and \( \text{erf}(z) = \left( 2/\sqrt{\pi} \right) \int_0^z \exp(-z^2) \, dz \)

### 2.3 Method III: Polynomial equation

The orthogonal polynomial is one of the most useful empirical equations. Its general form is:

\[
y(x) = \sum_{i=1}^n A_i \phi_i(x) \quad (10)
\]

where:

- \( A_i \) is the parameter to be determined, and
- \( \phi_i(x) \) is a function of \( x \). Here, \( \phi_i(x) \) - is taken as \( t^{1/2} \), and the leaching fraction is given by

\[
f = \sum_{i=1}^n A_i \, t^{1/2} \quad (11)
\]

To simplify the mathematical treatment, a five terms polynomial of the form

\[
f = A_0 + A_1 \, t^{1/2} + A_2 \, t^{3/2} + A_3 \, t^2 + A_4 \, t^3 \quad (12)
\]

was fitted to the leaching data. For this type of model, extrapolation to longer term leaching is not advisable since the arbitrary constants do not necessarily have any physical significance.

### III. PREPARATION OF SAMPLE FOR LEACHING TEST

The grout samples were prepared from a standard Portland cement. The cement was mixed with saturated wet non radioactive mix exchange resins (Lewatit S 100), additive-bentonite clay(63% SiO₂; 18% Al₂O₃; 4% Fe₂O₃; 2.6% MgO and 3.3% CaO). and water with artificial radioactivity of \(^{137}\)Cs, \( A_o = 60 \text{kBq} \), in the reason to simulate radioactive spent ion exchange resins. Mixing time was about ten minutes. The mixtures were cast into 50 mm diameter cylindrical molds with a height of 50 mm, which were then sealed and cured for 28 days prior to the leaching experiments. Leaching of \(^{137}\)Cs was studied using the method recommended by the IAEA,[1] The duration of leachant renewal period was 30 days. More then 100 different formulations of grout form were examined to optimize their mechanical and sorption properties. In this paper, we discuss four representative formulations. Grout composition formulas are shown in Table 1.

| Table I GROUT COMPOSITIONS (CALCULATED AS GRAMS FOR 1000 CM³ OF SAMPLES) |
|-----------------|------|------|------|------|
| Materials (g)   | G₁   | G₂   | G₃   | G₄   |
| Mix bead ion exchange resins | 315  | 325  | 330  | 340  |
| Portland cement  | 1445 | 1450 | 1485 | 1500 |
| Water with artificial radioactivity* | 250  | 260  | 280  | 300  |
| Bentonite       | 72   | 58   | 45   | 30   |
| (% of cement)   | 5%   | 4%   | 3%   | 2%   |

*artificial radioactivity of \(^{137}\)Cs, \( A_o = 60 \text{kBq} \), in each sample

### IV. RESULTS

Experimental data show the fractions of \(^{137}\)Cs leached from grout composite as a function of the square root of the leaching period. The linear relation between \( f \) and \( t \) is not observed throughout the test period. From the application of Method I to the leaching data we obtained:

\[
f(G_1) = 4.30 \times 10^{-1} t^{1/2} + 6.40 \times 10^9
\]

\[
f(G_2) = 4.80 \times 10^{-1} t^{1/2} + 6.92 \times 10^9
\]

\[
f(G_3) = 5.20 \times 10^{-1} t^{1/2} + 7.90 \times 10^9
\]

\[
f(G_4) = 6.60 \times 10^{-1} t^{1/2} + 9.20 \times 10^9
\]

The diffusion coefficients predicted by Method I are:

\[
D_e(G_1) = 4.20 \times 10^{-6} \text{ cm²/d}
\]

\[
D_e(G_2) = 4.80 \times 10^{-6} \text{ cm²/d}
\]

\[
D_e(G_3) = 7.10 \times 10^{-6} \text{ cm²/d}
\]

\[
D_e(G_4) = 8.70 \times 10^{-6} \text{ cm²/d}
\]

Method II was applied to the leaching data to obtain the unknown parameters \( D_e \) and \( k \). From this we obtained:

\[
D_e(G_1) = 2.70 \times 10^{-6} \text{ cm²/d}
\]

\[
D_e(G_2) = 3.90 \times 10^{-6} \text{ cm²/d}
\]
I. Plecas (Institute for Nuclear Sciences, Belgrade), S. Dimovic (Belgrade University, Chemical Engineering Faculty), and I. K. V. Jovanović (Institute for Nuclear Sciences, Belgrade) investigated the immobilization of radionuclides in concrete matrix using cement composites. They analyzed the leaching of cesium-137 from cement composites as a function of the square root of the leaching period [2,3,4,5]. In the data for cement composite as a matrix, linearity between \( f \) and \( t \) (d) is not observed throughout the time tested; however, there are two different linearities before and after a leaching time of about 10 days. The slope of the linear relation for the early stage is larger than for the latter one. This change in the leaching rate may be associated with the fact that, as the leaching time elapsed, the diffusion rate would gradually slow down as the diffusion path becomes longer [2,3]. Method I cannot describe the whole leaching process, but it is very convenient to simulate leaching over a long period because of its simplicity. Despite the very complex numerical treatment required, the fit obtained using Method II is no better than that obtained using Method I. Although Method I, is very similar to Method III, Method III provides the best approximation over the whole leaching period. In many cases, however, the leaching mechanisms are unknown and, therefore, it is convenient to use polynomial approximation. The results presented in this paper, give values that are similar to those reported in [6].

The solidification technique of spent mix bead (anion and cation) exchange resins is satisfied by cement immobilization. Finally, the results presented in this paper will define the design of our future engineered trenches disposal system for radioactive waste.

V. CONCLUSION

Results are presented in Fig. 1 and 2 which shows the fraction of \( ^{137}\text{Cs} \) leached from cement composites as a function of the square root of leaching period [2,3,4,5]. In the data for cement

\[
D_{30}(G_1) = 4.30 \times 10^{-6} \text{ (cm}^2/\text{d})
\]

\[
D_{30}(G_2) = 4.40 \times 10^{-8} + 3.85 \times 10^{-4} t^{1/2} + 3.24 \times 10^{-8} t + 7.45 \times 10^{-12} t^{3/2}
\]

\[
f_{\text{III}}(G_1) = 4.40 \times 10^{-8} + 3.85 \times 10^{-4} t^{1/2} + 3.24 \times 10^{-8} t + 7.45 \times 10^{-12} t^{3/2}
\]

\[
f_{\text{III}}(G_2) = 4.40 \times 10^{-8} + 3.85 \times 10^{-4} t^{1/2} + 3.24 \times 10^{-8} t + 7.45 \times 10^{-12} t^{3/2}
\]

\[
f_{\text{III}}(G_3) = 3.70 \times 10^{-8} + 5.95 \times 10^{-4} t^{1/2} + 4.50 \times 10^{-8} t + 8.15 \times 10^{-12} t^{3/2}
\]

\[
f_{\text{III}}(G_4) = 3.01 \times 10^{-8} + 6.65 \times 10^{-4} t^{1/2} + 5.44 \times 10^{-8} t + 9.22 \times 10^{-12} t^{3/2}
\]

\[
f_{\text{III}}(G_5) = 2.41 \times 10^{-8} + 8.45 \times 10^{-4} t^{1/2} + 7.63 \times 10^{-8} t + 9.95 \times 10^{-12} t^{3/2}
\]

\[
f_{\text{III}}(G_6) = 1.01 \times 10^{-8} + 8.45 \times 10^{-4} t^{1/2} + 7.63 \times 10^{-8} t + 9.95 \times 10^{-12} t^{3/2}
\]

Fig. 1 and Fig. 2 present plots of \( f \) against \( t \) (d) for leaching of \( ^{137}\text{Cs} \) from the four grout samples, for Methods I and Method III.

\[\text{Fig.1 } \quad \text{Plot of } f \text{ against } t \text{ (d) for leaching of radionuclides from concrete (Method I)}\]

\[\text{Fig.2 } \quad \text{Plot of } f_{\text{III}} \text{ against } t \text{ (d) for leaching of radionuclides from concrete (Method III)}\]

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