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

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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 (or other) waste 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 harmless. 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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Ion exchange resins may be used most successfully for the removal of radioactive and stable ions from dilute solutions. Ion exchange resins are polymers with cross-linking (connections between long carbon chains in a polymer). The resin has active groups in the form of electrically charged sites. At these sites ions of opposite charge are attracted but may be replaced by other ions depending on their relative concentrations and affinities for the sites. Spent mix bead exchange resins containing ^{60}Co and ^{137}Cs, represent a major portion of the solid radioactive waste in nuclear technology.[1,2,3,4,5]

Cement is used as a solidification material for the storage of intermediate-level radioactive waste. However, the retention of cesium, in the cement matrix is negligible. The sorption of cesium on cement is low and diffusivity of cesium in the hydrated cement is high. Only when the cement is mixed with a material having a significant sorption capacity, normally bead or powdered ion exchange resins, is the leachability of cesium and cobalt from the cement matrix low enough to be acceptable. Although cement has several unfavorable characteristics as a solidifying material, i.e. low volume reduction and relatively high leachability, it possesses many practical advantages: good mechanical characteristics, low cost, easy operation and radiation and thermal stability. It is generally assumed that the cement leachability of ^{137}Cs and other radionuclides can be reduced by adding minerals like bentonite, vermiculite and zeolite.[6,7]. The leaching process consists of physico-chemical phenomena, in which diffusion is anticipated to play an important role. Accordingly the IAEA suggested that the diffusion coefficient (leach coefficient) might be used for inter-comparison of leaching data.

At the "Vinca" Institute of Nuclear Sciences, a promising composite for the solidification of radioactive wastes has been developed. Leaching of ^{137}Cs from this material was studied using the method recommended by the IAEA [1]

II. Theoretical Methods

Three methods are compared with respect to their applicability to experimental leaching data [2,3,4,5,6]

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]

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

where Σa_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 (cm^2), t_n the duration of leachant renewal period (d) and D_e is the diffusion coefficient ($cm^2\ d^{-1}$)
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:

$$\frac{\sum a_n}{A_o} \text{ versus } \sqrt{\sum t_n} \tag{2}$$

If the model is applicable a plot of $\Sigma a_n/A_o$ versus $\sqrt{\Sigma t_n}$ is a straight line and the diffusion coefficient D_e is given by:

$$D_e = \frac{\pi}{4} m^2 \frac{V^2}{S^2} \tag{3}$$

where
$m=(\Sigma a_n/A_o)(1/\sqrt{\Sigma t})$,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:

$$\frac{\partial C}{\partial t} = D_e(\partial^2 C/\partial X^2) + g(C) \tag{4}$$

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,

$$t = 0,\ \alpha > x > 0, C = C_o \tag{5}$$

$$t = 0,\ x < 0, C = 0 \tag{6}$$

$$t > 0,\ x = 0, C = 0 \tag{7}$$

From this, the fraction leached from a specimen having a surface area S(cm^2) and volume V(cm^3) is

$$f = (S/V)\sqrt{D_e/k}\,[(kt+1/2)\,\mathrm{erf}\sqrt{kt} + \sqrt{kt/\pi}\,\exp(-kt)] \tag{8}$$

Where k is the rate constant of the first-order reaction and

$$erf(u) = (2/\sqrt{\pi})\int_o^u \exp(-z^2)\,dz \tag{9}$$

2.3 Method III: Polynomial equation
The orthogonal polynomial is one of the most useful empirical equations. Its general form is:

$$y(x) = \sum_{i=1}^{n} A_i\, \phi_i(x) \tag{10}$$

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

$$f = \sum_{i=1}^{n} A_i\, t^{1/2} \tag{11}$$

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

$$f = A_0 + A_1 \mathbf{t}^{1/2} + A_2\mathbf{t} + A_3\mathbf{t}^{3/2} + A_4\mathbf{t}^2 \tag{12}$$

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 bead exchange resins (Lewatit S 100), additive-bentonite clay(63% SiO_2 ; 18% Al_2O_3 ; 4% Fe_2O_3 ; 2,6% MgO and 3,3% CaO). and water with artificial radioactivity of ^{137}Cs, $A_{o=}$ 60(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 CM^3 OF SAMPLES)

Materials (g)	G_1	G_2	G_3	G_4
Mix bead ion exchange resins	315	325	330	340
Portland cement	1445	1450	1485	1500
Water with artificial radioactivity*	250	260	280	300
Bentonite (% of cement)	72 5%	58 4%	45 3%	30 2%

*artificial radioactivity of ^{137} Cs, $A_{o=}$60(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:

$$f_I(G_1) = 4{,}30\ 10^{-5}\,t^{1/2} + 6{,}40\ 10^{-9}$$
$$f_I(G_2) = 4{,}80\ 10^{-5}\,t^{1/2} + 6{,}92\ 10^{-9}$$
$$f_I(G_3) = 5{,}20\ 10^{-5}\,t^{1/2} + 7{,}90\ 10^{-9}$$
$$f_I(G_4) = 6{,}60\ 10^{-5}\,t^{1/2} + 9{,}20\ 10^{-9}$$

The diffusion coefficients predicted by Method I are:

$$D_I(G_1) = 4{,}20\ 10^{-6}\ (cm^2/d)$$
$$D_I(G_2) = 4{,}80\ 10^{-6}\ (cm^2/d)$$
$$D_I(G_3) = 7{,}10\ 10^{-6}\ (cm^2/d)$$
$$D_I(G_4) = 8{,}70\ 10^{-6}\ (cm^2/d)$$

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

$$D_{II}(G_1) = 2{,}70\ 10^{-6}\ (cm^2/d)$$
$$D_{II}(G_2) = 3{,}90\ 10^{-6}\ (cm^2/d)$$

$$D_{II}(G_3)=4{,}30\ 10^{-6}\ (cm^2/d)$$
$$D_{II}(G_4)=6{,}40\ 10^{-6}\ (cm^2/d)$$

Using the least squares procedure, Method III yielded:

$f_{III}(G_1) = 4{,}40\ 10^{-8}+3.85\ 10^{-4}\ \mathbf{t}^{1/2} +3{,}24\ 10^{-8}\ \mathbf{t}+7{,}45\ 10^{-12}\ \mathbf{t}^{3/2}+4{,}80\ 10^{-6}\ \mathbf{t}^2$

$f_{III}(G_2) = 3{,}70\ 10^{-8}+5.95\ 10^{-4}\ \mathbf{t}^{1/2} +4{,}50\ 10^{-8}\ \mathbf{t}+8{,}15\ 10^{-12}\ \mathbf{t}^{3/2}+5{,}85\ 10^{-6}\ \mathbf{t}^2$

$f_{III}(G_3) = 3{,}01\ 10^{-8}+6.65\ 10^{-4}\ \mathbf{t}^{1/2} +5{,}44\ 10^{-8}\ \mathbf{t}+9{,}22\ 10^{-12}\ \mathbf{t}^{3/2}\ 6{,}65\ 10^{-6}\ \mathbf{t}^2$

$f_{III}(G_4) = 2{,}41\ 10^{-8}+8.45\ 10^{-4}\ \mathbf{t}^{1/2} +7{,}63\ 10^{-8}\ \mathbf{t}+9{,}95\ 10^{-12}\ \mathbf{t}^{3/2}\ 7{,}43\ 10^{-6}\ \mathbf{t}^2$

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

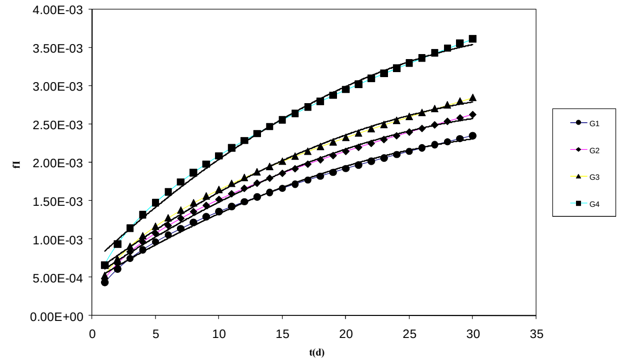

Fig.1 Plot of f_I against **t** (d) for leaching of radionuclides from concrete (Method I)

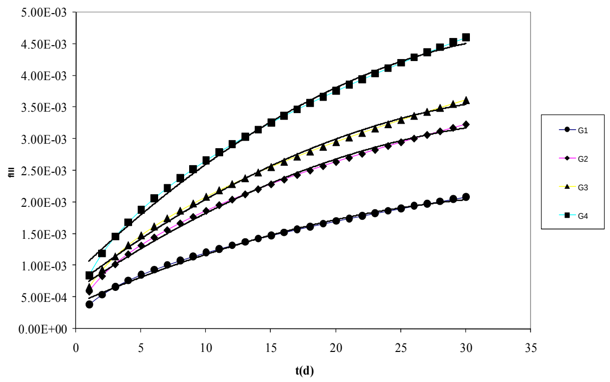

Fig.2 Plot of $fIII$ against **t** (d) for leaching of radionuclides from concrete (Method III)

V. Conclusion

Results are presented in Fig .1 and 2 which shows the fraction of ^{137}Cs leached from cement composites as a function of the square root of 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. Althought 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.

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