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MATHEMATICAL MODELLING OF TRANSPORT PHENOMENA IN CONCRETE MATRIX [†]

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Abstract. *Two fundamental concerns must be addressed when attempting to isolate low-level waste in a disposal facility on land. The first concern is isolating the waste from water, or hydrologic isolation. The second is preventing movement of the radionuclides out of the disposal facility, or radionuclide migration. Particularly, we have investigated the latter modified scenario. To assess the safety for disposal of radioactive waste-concrete composition, the leakage of* ^{60}*Co from a waste composite into a surrounding fluid has been studied. Leakage tests were carried out by original method, developed in Vinca Institute. Transport phenomena involved in the leaching of a radioactive material from a cement composite 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: *radioactive waste, cement, concrete, transport phenomena, leakage rate*

1. INTRODUCTION

Cement and concrete are widely used in low-level waste management both as a means of solidifying waste and for containment of dry or liquid wastes. At present there is also widespread interest in the use of near-surface concrete trench system for the disposal of radioactive waste materials. Typical concrete is a mixture of cement, sand, stone aggregate and water in various proportions that together determine the structural properties and tightness of the poured material. Water content is one of the critical parameters and must be carefully controlled during pouring and setting; to a large extent it will determine the porosity of the resulting material.

Engineered barriers are features of the disposal system made or altered by humans during the construction, operation and closure of a repository. Engineered barriers are

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intended to contribute to the overall performance of the disposal system by providing the level of containment required while the waste remains hazardous. In cases where the selected site or geological environment is not ideally suited for disposal, the repository can be heavily engineered so that, for meeting safety targets, reliance is placed primarily on the engineered barriers.

Engineering trenches system provides three biological protection barriers:

1. Mortar for immobilizing the waste and filling the concrete containers (enable its penetration into all cavities of solid radioactive waste and thus fix it permanently; permit no leakage of radionuclides - use of special cement or adsorbers and provide primary biological protection).
2. Concrete container (store and enable transport of low and intermediate level radioactive waste; provide secondary biological protection; provide safe keeping of radioactive waste for about 300 years).
3. Concrete for filling trenches (provide tertiary biological protection and prevent leakage of radionuclides which have penetrated the second barrier).

At the "Vinca" Institute of Nuclear Sciences, a promising composite for engineer trenches system, especially for concrete for filling trenches has been developed. Leakage test for leakage measurements of radionuclides from concrete was studied using the above method [1, 3, 7-9].

2. THEORETICAL METHODS

Three methods are compared with respect to their applicability to experimental leaching data [5-7].

2.1. Method I: Diffusion equation based on a plane source model [5, 7]

In this model the fraction f leached at time t (d):

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

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:

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

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 [5, 7]

In this model, the rate equation is:

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

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:

$$t = (S/V)\sqrt{D/K}\,[(kt+1/2) \bullet erf\sqrt{kt} + \sqrt{kt/\pi}\,\exp(-kt)] \tag{8}$$

Where k(time)$^{-1}$ is the rate constant of the first-order reaction and

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

2.3. Method III: Polynomial equation [5, 7]

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, $\varphi_i(x)$ - is taken as $t^{i/2}$, and the leaching fraction is given by

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

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

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

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.

3. PREPARATION OF SAMPLE FOR LEACHING TEST

More than 100 different formulations of concrete were examined to optimize their mechanical and sorption properties. The concrete samples were prepared with a standard Portland cement PC-20-Z-45 MPa. The concrete composition was mixed with artificial radioactivity of ^{60}Co, A_o=55-67(kBq). 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 ^{60}Co was studied using the method recommended by the IAEA [9]. The duration of leachant renewal period was 30 days. After each leaching period the radioactivity in the leachant was measured using EG&G - ORTEC spectrometry system and software. In this paper we discuss four representative formulations of concrete for filling trenches (T) : T_1, T_2, T_3 and T_4. Composition and initial radioactivity A_0 (B_q) per sample prepared for leakage test, is shown in Table 1.

4. RESULTS

Experimental data show the fractions of ^{60}Co leached from concrete 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:

$$f_I(T_1) = 2.2\cdot10^{-5}\,t^{1/2} + 7.6\cdot10^{-9}$$
$$f_I(T_2) = 3.9\cdot10^{-5}\,t^{1/2} + 5.8\cdot10^{-9}$$
$$f_I(T_3) = 4.4\cdot10^{-5}\,t^{1/2} + 6.3\cdot10^{-9}$$
$$f_I(T_4) = 5.5\cdot10^{-5}\,t^{1/2} + 7.5\cdot10^{-9}$$

The diffusion coefficients predicted by Method I are:

$$D_I(T_1) = 5.5\cdot10^{-6}\ (cm^2/d)$$
$$D_I(T_2) = 5.9\cdot10^{-6}\ (cm^2/d)$$
$$D_I(T_3) = 6.3\cdot10^{-6}\ (cm^2/d)$$
$$D_I(T_4) = 7.8\cdot10^{-6}\ (cm^2/d)$$

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

$$D_{II}(T_1) = 5.55\cdot10^{-6}\ (cm^2/d)$$
$$D_{II}(T_2) = 5.95\cdot10^{-6}\ (cm^2/d)$$
$$D_{II}(T_3) = 4.73\cdot10^{-6}\ (cm^2/d)$$
$$D_{II}(T_4) = 7.70\cdot10^{-6}\ (cm^2/d)$$

Using the least squares procedure, Method III yielded:

$$f_{III}(T_1) = 7.7\cdot10^{-8} + 3.7\cdot10^{-5}\,\mathbf{t}^{1/2} + 5.3\cdot10^{-8}\,\mathbf{t} + 9.5\cdot10^{-12}\,\mathbf{t}^{3/2}$$
$$f_{III}(T_2) = 5.7\cdot10^{-8} + 4.8\cdot10^{-5}\,\mathbf{t}^{1/2} + 6.6\cdot10^{-8}\,\mathbf{t} + 9.4\cdot10^{-12}\,\mathbf{t}^{3/2}$$
$$f_{III}(T_3) = 6.4\cdot10^{-8} + 5.4\cdot10^{-5}\,\mathbf{t}^{1/2} + 6.6\cdot10^{-8}\,\mathbf{t} + 9.7\cdot10^{-12}\,\mathbf{t}^{3/2}$$
$$f_{III}(T_4) = 7.6\cdot10^{-8} + 6.2\cdot10^{-5}\,\mathbf{t}^{1/2} + 9.8\cdot10^{-8}\,\mathbf{t} + 9.7\cdot10^{-12}\,\mathbf{t}^{3/2}$$

Figures 1 and 2 present plots of **f** against **t** for leakage of ^{60}Co through concrete for filling trenches (T) from the four concrete samples, for Methods I and III.

Table 1. Concrete compositions (calculated as grams for 1000 cm^3 of samples)

	Formula			
Materials	T_1	T_2	T_3	T_4
Cement (Portland), g	405	425	440	460
Sand (0-2 mm), g	640	580	680	660
Aggregate (2-4 mm), g	520	510	510	290
Aggregate (4-8 mm), g	430	680	590	870
Water, ml	185	190	210	250
Additive (Super Fluidal), ml	4	4	4	4
Initial activity A_o (kBq) ^{60}Co	Per sample ~60,0			

5. DISCUSSION AND CONCLUSION

The results are presented in Figure 1 and Figure 2, which show the fraction of ^{60}Co leached from cement composites as a function of the square root of the leaching period. In the data for cement composite as a matrix, linearity between f and t (d) is not observed throughout the time tested; however, linearity occurs before and after the leaching time of about 7 - 10 days. The slope of the linear relation for the early stage is larger than that for the latter one. This change in the leaching rate may be associated with the fact that as the leaching time elapses the diffusion rate would gradually slow down as the diffusion path becomes longer. Method I cannot describe the whole leaching process, but it is very convenient to simulate leaching over a long period because of its simplicity. Method II 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. Finally, the results presented in this paper will define the design of our future engineered trenches disposal system for radioactive waste.

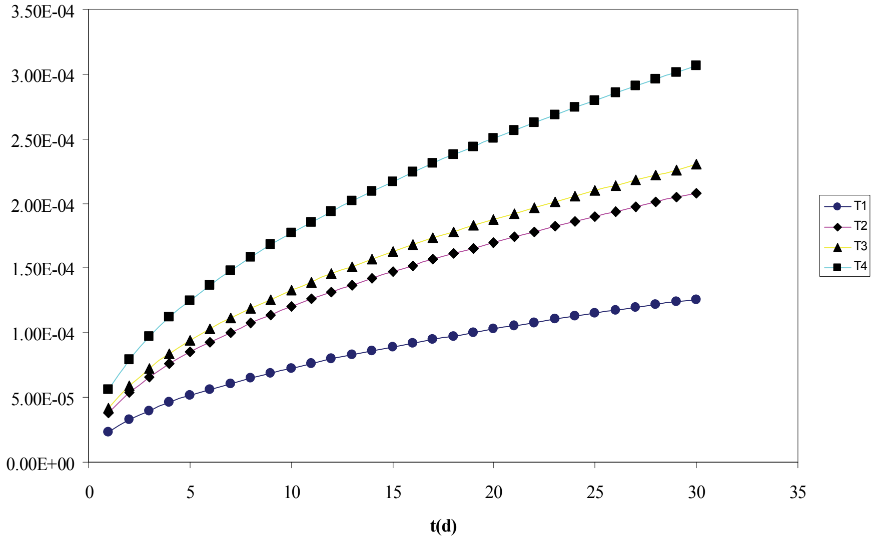

Fig. 1. Plot of **f** against **t** (d) for leakage rate of ^{60}Co from concrete (Method I)

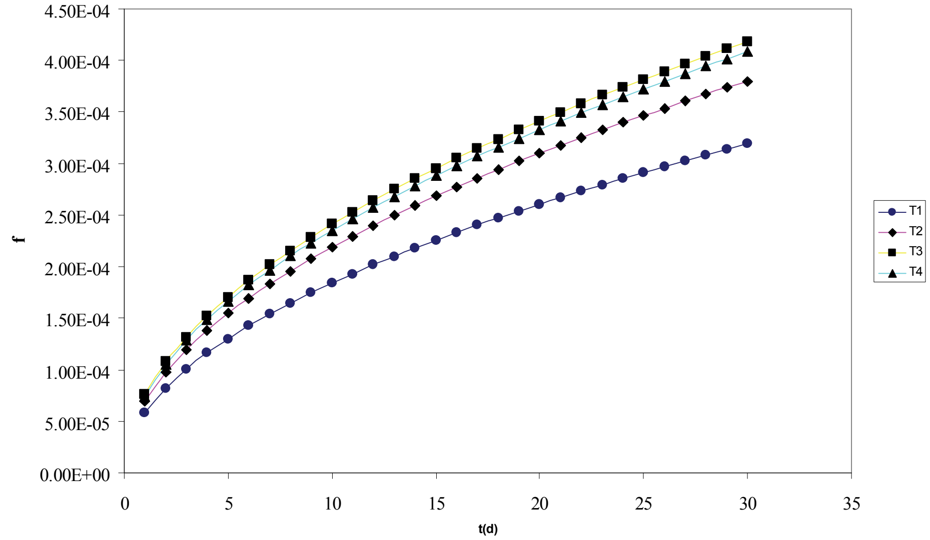

Fig. 2. Plot of **f** against **t** (d) for leakage rate of ^{60}Co from concrete (Method III)

We have also observed that Co^{60} cumulative amount of leached, f, decreased in order f (T_3) > f (T_4) > f (T_1) > f (T_2). Good explanation of this phenomenon is based on sorption properties of sand which amount decreased in the same way [2, 7, 10].

The system of engineered trenches permits secure preservation of radionuclides for more than 300 years in a future Serbian shallow land disposal system, with multiple safety barriers.

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MATEMATIČKO MODELOVANJE TRANSPORTNIH FENOMENA U BETONSKOJ MATRICI

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Postoje dva osnovna problema o kojima je neophodno voditi računa pri odlaganju nisko-radioaktivnog otpada u površinska odlagališta. Pre svega, potrebno je zaštititi otpad od vode, tj. izvršiti hidro-izolaciju. Zatim, neophodno je sprečiti izluživanje radionuklida iz odlagališta, tj. onemogućiti njihovu migraciju. U ovom radu je razmatrana problematika vezana za migraciju radionuklida. Da bi se utvrdio uticaj sastava betona na nivo bezbednosti pri odlaganju radioaktivnog otpada, proučavano je izluživanje ^{60}*Co. Izluživanje je praćeno košišćenjem originalne metode razvijene u Institutu Vinča. Transportni fenomeni vezani za izluživanje radioaktivnog materijala iz betonske matrice proučavani su korišćenjem tri teorijska modela bazirana na difuzionoj jednačina, kuplovanoj difuzionoj sa jednačinom za reakciju prvog reda, kao i empirijskoj polinomnoj jednačini. Rezultati obvde prezentovani su deo 25-godišnjeg rada na pripremi projekta za izgradnje trajnog odlagališta radioaktivnog otpada u Srbiji.*

Ključne reči: *radioaktivni otpad, cement, beton, transportni fenomeni, brzina izluživanja*