Mathematical Modelling of Immobilization of Radionuclides ^{137}Cs and ^{60}Co in Concrete Matrix

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Abstract: Transport phenomena involved in the leaching of a radioactive material from a cement composite matrix are investigated using an empirical method employing a polynomial equation. To assess the safety for disposal of radioactive waste-cement composition, the leaching of ^{137}Cs and ^{60}Co, from a waste composite into a surrounding fluid has been studied. Leaching tests were carried out in accordance with a method recommended by IAEA. Determination of retardation factors, K_F and coefficients of distribution, k_d, using a simplified mathematical model for analyzing the migration of radionuclides, has been developed. Transport phenomena involved in the leaching of a radioactive material from a cement composite matrix are investigated using an empirical method employing a polynomial equation. In our experiment we have analyzed mechanism of ^{137}Cs and ^{60}Co leaching values during a period of 60 days. Results presented in this paper are examples of values obtained in a 25 year mortar and concrete testing project, which will influence the design of the engineered trenches system for a future central Serbian radioactive waste storage centre.

Keywords: Leaching, retardation factor, immobilization, radioactive waste.

1. INTRODUCTION

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 here the latter modified scenario. Migration of radionuclides may occur when water comes into contact with low-level radioactive waste and carries the radionuclides into the surrounding soil/structure. The radionuclides are likely to migrate more rapidly when coarse-grained deposits, like sand and gravel, exist in the surrounding soil. Keeping water out of trenches reduces radionuclide migration. Disposal of low-level radioactive waste in a liquid form can increase migration of radionuclides away from the disposal facility. Liquid low-level waste has been found to be corrosive and can damage containers in which it is buried. If the liquid waste leaks from its container (concrete), it can migrate from the disposal facility [1].

Concrete is likely to be used in considerable quantities in repository construction for high and low level wastes. The hydrated cement will contact water and generate conditions that constitute a long-term chemical barrier to radionuclide migration as a result of decreased solubility and strong adsorption. The transport rate through engineered barriers is mainly diffusion controlled, but due to the strong sorption behaviour of the materials, the diffusion rate of the radionuclides is much slower than in pure water [1-4].

In order to prevent widespread dispersion of radionuclides into the human environment, the radioactive wastes have been incorporated in several kinds of matrixes. Incorporation of the low and intermediate level waste into cement and concrete has been routinely used [1, 2, 5, 6]. Although cement has several unfavourable characteristics as a solidifying material, i.e. low volume reduction it possesses many practical advantages. Information about the leachability of radionuclides contained in cement-waste composites are necessary to assess their safety for storage for a period long enough to allow the radioactivity to decay to a negligible level and final disposal. The leaching process consists of physicochemical transport phenomena, in which diffusion is anticipated to play an important role, and IAEA therefore suggested that the diffusion coefficient (leach coefficient) might be used for inter-comparison of leaching data [5].

2. RADIONUCLIDE MIGRATION THROUGH POROUS MATERIALS AND MODELLING OF LEACHING PHENOMENA

The dispersion of radionuclides in porous materials, such as grout or concrete, is described using a one dimensional differential model [1-3].

$$D\frac{\partial^2 A}{\partial X^2} - V_V\frac{\partial A}{\partial X} - \left(1+\frac{1-f}{f}\rho_T k_D\right)\frac{\partial A}{\partial t} = 0 \quad (1)$$

or

$$D\frac{\partial^2 A}{\partial X^2} - V_V\frac{\partial A}{\partial X} - K_F\frac{\partial A}{\partial t} = 0 \quad (1')$$

where:

K_F - retardation factor

D - diffusion coefficient (cm^2/d)

A - concentration in liquid (Bq)

X - length (cm)

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V_v - velocity of leachant fluid (cm/d)

f - porosity (=)1

ρ_T - solid density (g/cm^3)

k_d - distribution coefficient (ml/g)

t - time variable (d).

Using Laplace transformation method, Eq. (1') becomes:

$$\frac{A_n}{A_0} = \frac{1}{2}\operatorname{erf} a \left| \sqrt{\frac{V_V X}{4D_e}} \cdot \frac{1-\frac{V_V t}{K_F X}}{\sqrt{\frac{V_V t}{K_F X}}} \right| \tag{2}$$

From which we can calculate a retardation factor, K_F. The coefficient of distribution, k_d, can be calculated:

$$k_d = \frac{(K_F - 1)f}{(1-f)\rho_T}(=)\ \text{(ml/g)} \tag{3}$$

In which: V_v is average linear velocity of flow in the X direction, X is the length, t is the time and A_o are known. A_n and D_e can be determined experimentally using a leaching test procedure [5].

For the interpretation of the results of leach tests, leach coefficient D_e, is used, and it is defined as:

$$D_e = \frac{\pi}{4} m^2 \frac{V^2}{S^2}\ \ (\text{cm}^2/\text{d}) \tag{4}$$

where:

D_e - leach coefficient (diffusion) (cm^2/d) or (cm^2/s);

m - $(\Sigma A_n/A_o)\cdot(1/\sqrt{\Sigma t})$, slope of the straight line (d$^{-1/2}$);

A_o - initial sample activity at time zero (Bq); (Table **1**)

A_n - activity leached out of sample after leaching time t, (Bq);

t - duration of leaching renewal period (d); (1, 2, 3, 4, 5, 6, 7, 15, 30, 60)

V - sample volume (cm^3);

S - sample surface (cm^2).

Table 1. Concrete Compositions (Calculated as Grams for 1000 cm^3 of Concrete)

Materials (g)	Concrete Compositions			
	C_I	C_{II}	C_{III}	C_{IV}
Cement (Portland)	410	420	430	450
Sand, 0-2 mm	840	600	600	470
Granulate,2-4 mm	95	77	77	55
Granulate,4-8 mm	535	565	435	465
Granulate,8-15 mm	490	690	840	920
Water	160	160	160	160
Bentonite Clay	10	10	10	10
Initial Activity A_o(kBq)	Per Sample (95 cm^3)			
^{60}Co		60		
^{137}Cs		65		

The development of a model that takes into account all the leaching phenomena is mathematically very complex and the resultant expression is not likely to have practical application. To overcome this problem, should adopt a semi-empirical method to obtain a model that describes the long-term leaching characteristics of a waste component by polynomial equation [6, 7]. In this model, the cumulative amount of contaminant leached is expressed by:

$$f = A_o + A_1 t^{1/2} + A_2 t \tag{5}$$

where, A_o is a constant representing the immediate dissolution, A_1 is a constant representing the diffusion controlled transport mechanism, and A_2 is a constant representing the long-term kinetically controlled dissolution.

Second partial in equation (5), represent the leach coefficient of transport mechanism, D_e(cm^2/d) [8-11].

3. EXPERIMENTAL

Concrete samples were made of: Portland cement PC-20-Z-45 MPa; Sand fraction 0-2 mm; Granulate 2-4, 4-8 and 8-15 mm; Water and Bentonite clay.

The grout samples were prepared with a standard Portland cement PC-20-Z-45 MPa. The cement was mixed with artificial radioactivity of ^{137}Cs, as $CsNO_3$, A_o = 55-67(kBq), and ^{60}Co, as $Co(NO_3)_2$, A_o = 54- 66 (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 ^{137}Cs and ^{60}Co ^{137} was studied using the method recommended by the IAEA [5]. 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. 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**.

4. RESULTS

The results are obtained after 60 days. Using equation (4), coefficients of diffusion are calculated for four experimental samples. Using equations (2) and (3), retardation factors, K_F, and distribution coefficients, k_d(ml/g) are calculated. Table **2**, gives ^{60}Co and ^{137}Cs, leach coefficients in different concrete samples.

Table 2. Leach Coefficients D_e(cm^2/d) in Different Concrete Samples After 60 Days, Using Eq. (4)

Leach Coefficient	Concrete Compositions			
	C_I	C_{II}	C_{III}	C_{IV}
D_e, ^{60}Co	$3.20\cdot10^{-6}$	$6.20\cdot10^{-6}$	$2.10\cdot10^{-6}$	$5.20\cdot10^{-6}$
D_e, ^{137}Cs	$5.60\cdot10^{-5}$	$8.20\cdot10^{-5}$	$4.60\cdot10^{-5}$	$6.40\cdot10^{-5}$

Table **3**, gives the results of retardation factors, K_F and coefficients of distribution, k_d(ml/g), for four concrete formulations for each radionuclide, during 60 days. In accordance with what previously mentioned, the modelling of the radionuclides transport mechanism have been treated in a simplified way.

Table 3. Retardation Factor K_F and Coefficients of Distribution k_d(ml/g), After 60 days, ρ_T = 2.4 (g/cm^3). f = 0.20-0.35

Retard. Factor	Concrete Compositions			
	C_I	C_{II}	C_{III}	C_{IV}
K_F, ^{60}Co	95.0	100.0	92,0	102.0
k_d, ^{60}Co	6-15	7-16	6-13	7-16
K_F, ^{137}Cs	25	35	13	27
k_d, ^{137}Cs	1-5	6-10	1-5	5-9

Using the least squares procedure, for ^{137}Cs, polynomial equation yielded:

$f(C\text{-}I) = 3{,}20\ 10^{-8}+7.60\ 10^{-5}\ \mathbf{t}^{1/2} +5{,}30\ 10^{-8}\ \mathbf{t}$

$f(C\text{-}II) = 3{,}60\ 10^{-8}+3.20\ 10^{-5}\ \mathbf{t}^{1/2} +4{,}40\ 10^{-8}\mathbf{t}$

$f(C\text{-}III)\ ) = 2{,}30\ 10^{-8}+8.40\ 10^{-5}\ \mathbf{t}^{1/2} +7{,}50\ 10^{-8}\ \mathbf{t}$

$f(C\text{-}IV) = 4{,}30\ 10^{-8}+5.50\ 10^{-5}\ \mathbf{t}^{1/2} +3{,}15\ 10^{-8}\ \mathbf{t}$

Using the least squares procedure, for ^{60}Co, polynomial equation yielded:

$f(C\text{-}I) = 3{,}20\ 10^{-8}+4.50\ 10^{-5}\ \mathbf{t}^{1/2} +7{,}40\ 10^{-8}\ \mathbf{t}$

$f(C\text{-}II) = 9{,}10\ 10^{-8}+1.23\ 10^{-5}\ \mathbf{t}^{1/2} +9{,}50\ 10^{-8}\ \mathbf{t}$

$f(C\text{-}III) = 6{,}30\ 10^{-8}+5.20\ 10^{-5}\ \mathbf{t}^{1/2} +8{,}15\ 10^{-8}\ \mathbf{t}$

$f(C\text{-}IV) = 6{,}10\ 10^{-8}+2.00\ 10^{-5}\ \mathbf{t}^{1/2} +2{,}30\ 10^{-8}\ \mathbf{t}$

Figs. (**1**, **2**), represents plots of f against t ^{for} leaching of ^{137}Cs and ^{60}Co from the four samples.

5. CONCLUSION

The analysis of the results presented in Tables **2** and **3**, shows that the values of retardation factors and coefficients of radionuclides ^{60}Co and ^{137}Cs, are similar to the literature data, and proves that the one-dimensional model can be used for calculating parameters of the migration process. We found very good similarity with leach coefficient, D_e, from our previous work [10, 11]. The results well fitted to semi empirical model proposed by author [7, 9]. A linear regression fitting the experimental results leads to minor influence of variable t, which parameter A_2 is not significant in the linear regression analysis. It was therefore concluded that the dissolution rate was not a controlling factor in any of the leaching intervals. Leaching mechanism can be classified into two general categories: 1) initial wash off and 2) diffusion control. On the basis of parameters A_1 and leaching coefficient D_e [8], in different cement matrix formulations, we have noticed that leaching rate of Cs^{137} > Co^{60} which is matched with other studies [1-4]. We have also observed that Cs^{137} and Co^{60} cumulative amount of leached, f, decreased in order f (C-II) > f (C-IV) > f (C-I) > f (C-III). Good explanation of this phenomenon is based on sorption properties of sand which amount decreased in the same way.

The mathematical analysis (cumulative amount of contaminant leached) of the results presented in Figs. (**1**, **2**), shows that polynomial equations (2), described quite good leaching phenomena of ^{60}Co and ^{137}Cs, and prove that the one-dimensional model can be used for calculating parameters of the migration process.

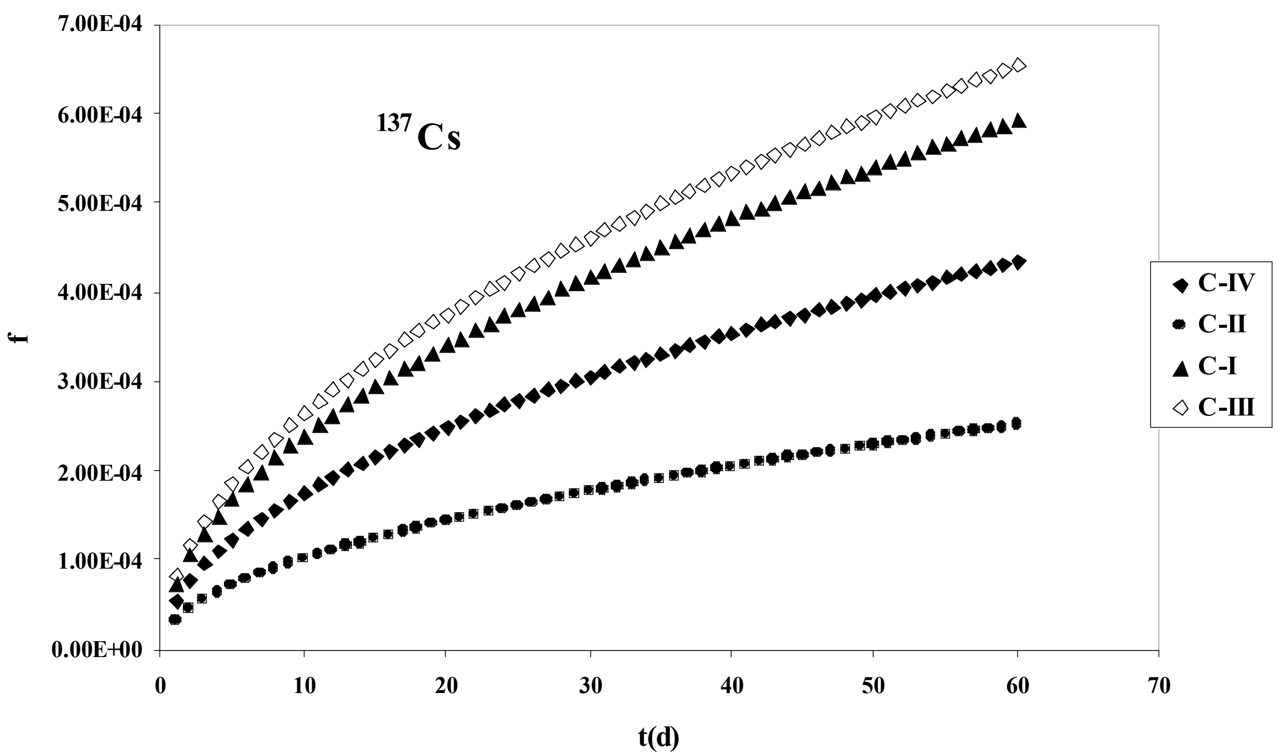

Fig. (1). Plots of f against t for leaching of ^{137}Cs from the four samples.

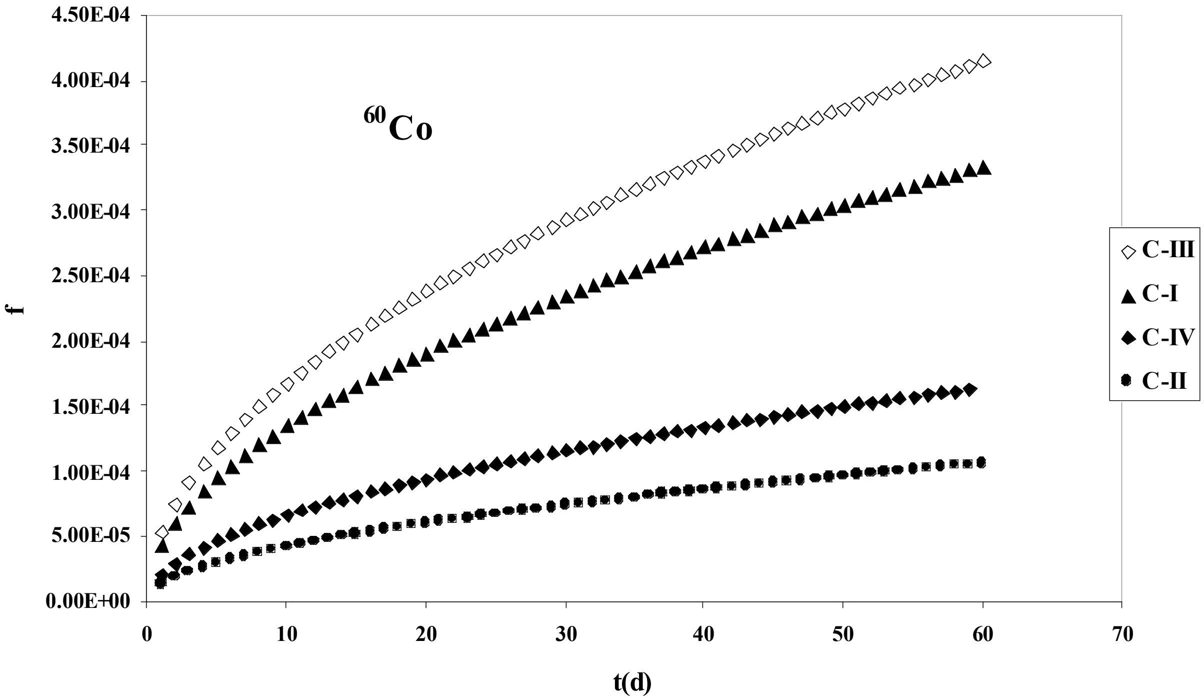

Fig. (2). Plots of f against t for leaching of ^{60}Co from the four samples.

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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