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Leaching kinetics of ^{137}Cs and ^{60}Co radionuclides fixed in cement and cement-based materials

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Abstract

Leach characteristics of ^{137}Cs and ^{60}Co radionuclides from both ordinary Portland cement and cement mixed with two different ratios of silica fume and ilmenite have been studied using International Atomic Energy's (IAEA) standard leach method. A mathematical model has been simulated to predict the release rate of each nuclide from cubic geometry waste matrix and the predicted values are discussed in relation to experimentally observed leach rates to confirm the validity of the proposed mechanism in the model. The effect of temperature on the radionuclides leaching rates was also studied and the effective diffusion coefficients were obtained at different temperatures. The net fractional release of the two radionuclides from different waste forms showed a decreasing pattern as $^{137}Cs > ^{60}Co$, indicating the largest diffusion coefficient for cesium in all waste matrices.

Keywords: Kinetics; Modeling; Radioactive waste; Portland cement; Silica fume

1. Introduction

Cement represents the most known material for solidification of low- and intermediate-level radwastes. The solidified blocks should have adequate characteristics to withstand the operating conditions. Some additives such as blast furnace slag, silica fume and ilmenite [1–5] have been found to be a very effective ingredients of cement-based grout to improve the characteristics of the waste matrix towards the safety requirements.

The disposal of low- and intermediate-level radwaste in shallow land burial is based on encapsulation of these wastes with cement and cement-based materials. Radionuclides can escape from the waste matrix through diffusion migration under water-saturated conditions. Hence, there is considerable interest in understanding the diffusive transport of radionuclides through cement matrix. Several leaching studies [6–8] have been reported using different methods to study the temporal distribution of radionuclides in the leachant medium. However, leaching tests are conducted over short periods of time and the extrapolation of these measured values is therefore subject to large uncertainties. The mathematical modeling is then used to assess the long-term behaviour of embedded radioactive wastes through mechanistic studies and annually radionuclide fraction calculations. Krishnamoorthy et al. [9] proposed an iterative model to simulate the release rates of radionuclides from cylindrical cement blocks. Pescatore [7] derived two leach rate expressions for the diffusive release of radioactive constituents from both cylindrical- and rectangular-shaped waste forms.

In the present study, the International Atomic Energy's (IAEA) standard leach method proposed by Hespe [10] has been employed to study the leach pattern of ^{137}Cs and ^{60}Co radionuclides encountered in low- and intermediate-level radwastes solidified in cement and cement mixed with two different ratios of locally produced silica fume and ilmenite. The leaching of these radioactive materials can be related to the diffusion transport from the cementitious materials. Also, the study is directed to achieve a simple mathematical model, based on diffusion mechanism for cubic geometry waste matrix, to predict the release rate of

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Table 1
Chemical compositions of cement and additives

Chemical composition	Material		
	Ordinary Portland cement	Silica fume	Ilmenite
CaO	61.0	0.2	0.2
SiO_2	21.0	97.0	4.0
Al_2O_3	4.74	0.2	1.07
Fe_2O_3	4.00	0.5	27.0
MgO	2.5	0.5	2.0
K_2O	0.6	0.5	–
SO_3	2.43	0.15	–
Cl	–	0.5	–
H_2O	–	–	–
K_2O+Na_2O	–	–	0.25
TiO_2	–	–	37.0
FeO	–	–	26.0
S	–	–	0.2
P	–	–	0.02

Table 2
Chemical analysis of the ground water

TDS (mg/l)	pH	Soluble cations (ppm)				Soluble anions (ppm)		
		K^+	Na^+	Mg^+	Ca^{++}	Cl^-	SO_4^-	HCO_3^-
1.05	7.2	23	149	13	74	137	317	272

each nuclide from the cement and cement based materials waste forms.

2. Experimental

2.1. Materials

All materials used in this study were locally produced. Their chemical compositions were given in Table 1.

2.2. Static leaching test

Static leaching tests were preformed using ground water solution obtained from Abu Zaabal well no. 202, which is one of the nearest ground water wells to Inshas nuclear site, to study the desorption of ^{137}Cs and ^{60}Co radionuclides from hardened blocks of cement and cement mixed with additives. The chemical analysis of the ground water was given in Table 2.

The IAEA's standard test proposed by Hespe [10] was applied. All prepared samples, cubic moulds $2\times2\times2$ cm^3 dimensions, were stored in laboratory at ambient temperature (25 ± 3 °C) for 28 days curing time. Detailed description of sample preparation is presented in Ref. [11]. Each sample was immersed in beaker containing 25-ml ground water for certain time intervals and 1 ml of leachant was taken, dried and counted. The gamma spectra of studied nuclides were measured using a gamma spectrometer with 4×4 in. NaI crystal activated with thallium. The crystal is connected to a multichannel analyzer. The cumulative leach fraction was calculated according to the following equation,

$$\text{Cumulative leach fraction} = \left(\frac{\sum A(t)}{A_0}\right)\left(\frac{V}{S}\right)$$

where $\sum A(t)$ = cumulative radioactivity leached, A_0 = initial radioactivity present in specimen, V = volume of specimen (cm^3), S = exposed surface area of specimen (cm^2).

3. Mathematical model

Radionuclides from the cement block are transferred to the surrounding water by dissolution to the interstitial water, diffusion through interstitial water to the surface of the cement block and eventual release to the water. Since the geometry of the cement block is well defined, the following equation is used to represent the migration of nuclides from the cubic cement block to the surrounding water:

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial x^2}\right] \tag{1}$$

where C = concentration of radionuclide in cement block (mol/l), D = diffusion coefficient (cm^2/s), x = spatial coordinate in the direction of flow (cm), t = time (s).

The initial and boundary conditions for Eq. (1) are given by:

$$C(x,0) = C_0 \tag{2}$$

$$C(0,t) = 0 \tag{3}$$

$$C(a,t) = 0 \tag{4}$$

Table 3
Physical characteristics of studied specimens

Nuclide	Sample no.	Sample form	S/V (cm^{-1})	W/C	Initial activity (cps)	Leachant volume (ml)	Curing time (days)
^{137}Cs	1	Cement	3.225		29,955		
	2	Cement + 10% S.F.	3.163		239,637		
	3	Cement + 15% S.F.	3.163	0.3	79,879	25	28
	4	Cement + 10% ilmenite	3.183		239,637		
	5	Cement + 15% ilmenite	3.387		79,879		
^{60}Co	1	Cement	3.047		26,320		
	2	Cement + 10% S.F.	3.176		26,320	25	28
	3	Cement + 10% ilmenite	3.052		26,320		

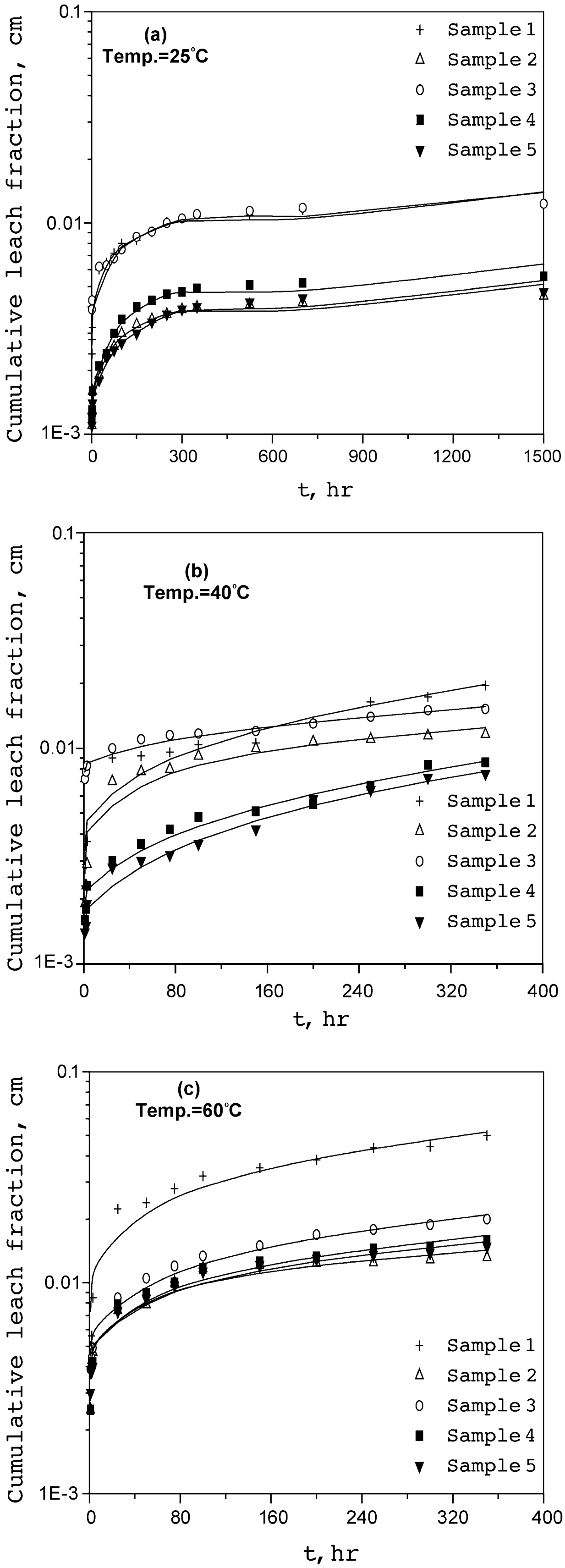

Fig. 1. Cumulative leach fraction of ^{137}Cs for cement and cement mixed with additives at different temperatures.

where C_0 is the initial concentration of radionuclide in the cement block and a is the dimension of the cement block.

Using initial and boundary conditions, the solution for Eq. (1) can be written as:

$$C(x,t) = \sum_{n=1}^{\infty} \frac{2C_0}{\pi} \left[\frac{1+(-1)^{n+1}}{n} \right] \sin \frac{n\pi}{a} x \exp\left[-\frac{Dn^2\pi^2}{a^2} t \right]. \quad (5)$$

The leaching flux $F(t)$ from the surface of the cement block can be evaluated from the relation $F(t) = SD\partial C/\partial x$ at $x = a$ as:

$$F(t) = \frac{2C_{o}SD}{a} \sum_{n=1,3,\ldots}^{\infty} \exp\left[-\frac{Dn^2\pi^2}{a^2} t \right] \quad (6)$$

where S is the surface area of the cement block.

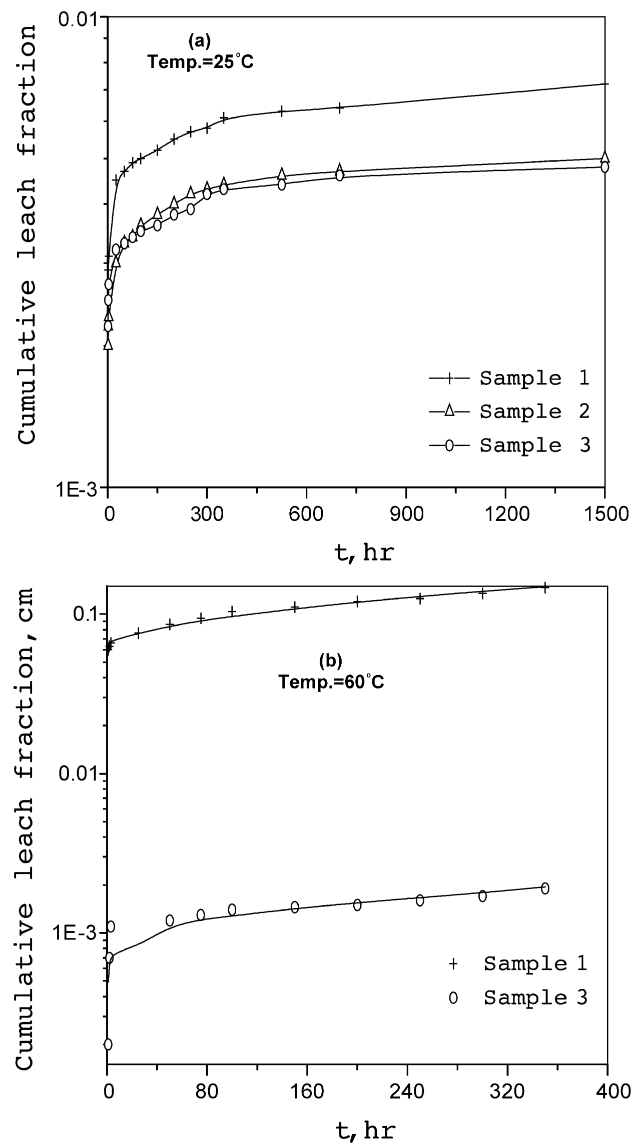

Fig. 2. Cumulative leach fractions of ^{60}Co for cement and cement mixed with additives at different temperatures.

The cumulative radioactivity A (Bq) in the leachant can be evaluated by integrating Eq. (6) with respect to t. Since $C_0 = A_0/V$, where A_0 is the initial radioactivity added to the cement block and V is the volume of the cement block, the fraction of the activity released to the leachant can be obtained as:

$$\frac{A(t)}{A_0} = \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\left[1 - \exp\left(-\frac{Dn^2\pi^2}{a^2}t\right)\right]. \tag{7}$$

4. Results and discussion

4.1. Leaching characteristic of ^{137}Cs and ^{60}Co radionuclides

The shallow land burial waste forms contain fairly high concentrations of short-lived radionuclides and very low concentrations of long-lived radionuclides. Various radionuclides and salts make chemical bondage with cement components, or they exist dispersively in the state of sole crystals in concrete. When the cemented waste forms come in contact with water, the movement of soluble materials from the waste to the surrounding water is caused by dissolution or chemical reaction with chemical components of water. In this study, the radionuclides chosen for the leach test are intended to represent the desorption (leaching) behaviour of some of the typical radionuclides encountered in low-level solid waste forms.

The physical characteristics of the different cementitious block samples along with other relevant parameters are given in Table 3. The variation of cumulative leach fractions of ^{137}Cs radionuclide incorporated in cement and cement mixed with two different ratios (10% and 15%) of locally produced silica fume and ilmenite at different studied temperatures (25–60 ± 3 °C) are depicted in Fig. 1a–c. The results showed that addition of 10% silica fume decreases the leaching rate and this can be attributed to the extreme fineness and high surface area of silica fume, capable of reducing the volume of large pores and capillar-

Table 4
Cumulative leach fractions of ^{137}Cs and ^{60}Co nuclides from cement and cement mixed with silica fume and ilmenite at different temperatures

Nuclide	Sample no.	Material	Cumulative leach fraction $\times 10^{3-}$ (cm)		
			25 ± 3 °C	40 °C	60 °C
^{137}Cs	1	Cement	12.3	19.5	50.0
	2	Cement + 10% S.F.	4.5	11.6	13.2
	3	Cement + 15% S.F.	12.3	15.2	20.0
	4	Cement + 10% ilmenite	5.6	8.6	15.9
	5	Cement + 15% ilmenite	4.7	7.6	14.8
^{60}Co	1	Cement	7.2		11.1
	2	Cement + 10% S.F.	5.0		
	3	Cement + 10% ilmenite	4.8		0.58

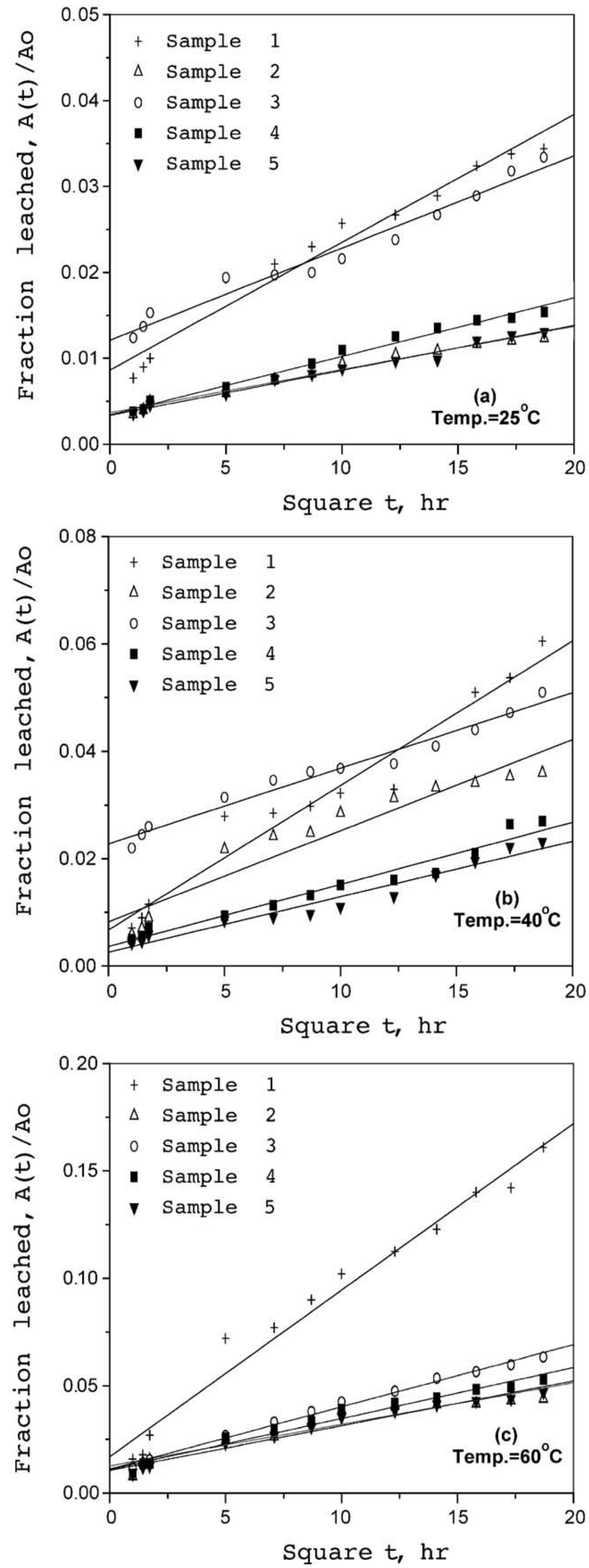

Fig. 3. Variation of fraction leached of ^{137}Cs from cement and cement mixed with additives versus square root leaching time at different temperatures.

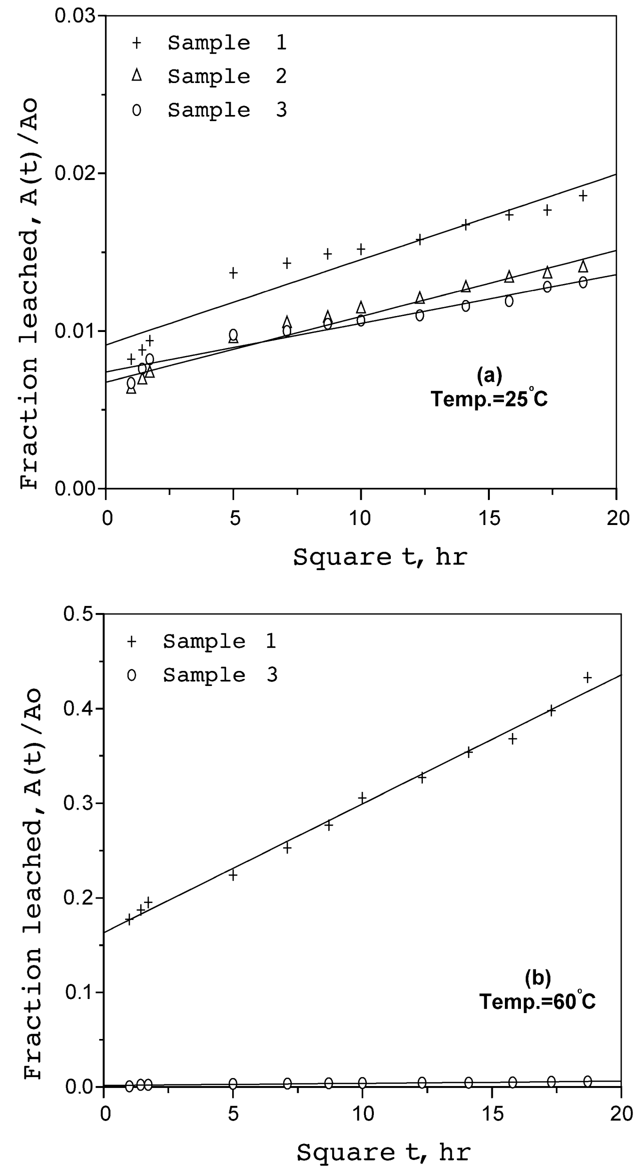

Fig. 4. Variation of fraction leached of ^{60}Co from cement and cement mixed with additives versus square root leaching time at different temperatures.

ies that are normally found in cement pastes and refinement in pore structure [12].

For 15% silica fume, the leaching rate increases due to the high specific surface area of silica fume particles and their tendency to absorb water, which decreases the gel formation and increases the void formation in the matrix. Also, adding of ilmenite up to 15% decreases the leaching rates and this can be explained by the presence of titanium oxide (TiO_2), which forms with water a gelatinous material leading to filling the pores and decreasing the leaching rates.

The results of the leaching rates (cumulative fractions) of ^{60}Co nuclide incorporated in cement and cement mixed with 10% silica fume and 10% ilmenite at two different temperatures (25 and 60 ± 3 °C) are depicted in Fig. 2a–b. These results indicated that all leaching rates are slightly decreased and this may be attributed also to the formation of gel and the reaction between TiO_2 and water, which form a gelatinous material filling the pores. The effect of temperature on the leaching rates of both studied nuclides is clearly shown from the previous results. In all cases, the leaching rate increases with increasing temperature except in the case of ^{60}Co nuclide incorporated in cement mixed with 10% ilmenite. This exception may be due to ionic substitution, in which many ions were involved in the space lattice of illuminate. In such case, ^{60}Co may substitute Ti^{2+} and/or Fe^{2+} at high temperatures resulting in a decrease of leaching rate [13].

Table 4 reported the maximum cumulative leaching fractions of ^{137}Cs and ^{60}Co nuclides incorporated in cement and cement mixed with different ratios of silica fume and ilmenite at different temperatures. The magnitude of the cumulative leach fraction is an index for the release of the nuclide from the cement matrix. In all studied cases, ^{137}Cs have the highest values of cumulative leach fraction than ^{60}Co.

4.2. *Effective diffusion coefficient and thermodynamic parameters*

Leaching is assumed to be a diffusion-controlled process. The mechanism of this diffusion could not be completely studied due to the complex microstructure of composite and the presence of multivariables, which affect the rate of leaching such as matrix composition, temperature, chemical nature of leaching solution, chemical nature of the element diffused out and radiation effects. Several methods are used to measure leaching data and IAEA suggested that diffusion coefficients may be used to compare leaching data [14], where the quantity of radionuclide leached out from a unit surface area during time t_n is given by:

$$A_n = 2A_0 \frac{\sqrt{Dt_n}}{\sqrt{\pi}} \quad (8)$$

where A_n = activity leached out after time t_n (Ci), A_0 = initial activity in the composite (Ci), D = diffusion coefficient ($m^2\ s^{-1}$).

Table 5
Effective diffusion coefficients of ^{137}Cs and ^{60}Co at different temperatures

Nuclide	Sample no.	Effective diffusion coefficient, D (m^2/s)		
		25 ± 3 °C	40 °C	60 °C
^{137}Cs	1	4.6×10^{-7}	1.52×10^{-6}	1.26×10^{-5}
	2	5.7×10^{-8}	6.27×10^{-7}	6.72×10^{-7}
	3	2.6×10^{-7}	4.32×10^{-7}	1.89×10^{-6}
	4	1.02×10^{-7}	2.87×10^{-7}	1.22×10^{-6}
	5	5.4×10^{-8}	2.02×10^{-7}	8.3×10^{-7}
^{60}Co	1	6.9×10^{-8}	5×10^{-7}	4.37×10^{-6}
	2	3.75×10^{-8}		
	3	2.2×10^{-8}	1.8×10^{-8}*	1.1×10^{-8}

* Calculated based on Arrhenius plot.

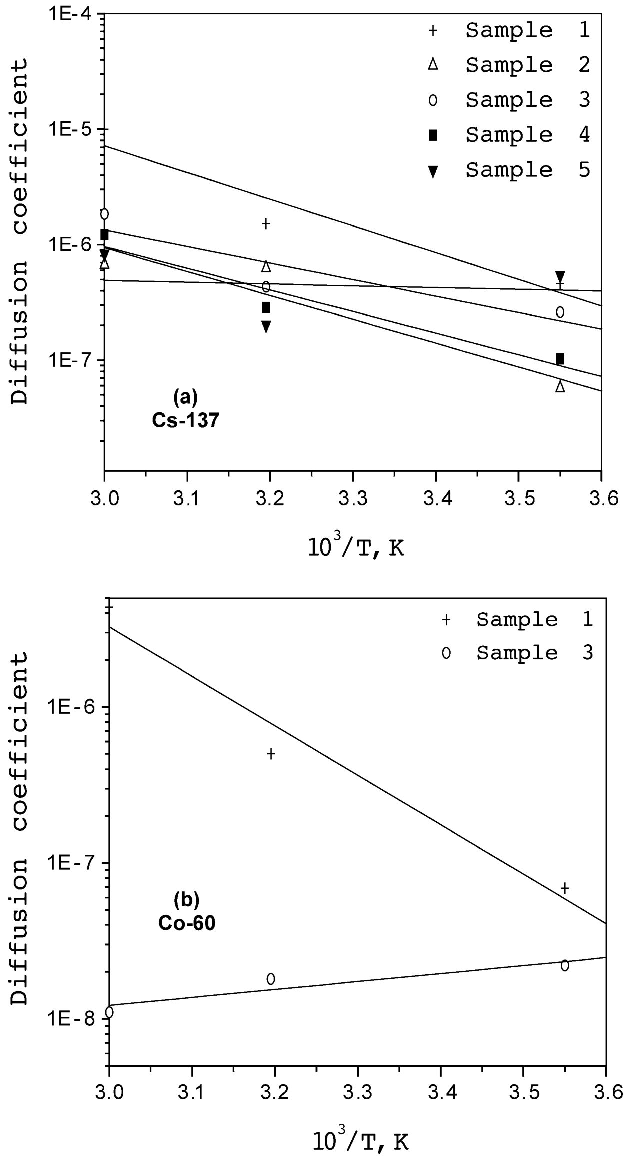

Fig. 5. Arrhenius diagram of ^{137}Cs and ^{60}Co leached from different cement matrices.

From the above equation, the cumulative fraction leached out from the composite can be expressed as:

$$\left[\frac{\sum A_n}{A_0}\right]\left[\frac{S}{V}\right] = \frac{2SA_0(D\sum t_n)^{0.5}}{A_0 V} \tag{9}$$

$$\frac{\sum A_n}{A_0} = 2\left(\frac{S}{V}\right)\left(\frac{D\sum t_n}{\pi}\right)^{0.5} \tag{10}$$

where $\sum A_n$ = cumulative amount of radioactivity leached during cumulative time t_n. Thus, a plot of $[\sum A_n/A_0]$ versus $\sqrt{t_n}$ should give a straight line if D remains constant. The value of D can be calculated from the slope m of the line, i.e.,

$$D = \frac{\pi m^2 V^2}{4S^2}. \tag{11}$$

Figs. 3a–c and 4a–b represent the plotting of the fraction leached of ^{137}Cs and ^{60}Co nuclides from different samples versus square root of leaching time at different studied temperatures, respectively. The calculated diffusion coefficients for both nuclides are presented in Table 5. These data indicated that ^{137}Cs have the largest values of diffusion coefficients in all waste matrices at different temperatures compared to ^{60}Co nuclide.

Energies of activation, E_a, for the leaching process were obtained using the Arrhenius equation:

$$D = D_0 e^{-E_a/RT} \tag{12}$$

where D_0 is the pre-exponential constant and R is the gas constant.

Arrhenius plots for leaching of ^{137}Cs and ^{60}Co are shown in Fig. 5a–b and the calculated values of E_a are presented in Table 6. Such a high values of the leaching activation energy in all cement matrices suggested that the temperature has a great effect on the rate of leaching and the system is controlled by temperature. The Arrhenius equation would be also used to calculate D_0, which in turn is used for the calculation of entropy change, ΔS, of the leaching process using:

$$D_0 = \frac{2.72 d^2 KT}{h} e^{\Delta S/R} \tag{13}$$

where K is the Boltzmann constant, h is the Plank constant, d is the distance between two adjacent sites in cement and T is the absolute temperature.

Assuming that the value of d is equal to 5×10^{-8} cm [11], the calculated values of the entropy change, ΔS, are presented in Table 6. The free energy of the leaching process is also calculated using the relation,

$$\Delta G = E_a - RT - T\Delta S \tag{14}$$

and the calculated values are shown in Table 6. The positive values of G indicated that the reaction occurs in the forward direction and the system does not reach equilibrium.

Table 6
Thermodynamic parameters of studied leaching systems

Nuclide	Sample no.	E_a (kJ/mol)	S (J/mol K)	G (kJ/mol)
^{137}Cs	1	131.6	343.27	26.83
	2	109.94	227.49	39.76
	3	75.87	133.12	33.63
	4	99.49	196.59	38.43
	5	111.24	224.14	41.97
^{60}Co	1	168.71	456	30.35
	2			
	3	− 29.11	− 292.21	55.49

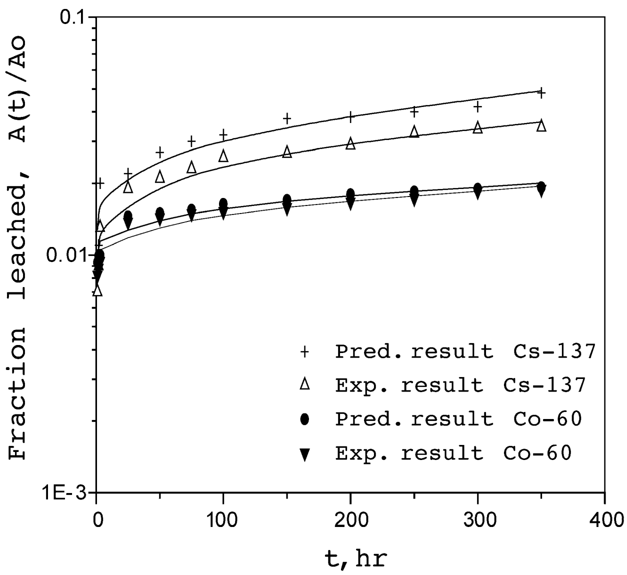

Fig. 6. Experimental and predicted fraction leaching of ^{137}Cs and ^{60}Co from Portland cement matrix (sample no. 1) versus leaching time.

4.3. Prediction of time–profile leach fraction

Temporal profiles of leach fractions of ^{137}Cs and ^{60}Co from Portland cement waste form (sample no. 1) measured under laboratory condition are shown in Fig. 6. The predicted curves by the simulated model (Eq. (7)) using the evaluated diffusion coefficients are also presented in this figure. The simulation gives an acceptable representation of experimental data; thereby demonstrating that the proposed mechanism in the model can represent the leaching kinetics of studied radionuclides from cubic geometry cement matrix. The observed difference in data can be related to the discrepancies in calculating the diffusion coefficients. The obtained results, in all studied leaching tests, indicated an initial fast leaching during the first period followed by slow leaching in the subsequent periods. This behaviour suggests the presence of two different values of diffusion coefficient for the fast and slow components. Further work is under investigation to rectify this model.

5. Conclusion

The addition of silica fume and ilmenite to cement affects the characteristics of waste form towards the safety requirements. The leaching tests of ^{137}Cs and ^{60}Co radionuclides represent the leaching behaviour of some of the typical radionuclides encountered in low-level solid waste forms. The obtained results showed that the addition of 0–15% silica fume and ilmenite to cement decreases the leaching rate of each nuclide at different studied temperatures and suggested a rapid release of radioactivity in the beginning (fast component) followed by slow release for long periods of time (slow component). The simulation model gives an acceptable representation of the experimental data.

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