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Modeling the long-term leaching behavior of ^{137}Cs, ^{60}Co, and ^{152,154}Eu radionuclides from cement–clay matrices

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Abstract

Leaching characteristics of some radionuclides that are commonly encountered in radioactive waste streams from immobilized waste matrices in different cement–clay grouts have been assessed to investigate the influence of the clay additives on the leaching behavior of the solid waste matrices. The International Atomic Energy's Agency (IAEA) standard leach method has been employed to study the leach pattern of ^{137}Cs, ^{60}Co, and ^{152,154}Eu radionuclides immobilized in ordinary Portland cement (OPC), OPC–bentonite, and OPC–red clay grouts. The examination of the leaching data revealed that adding clays to OPC reduces the leach pattern as OPC–bentonite < OPC–red clay < OPC for all studied radionuclides. The controlling leaching mechanism has been found to be diffusion and the mean apparent diffusion coefficients and leachability indices have been calculated for the studied waste matrices. Simplified analytical models have been derived to predict the cumulative leach fraction (CLF) of radionuclides over the studied experimental period. These simplified research models could be used as a screening tool to assess the performance of the waste matrix under repository conditions.

Keywords: Radioactive wastes; Cement grouts; Leaching mechanism; Diffusion coefficients; Mathematical models

1. Introduction

In Egypt, low and intermediate level radioactive wastes are produced during research activities of the radiochemical laboratories, research reactors, radioisotope and metallurgical laboratories, activation analysis units, nuclear medicine divisions in hospitals, universities and research institutes as well as industrial activities [1]. The treatment of these wastes is needed to produce a waste product suitable for long-term storage and disposal. Chemical precipitation, coagulation, ion exchange and evaporation processes are used as treatment techniques at Inshas radioactive waste treatment plant. The process flow sheet of this plant is illustrated in Fig. 1 [2]. The chemical treatment processes are achieved at high pH (>9) using either ferric sulphate or zinc sulphate for the removal of ^{60}Co and ^{152,154}Eu, where ^{137}Cs is removed using hexa cyanocobalt ferrate. The produced sludge and/or concentrate is immobilized in cement grout matrices, then poured in 200 L steel drums or in one cubic meter concrete containers. The solidified waste matrices are then transported to be disposed at shallow land disposal facility. These wastes must be structurally stable to ensure that they does not degrade and/or promote slumping, collapse or other failure. Chemical and physical immobilizations provide the required structural stability and minimize the contaminant migration [3].

Immobilization techniques consist of entrapping the contaminant within a solid matrix, i.e. cement, cement-based material, glass, or ceramic. Despite the existence of several disadvantages in the utilization of cement immobilization technique such as its low volume reduction and relatively high leachability, the choice of this technique has been worldwide employed for the immobilization of low and intermediate level radioactive wastes because of its compatibility with aqueous waste streams, capability of activated several chemical and physical immobilization mechanisms for a wide range of inorganic waste species [4–6]. Also, cement immobilization possesses good mechanical characteristics, radiation and thermal stability, simple operational conditions, availability, and low cost.

Reported studies on leaching of lanthanides, actinides, and alkali metals from cement waste matrices confirm that the solubility of the lanthanides and actinides are low, while alkali

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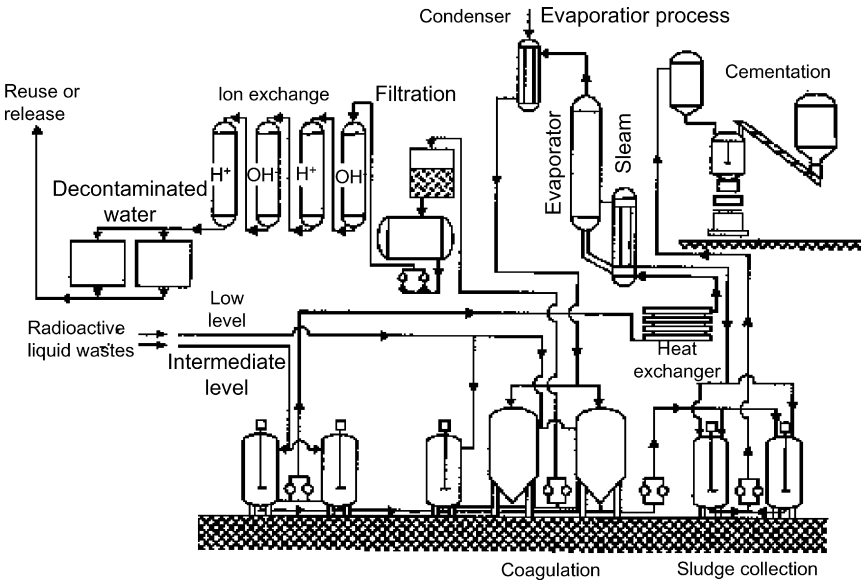

Fig. 1. Process flow sheet of Inshas liquid radioactive waste treatment plant.

metals remain substantially soluble in the high pH environment of the hydrated cement [6–9]. Recently, an extensive array of leaching studies has been addressed to reduce the leachability of different radionuclides from immobilized waste matrices by mixing the cement with different materials having significant sorption capacity such as fly ash, silica fume, ilmenite, blast furnace slag, kaolin, and zeolites [10–22]. These additives were utilized either to enhance the compressive strength of the grout mixture or increase its resistibility to leaching. It was found that adding these mixing materials could increase the resistibility of the studied waste matrices to the leaching of different radionuclides, e.g. ^{137}Cs, ^{60}Co, and ^{90}Sr. Also, the sportive behavior of different alkali radionuclides and europium, as a model for trivalent actinides, has been investigated on bentonite [23–25]. It was found that the sorption of these radionuclides on bentonite is an increasing function of pH.

In the present work, natural local clays known with their high sorptivity have been investigated to determine their efficiency as cement-based materials and to evaluate the effects of their addition on the leaching properties of the immobilized waste matrix. In this concern, the International Atomic Energy's (IAEA) standard leach method has been employed to study the leach pattern of ^{137}Cs, ^{60}Co, and ^{152,154}Eu radionuclides immobilized in OPC, OPC–bentonite, and OPC–red clay. Cumulative leach fractions, diffusion coefficients and leachability indices of all radionuclides were determined using diffusion release models.

2. Experimental

2.1. Materials

OPC was provided from Seuz Cement Company, Seuz, Egypt and its chemical composition is given in Table 1. The clay minerals used were obtained form natural deposits in Aswan, Upper Egypt, and the dried radioactive waste sludge samples were collected from the Egyptian low and intermediate level radioactive waste treatment plant. The chemical compositions of these natural clay minerals were also given in Table 1. The BET surface area of the solid powder, measured after the thermal treatment for 2 h at 473 K, were 25.13 and 20.63 m^2/g for bentonite and red clay, respectively.

2.2. Preparation of specimens

2.2.1. Mixing

Cement clay based matrices were prepared by mixing the OPC with different weights of clay minerals ranged from 5 to 20 wt.% at water/cement (w/c) ratio of 0.4. The required amount of cement was placed on a smooth non-absorbent surface, and a crater was formed in the center. The required amount of mixing water was poured into the crater by the aid of a trowel. The mixing operation was then completed by continuous vigorous mixing using a helix grout mixer at a 1500-rpm speed for duration of 4 min. At the end of mixing, paste was directly poured into moulds.

2.2.2. Moulding and curing

Polyethylene cylindrical shape moulds with internal height/diameter ratio of 1.0 (3.0 cm diameter and height) was

Table 1
Chemical composition of cement and additives

Chemical composition	OPC	Bentonite	Red clay
SiO_2	20	62.9	62.9
Al_2O_3	6.0	19.6	24.7
Fe_2O_3	2.1	2.25	3.3
FeO	0.9	0.32	0.8
MgO	1.5	3.05	1.16
CaO	63	2.68	1.2
Na_2O	0.5	5.53	0.9
Others	6.0	13.67	5.04

used to prepare cement pastes [13,21,26]. Paste was placed in the moulds in two approximately equal layers. Each layer was compacted and passed along the surface of the moulds until homogenous specimen was obtained. After the top layer was compacted, the moulds was then vibrated for 2 min to remove any air bubbles and to have a better compaction of the paste and even the top surface of the mould was smoothed by the aid of thin edged trowel. Immediately after moulding, moulds were kept in air for 24 h. The moulds were demoulded and were cured during 28 days in a humid atmosphere (100% RH) at 25 ± 2 °C.

The compressive strength of the cured cement based matrices were measured using a load compressive strength machine, it was found that the compressive strength of the solidified matrices have the highest value for the matrices that contained 10 wt.% clay addition. This result is compatible with the former obtained by Osmanlioglu [13].

2.3. Static leaching test

The IAEA standard leach test was applied to determine the leaching characteristic of the ^{137}Cs, ^{60}Co, and ^{152,154}Eu radionuclides from the solidified waste [27]. The waste matrices, as prepared above, were immersed in beaker containing 300 mL-distilled water. Leachant was exchanged and analyzed for radioactivity daily during the first week, and then after every week for 1 month and from therefore a month till 90 days. The ratio of leachant volume to the total exposed surface area of the specimen was always kept constant at 10 cm [28,29]. The samples were analyzed using gamma spectrometer with 2 in. × 2 in. sodium iodide (NaI) crystal activated with thallium. The crystal was connected to a multi-channel analyzer which had 256 channels attached with preamplifier. The equipment was manufactured by the Nuclear Excellence in Nuclear Instrumentation, Model 800A. All the leachate analyses were carried out on duplicate matrices at room temperature 25 ± 2 °C. The CLF (cm) was calculated according to the following equation:

$$\mathrm{CLF} = \left(\frac{\Sigma A(t)}{A_0}\right)\left(\frac{V}{S}\right) \quad (1)$$

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

3. Results and discussion

3.1. Leaching charachterisitcs of ^{137}Cs, ^{60}Co, and ^{152,154}Eu radionuclides

The objective of performing the IAEA standard leach method is to measure the CLF that represents the leaching rate of some radionuclides of potential concern from immobilized waste matrix under continuously saturated conditions that represents the worst case. The result of this method is used to estimate the intrinsic mass transfer parameters such as the apparent diffusivity of the studied radionuclides, which are used in conjunction with mathematical models to estimate the long-term leaching behavior.

The influence of natural clay additives on the CLF of ^{137}Cs, ^{60}Co, and ^{152,154}Eu from the studied immobilized waste matrices are depicted in Fig. 2. The examination of this figure indicates that:

(a) The CLF is less than 5% for each of the studied cases.
(b) The addition of 10% of natural clays decrease the CLF for the studied radionuclides, and this can be attributed to the low porosity of these additives that can reduce the overall porosity of the waste matrix when compared with that of plain cement matrix and also to the high sorption capacity of those natural clays for the studied radionuclides [18–20].
(c) The CLF from OPC–bentonite waste matrix is lower than that from OPC–red clay and this may be related to the higher sorption capacity of bentonite, towards all the studied radionuclides, than red clay.
(d) ^{152,154}Eu has the smallest leachability; this can be attributed to the low solubility of lanthanides and actinides in the high pH environment of the hydrated cement. On the other hand, ^{137}Cs has the highest leachability because of its low field strength that keeps it substantially soluble in the high pH environment [8–10].

Various leaching studies assessed the effect of different additives on the leachability of ^{137}Cs from cement based matrices, a comparison between the performance of these matrices and the OPC–bentonite, and OPC–red clay matrices could be held by comparing the CLF of ^{137}Cs measured after 90 days in a static leach test using distilled water. It was found that the CLF (cm) from OPC–bentonite and OPC–red clay matrices are lower than that of OPC–zeolite (0.012) and OPC–tobermorite (0.014) [19,30].

3.2. Controlling leaching mechanism

In general, any leaching phenomena from cementitious material can be explained as a combination of the diffusion and dissolution mechanisms. Various studies in the literature, divide the leaching phenomena into three regions [19,21,30]. The first is controlled by the rapid release of dissolved soluble materials that exists on the surface of the waste matrix, which is known as surface wash-off. Following surface wash-off, the material release is controlled by diffusion through the pore space of the waste matrix. At the last region, the slow portion of dissolution control the leaching phenomena, in this case, the dissolution of materials from the surface proceeds faster that the diffusion through the pores. Both the rapid and slow portion of dissolution will result in the release of highly soluble materials but it will not cause depletion of material. The examination of the plot of incremental leach fractions form the studied immobilized waste matrices loaded by ^{137}Cs, ^{60}Co, and ^{152,154}Eu expressed as cm/day on log scale versus time (Fig. 3), indicate that the leaching pattern can be divided into two regions. Region I shows initial rapid release of radionuclides within the first 5 days, then a drastic reduction in the release take place over a longer period of time. From this figure, it is clear that the leaching of the studied radionuclides

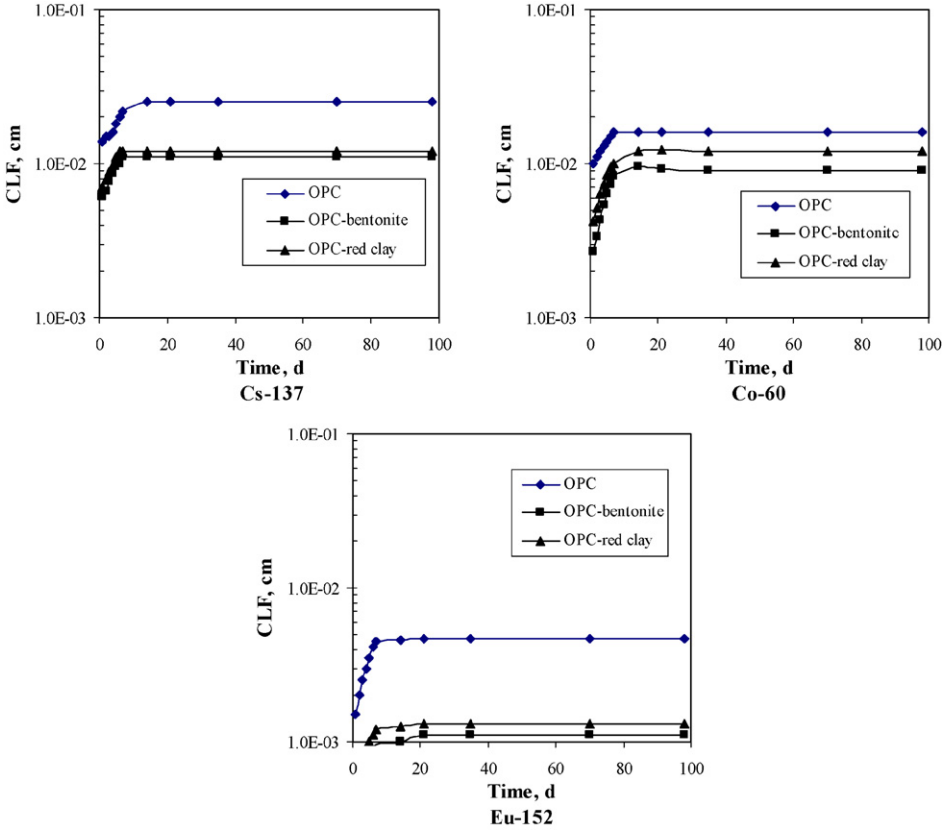

Fig. 2. Cumulative leach fractions of ^{137}Cs, ^{60}Co, and ^{152,154}Eu radionuclides from plain OPC, OPC–bentonite and OPC–red clay waste matrices.

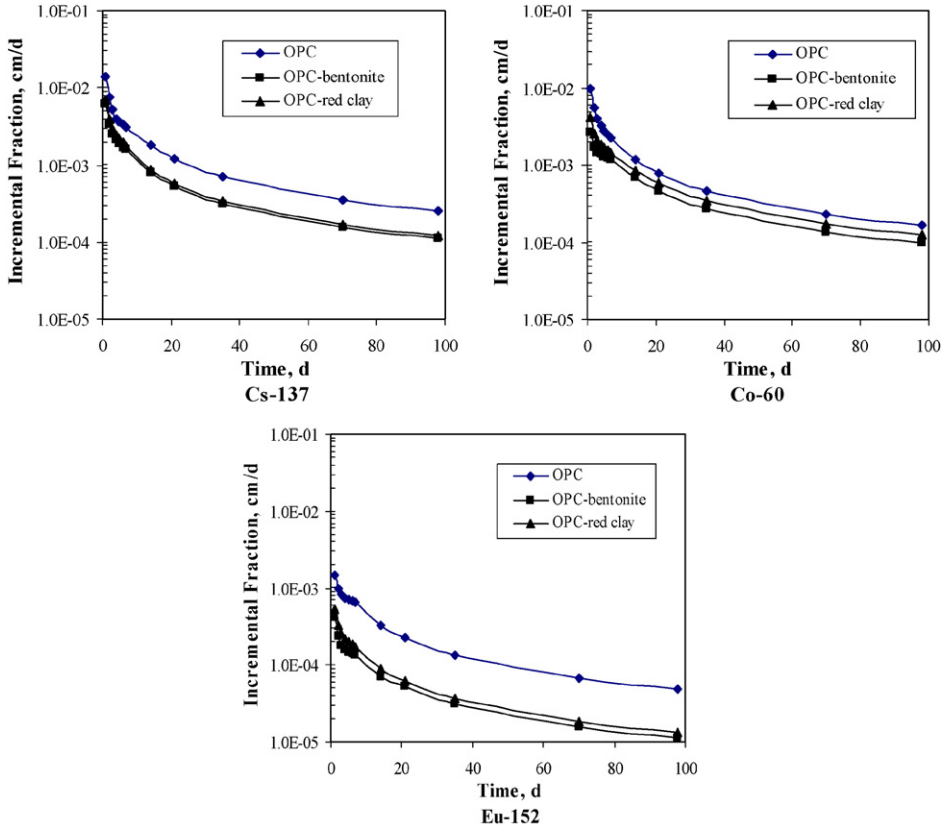

Fig. 3. Incremental leach fraction of ^{137}Cs, ^{60}Co, and ^{152,154}Eu radionuclides from immobilized cement matrices as a function of time.

Table 2
Slope of the linear regression of log(CLF) vs. log(time) in the second region (5–90 days)

Radionuclide	OPC	OPC–red clay	OPC–bentonite
Cs-137	0.35	0.36	0.38
Co-60	0.37	0.43	0.44
Eu-152,154	0.40	0.49	0.51

is due to surface wash-off and diffusion, where the slow portion of dissolution did not take place.

The determination of the controlling leaching mechanism could be conducted based on the slope of the linear regression of the logarithm of CLF versus the logarithm of time. If the slope is less than 0.35 the controlling leaching mechanism will be the surface wash-off, for the slope values ranging from 0.35 to 0.65 the controlling mechanism will be the diffusion, and higher slope values represent the dissolution mechanism [31]. To eliminate interpretative errors in the analysis due to the surface wash off mechanism, the initial leached fraction has been excluded. The result of the linear regression in the second region (5–90 days) is listed in Table 2, it is clearly shown that the slop values lies between 0.35 and 0.65 which indicate that the diffusion is the controlling leaching mechanism for all studied cases.

3.3. Apparent diffusion coefficient

As revealed from the previous sections, the leaching of ^{137}Cs, ^{60}Co, and ^{152,154}Eu radionuclides from the studied immobilized waste matrices are controlled by the diffusion mechanism. To assess the long-term leaching behavior of these radionuclides, the apparent diffusion coefficient has been determined based on the solution of Fick's second law in semi-infinite medium, which gives the relative concentration as follows:

$$\frac{C}{C_0} = erf\left(\frac{x}{2\sqrt{Dt}}\right) \tag{2}$$

The flux of the diffusing materials through the matrix is given by Fick's first law:

$$J(t) = -D\left.\frac{\partial C}{\partial x}\right|_{x=0} = -C_0\sqrt{\frac{D}{\pi t}} \tag{3}$$

The leached activity from a unit surface area during time t is expressed by

$$A_n(t) = \int_0^t J(t)\ \mathrm{d}t = 2A_0\sqrt{\frac{Dt}{\pi}} \tag{4}$$

where A_n is the activity leached out after time t_n (Bq), A_0 the initial activity in the composite (Bq), and D is the diffusion coefficient (cm^2/s).

From the above equation, the CLF out from the waste matrix can be expressed as

$$\frac{\sum A_n}{A_0} = 2\left(\frac{S}{V}\right)\sqrt{\frac{Dt}{\pi}} \tag{5}$$

Table 3
Mean apparent diffusion coeffecient of ^{137}Cs, ^{60}Co, and ^{152,154}Eu through the studied matrices (cm^2/s)

Radionuclide	OPC	OPC–red clay	OPC–bentonite
Cs-137	3.1×10^{-9}	2.6×10^{-11}	1.8×10^{-12}
Co-60	1.4×10^{-9}	1.0×10^{-11}	6.6×10^{-12}
Eu-152,154	1.44×10^{-11}	8.6×10^{-14}	8.6×10^{-14}

where ΣA_n is the cumulative amount of radioactivity leached during cumulative time t_n.

The value of the apparent diffusion coefficient (D) can be calculated from the slope (m) of the straight line of the plot of $[\Sigma A_n/A_0]$ versus $(t_n)^{1/2}$, i.e.

$$D = \pi\left(\frac{mV}{2S}\right)^2 \tag{6}$$

Fig. 4 represents the plotting of the fraction leached of ^{137}Cs, ^{60}Co, and ^{152,154}Eu from studied matrices versus square root of leaching time. As can be seen from these plots, for all studied leaching cases, the results indicated an initial fast leaching during the first period followed by slow leaching in the subsequent periods. This behavior suggests the presence of two different values of diffusion coefficient for the fast and slow components.

This approach in determining the apparent diffusion coefficient is valid for leached fraction less than 20%. The mean apparent diffusion coefficients calculated using Eq. (6) for the slow component was obtained by conducting a linear regression analysis between $(\Sigma A_n/A_0)$ and the square root of time in the period form 5 to 90 days. The obtained values of the mean apparent diffusion coefficients are listed in Table 3. From these data, it was found that the diffusion coefficient values of the studied radionuclides were significantly reduced upon the addition of both bentonite and red clay. The diffusion coefficients values generally range from 10^{-5} cm^2/s for very mobile species to 10^{-15} cm^2/s for immobile species [31]. Therefore, it could be concluded that the mobility of the studied radionuclides in OPC–bentonite matrices showed a decrease of two to three order of magnitude compared to that of plain OPC matrices.

The leachability index is a material parameter of the leachability of diffusing species, which used to catalogue the efficiency of a matrix material to solidify a waste and is given by [10,29]:

$$L = -\log(D) \tag{7}$$

The value of 6 is the threshold to accept a given matrix as adequate for the immobilization of radioactive wastes. As it is shown in Table 4, the mean leachability indices for all radionuclides in all studied matrices are in the range from 8.57 to 13.06, which exceed the value of 6. These values indicated that all studied

Table 4
Mean lecahability index of ^{137}Cs, ^{60}Co, and ^{152,154}Eu

Radionuclide	OPC	OPC–red clay	OPC–bentonie
Cs-137	8.57	11.55	11.74
Co-60	8.85	10.98	11.17
Eu-152,154	9.84	13.06	13.06

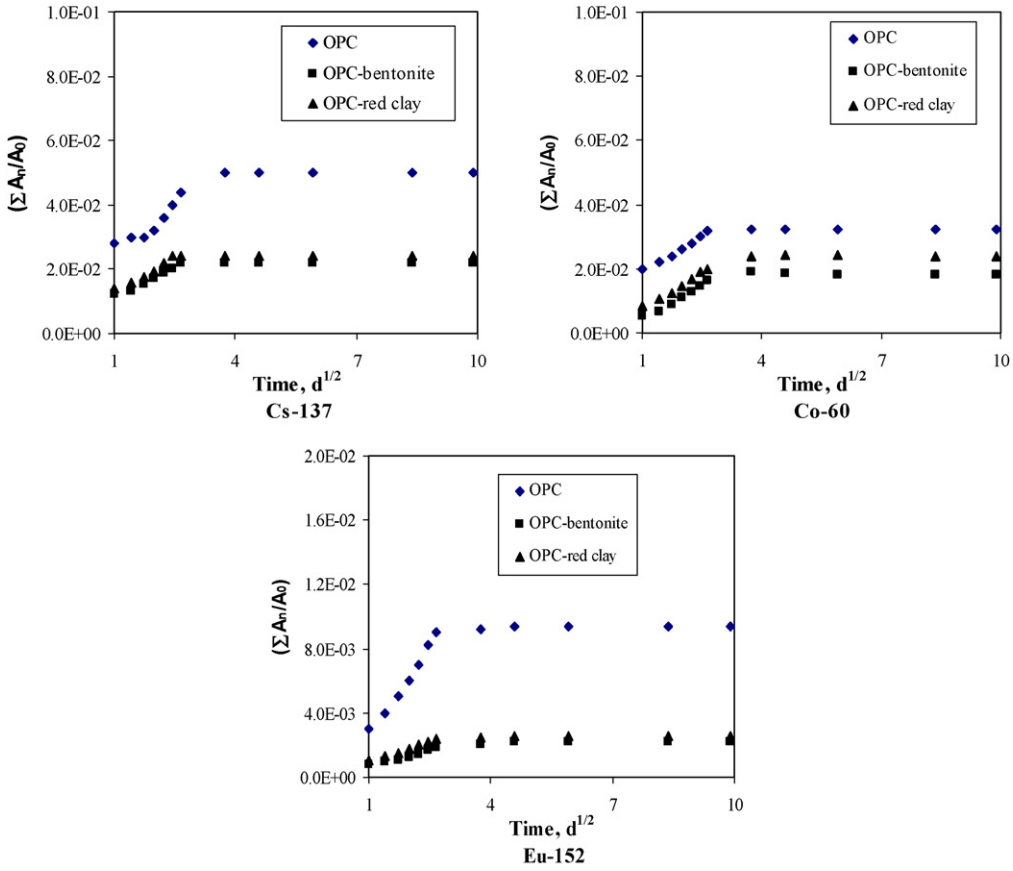

Fig. 4. Variation of fraction leached of ^{137}Cs, ^{60}Co, and ^{152,154}Eu radionuclides from different cement based matrices vs. square root of time.

OPC matrices, especially OPC–bentonite, can be catalogued as efficient materials for immobilizing cesium from radioactive wastes.

4. Long-term leaching behavior modeling

Mathematical models are being developed and used to assess the radiological safety implications of buried solidified radioactive wastes. The modeling efforts in this safety assessment can be divided to research (process) and assessment modeling. Research models are used in conjunction with laboratory and field experiments to understand, quantify and rank which is the most important processes that take place in a subsystem, i.e. waste matrix, engineering barrier, geosphere, or biosphere. Where in assessment modeling, the important processes are linked together to predict the overall performance of the disposal system or of sub-systems [2]. The aim from this section is to derive simple screening mathematical tools that could be utilized to compare the release of radionuclides from solidified waste matrices and check the validity of these derived models to simulate the complicated leaching phenomena.

4.1. Conceptual model development

The planned Egyptian disposal facility consists of a reinforced concrete closed vault covered with a one-layer cover and placed above the groundwater table so that any fluctuation in the groundwater table will not lead to the penetration of water into the facility (Fig. 5a). The solidified waste matrices placed in labeled steal containers will be placed in the concrete vaults, and it is planed to backfill the vault with a mixture of bentonite and crushed rock [2,32,33]. In order to optimize the most suitable composition between the studied matrices, it is assumed that bare cylindrical waste matrices are placed in the facility without backfill, to eliminate the delay and retardation effects of the container and backfill on the radionuclide transport. The penetration of water into the facility is assumed to occur due to percolation of rainfall through the one-layer after the degradation of the reinforced concrete cap due to cracks resulting from the thermal stress (freeze/thaw cycles), corrosion of reinforcement, sulfate attack, alkali aggregate reaction, and water leaching (Fig. 5b). The amount of percolating water inside the disposal vault is assumed to be large enough to attain the saturation after the water penetration.

4.2. Mathematical model development

There are several models to study the leaching behavior of radionuclides from solid waste matrices [33–39]. Simplified one and two-dimensional analytical leaching models that are corrected to consider the decay based on internal diffusion controlled kinetics have been developed. For a leaching system consists of a finite cylinder, Fick's second law gives the leaching

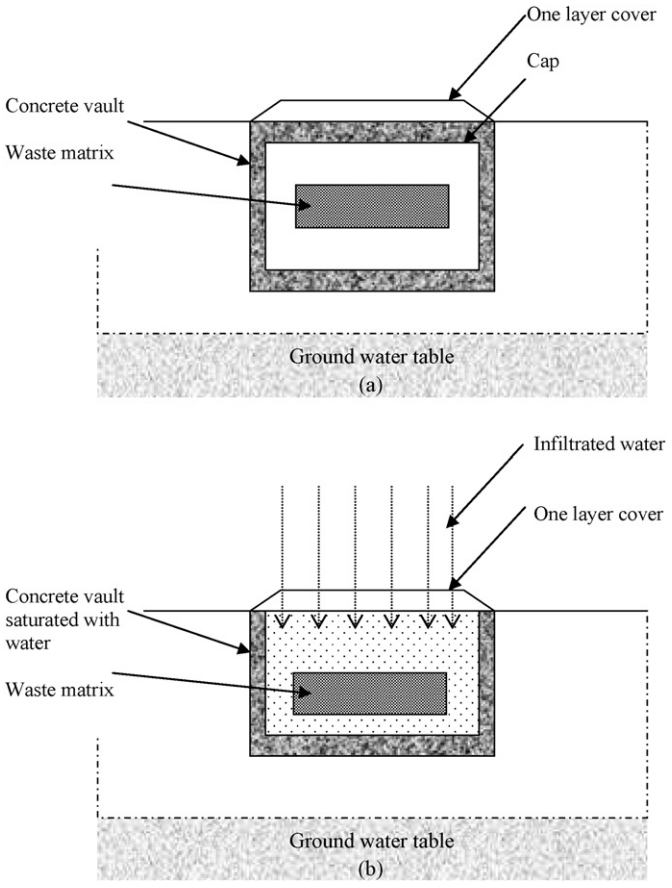

Fig. 5. Conceptual model of the studied disposal vault (a) no water penetration and (b) water infiltration into the disposal vault.

rate as follow:

$$\frac{\partial C}{\partial t} = D\nabla^2 C - \lambda C,$$

$$\text{for one-dimension}: \quad \nabla^2 = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right), \quad 0 \le r \le R,$$

$$\text{for two-dimension}: \quad \nabla^2 = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{\partial^2}{\partial z^2},$$

$$0 \le r \le R, \ \ 0 \le z \le H \tag{8}$$

where C is concentration of radionuclides in the waste matrix (Bq/cm^3), D the apparent diffusion coefficient (cm^2/year), r the radial distance from the center of the matrix (cm), z the axial distance from the bottom of the matrix (cm), and λ is the decay constant (year^{-1}).

Assuming that, the radionuclides are uniformly dispersed through the immobilized waste matrix on the macroscopic view, and the matrix is surrounded by semi-infinite leachant liquid having a homogenous composition. Also, given that the mass transfer external to the waste matrix is faster than the internal transfer in the matrix, the initial and boundary conditions can be written as following:

$$\text{for one-dimension}: \quad C(r,t) = C_0,$$

$$\text{for two-dimension}: \quad C(r,z,t) = C_0, \quad t = 0 \tag{9}$$

$$\text{for one-dimension}: \quad C(R,t) = 0,$$

$$\text{for two-dimension}: \quad C(R,\ z,t) = 0, \quad t > 0 \tag{10}$$

$$\text{For two-dimension}: \quad C(r,H,\ t) = 0, \quad t > 0 \tag{11}$$

where C_0 is the initial concentration of radionuclides in the waste matrix, R the radius of the cylinder (cm), and H is the height of the cylinder (cm).

4.2.1. One-dimensional leaching model

The amount of radionuclide leached from cylindrical waste matrix without considering the decay of radionuclides is given in various studies as follow [12]:

$$\frac{A(t)}{A_0} = \sum_{m=1}^{\infty} \frac{2R}{\alpha_m^2} J_0(k_m r)\ \ \exp[-(Dk_m^2 t)] \tag{12}$$

This analytical expression is valid as long as the time framework for conducting the leaching simulation is short compared with the radionuclide half-life.

The one-dimensional analytical expression for the amount of radionuclide leached from cylindrical waste matrix corrected for the decay can be derived as follow.

The solution of Eq. (8) that satisfies the initial condition (Eq. (9)) and the boundary condition (Eq. (10)) could be obtained using the separation of variables method. The distribution of the radionuclide concentration within the waste matrix can be written as:

$$C(r,t) = \sum_{m=1}^{\infty} A_m J_0(k_m r)\ \ \exp[-((Dk_m^2 + \lambda)t)] \tag{13}$$

where A_m are the coefficient of the concentration function, J_0 the first kind of Bessel functions of order 0, and k_m are the roots of $J_0(\alpha) = 0$ divided by the radius of the waste matrix. Using the initial condition (Eq. (9)) and the orthogonality properties of Bessel function, C_0 can be expended in Bessel function, the coefficients A_m are given by:

$$A_m = \sum_{m=1}^{\infty} \frac{2C_0}{\alpha_m R J_1(\alpha_m)}$$

where J_1 is the first kind of Bessel functions of order 1, and α_n are the roots of first kind of Bessel function of order zero ($J_0(\alpha) = 0$). The leaching flux $F(t)$ from the surface of the waste matrix can be evaluated as follow:

$$F(t) = -SD\left(\frac{\partial C}{\partial r}\right)\Big|_{r=R} = \frac{2C_0 SD}{R} \sum_{m=1}^{\infty} \exp[-((D\,k_m^2 + \lambda)t)] \tag{14}$$

where S is the surface area of the cement block. And $C_0 = A_0/V$, where A_0 is the initial radioactivity added to the waste matrix, and V is the volume of the waste matrix

The cumulative radioactivity, A (Bq) in the surrounding water can be evaluated by integrating the leaching flux (Eq. (14)) with respect to time. By assuming that the waste matrix will be intact

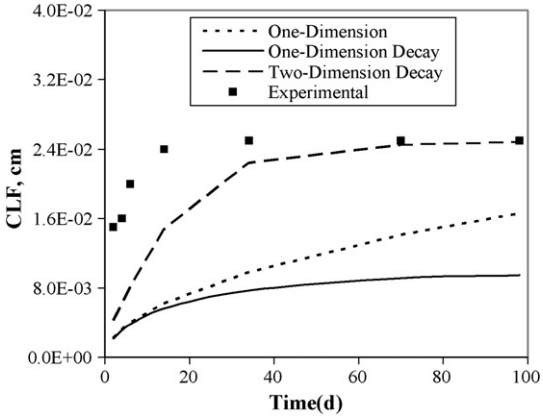

Fig. 6. Comparison between the experimental and predicted values of the temporal CLF of ^{137}Cs from OPC waste matrix.

in terms of shape over the duration of radionuclide release process, *S*/*V* ratio will has a constant value. Amount of radionuclide leached from cylindrical waste matrix to the surrounding water can be obtained as

$$\frac{A(t)}{A_0} = \sum_{m=1}^{\infty} \frac{2}{R} \left(\frac{1}{k_m^2 + \lambda/D} \right) [1 - \exp(-(Dk_m^2 + \lambda)t)] \quad (15)$$

4.2.2. Two-dimensional leaching model

Using the boundary conditions, the solution for Eq. (8) in two-dimensional coordinates can be written as follows:

$$C(r,t) = \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} A_{nm} J_0(k_m r) \ \sin(l_n z) \ \exp[-(D\eta_{nm}^2 + \lambda)t)],$$

$$k_m = \frac{\alpha_m}{R}, \ \ l_n = \frac{n\pi}{H}, \ \ \eta_{mn}^2 = \left(\frac{n\pi}{H}\right)^2 + \left(\frac{\alpha_m}{R}\right)^2 \quad (16)$$

where A_{nm} are the coefficient of the concentration function, J_0 is the first kind of Bessel functions of order zero.

Using the initial condition (9) and the orthogonal characteristics of Bessel function C_0 can be expended in Bessel function, the coefficients A_m are given by

$$A_{nm} = \begin{cases} \displaystyle\sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \frac{8C_0}{\pi n \alpha_m J_1(\alpha_m)} & \text{odd } n \\ 0.0 & \text{even } n \end{cases}$$

where J_1 is the first kind of Bessel functions of order 1, and α_n are the roots of $J_0(\alpha) = 0$.

The amount of radiocontaminant leached (diffused) from the immobilized waste matrix can be given by:

$$\frac{A(t)}{A_0} = 1 - \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} \frac{32R^2H}{\pi n^2 \alpha_m^2} \exp(-D\lambda^2 t) \quad (17)$$

4.3. Prediction of time-profile leach fraction

Temporal profiles of leach fraction of ^{137}Cs from OPC waste matrix measured under laboratory conditions (as previously mentioned in Section 3.1) are shown in Fig. 6. The predicted curves obtained using one and two-dimensional analytical models are also presented in this figure. The simulation obtained from the two-dimensional analytical model gives an acceptable representation of the experimental data; thereby demonstrating that the proposed analytical model can represent the leaching kinetics of the studied radionuclide from cylindrical geometry cement matrix. A considerable divergence between the experimental and predicted data is noticed at the beginning of the simulation, this behavior could be attributed to the occurrence of the surface wash-off mechanism that is not included in the assumption of the analytical models. Further work will be carried out to investigate other mechanisms (chemical reaction and dissolution) that probably will occur at longer time to rectify the proposed model.

5. Conclusion

Long-term modeling of the ^{137}Cs, ^{60}Co, and ^{152,154}Eu leachability from different immobilized waste matrices were evaluated. The specific conclusions pertaining to the results presented herein can be drawn as follow:

(1) The CLF of studied radionuclides were significantly reduced by adding bentonite and red clay to the cement grouts due to their low porosity and the high sorption capacity of these clays.
(2) The OPC–bentonite matrix show a pronounced increasing in all studied radionuclides resistibility to leaching compared with red clay matrix and this is most probably due to the higher sorption capacity of bentonite than red clay.
(3) The controlling release mechanism for leaching the studied radionuclides was found to be diffusion.
(4) The mobility of the studied radionuclides in OPC–bentonite matrices showed a decrease of two to three order of magnitude compared to that of plain OPC matrices.
(5) All studied waste matrices have high leachability indices that allow their acceptance for disposal.
(6) Derived analytical models show acceptable agreement with the experimental work after nearly 40 days, which make them applicable for predicting the CLF of radionuclide from solidified waste matrices.

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