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Immobilization of radioactive borate liquid waste using natural diatomite

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ABSTRACT

In this article, influence of diatomite as a natural adsorbent in immobilization of radioactive borate liquid waste in the cement-diatomite matrix was investigated. Cylindrical concrete mixtures were prepared with different amounts of diatomite additives at three different w/c values. Mechanical strength tests were carried out to determine the uniaxial compressive strength of the samples. A new dynamic column type leaching tests were applied to the solidified waste forms, and leach rates of ^{137}Cs and ^{60}Co were determined according to different diatomite additives. The experimental results indicated that the increasing of the diatomite additive amounts resulted high isolation performance of the solidified waste form. However, the results revealed that mechanical strength decreases with increasing borate diatomite amount. Results show that 9% amount of natural diatomite is effective as an admixture of the cementation process for achieving long-term stability of solidified borate waste. Optimum strength and leach values were determined as 11.5 MPa with leaching rates of 7.5×10^{-4} and 3.2×10^{-5} cm/d for ^{137}Cs and ^{60}Co, respectively.

Keywords: Radioactive; Borate; Waste; Diatomite; Solidification; Immobilization

1. Introduction

Radioactive liquid wastes are generated by the cleanup of primary coolants and spent fuel storage pond of several nuclear reactors. In addition, decontamination operations in these reactors generate liquid wastes. In radioactive waste management applications, generally liquid wastes are converted to fixed form. Because of the fixed form of the radioactive waste is safer than fluid form, radioactive liquid wastes should be treated with one of the various treatment techniques. Major techniques are filtration, ion exchange, evaporation, and solidification. Generally, one of the solidification matrixes (cement, bitumen, and polymer) has been used for immobilization of radioactive liquid waste. Converting liquid radioactive waste in the safe and stable form of radioactive waste is a basic requirement for long-term disposal. By this way, radioactive waste in the solidified waste form can be safely isolated from the environment for a long time in a disposal facility. In contact with groundwater, release of the radionuclide from the radioactive waste would occur by leaching. For this reason, leaching property of the waste form is a basic parameter for long-term safety. In addition, mechanical strength of the waste form is another important parameter for long-term stability in underground disposal conditions.

Radioactive liquid borate waste is one of the radioactive waste types, which were generated from certain type of nuclear power plants. WWER reactors differ from pressurized water reactor (PWR) reactors with the use of boric acid in their primary coolant circuit and in related safety systems. A certain amount of boric acid can get into waste stream and consequently into the concentrate during liquid waste treatment. Due to specific design features of WWER reactors, the generation of concentrate is relatively high and its value in most cases ranges approximately 50–150 m^3/y for one reactor unit. Further treatment of concentrate is complicated by the limited solubility of borates (boric acid salts) contained in the waste together with the fact that discharges of waste stream containing boric acid into the environment are strictly limited [1]. Various solidification processes have been applied for immobilization of radioactive waste in cement, glass, polymer, or ceramic matrices in order to provide stable and durable materials for long-term safety. Related to this processes, numerous studies have been carried out.

Effective factors such as leaching and mechanical properties of matrices in contact with aqueous solutions are studied for the performance of solidification process [2–4]. Developing a glass formulation for radioactive waste is another research area. Several approaches have been carried out to determine the optimum formulation by changing ingredients of the glass using coal fly ash [5]. Previous studies on the long-term performance of cement–polymer composite for solidification of borate radioactive waste. These studies show that mechanical integrity and leaching properties are acceptable for long-term safety [6,7]. Many studies have been made on cement matrix for radioactive waste solidification [8–11] and Ordinary Portland Cement (OPC) was used with various pozzolanic materials as an additive for solidification in plant scale applications [12,13].

Investigation on the solidification of borate radioactive resins using sulfoaluminate cement (SAC) blending with zeolite showed that SAC-zeolite matrix is appropriate for the solidification of borate radioactive resins and borate radioactive liquid waste [14,15]. Study on solidification of the radioactive evaporator concentrates by SAC blending with zeolite, blast-furnace slag, silica fume, and fly ash was carried out, and admixtures showed positive effects on the leachability index. The results showed that the effect of zeolite was most significant, followed by blast-furnace slag, fly ash, and silica fume in sequence [16]. Influence of bentonite and zeolite as natural sorbents on immobilization of evaporator concentrates in the cement matrix has been studied, and reduction of leaching rate is determined by the increasing amount of bentonite and zeolite, as ordinary sorption materials for ^{137}Cs, ^{60}Co, and ^{85}Sr [17].

2. Materials and methods

Radioactive liquid borate waste is generally generated from the cooling circuit of PWRs. This type of waste mainly includes boric acid and sodium metaborate besides of radioactive species. Generally, this type of liquid radioactive waste has 9–12 pH with 250–300 g/L sodium-potassium metaborate. Radioactive liquid borate waste has two gamma emitters, radio cesium (^{137}Cs, $T_{1/2} = 30.5$ y) and radio cobalt (^{60}Co, $T_{1/2} = 5.27$ y).

In this study, a mixture was prepared using tetra borate hexahydrate, potassium nitrate, sodium hydroxide, and sodium in addition of radioactive liquid as radioactive liquid borate waste. Chemical and radiological composition of the borate liquid waste and specific activities of radionuclides were listed in Table 1.

Diatomite is an extremely fine-grained light-colored sedimentary rock. It is the consolidated accumulation of microscopic siliceous shell fragments (Fig. 1). The skeletal remains of single-celled plants are called diatoms. Natural diatomite is comprised of 85% silica and other inert oxides. Natural diatomite is odorless and non-toxic. Main component is the silica and it is strong and chemically inert natural material. Previous studies on diatomite in this field generally based on removal of contaminants by sorption [18–22].

In this study, radioactive borate concentration was solidified using OPC with the addition of natural diatomite. The specific surface area of diatomite is 21 m^2/g and the medium particle size d50 = 0.6 μm. Composition of the OPC is presented in Table 2. Water-to-solid material ratio is used to maintain fluidity of the concrete. However, durability and permeability properties to the concrete were affected by increasing the w/c ratio. Samples were prepared in three water–cement (w/c) ratios (0.35, 0.45, and 0.50).

Table 1
Chemical and radiological composition of radioactive borate liquid waste

Component	Amount (g/L)	Specific activity (Bq/L)
B	30	
Na^+	80	
Ca^{2+}	0.5	
Mg^{2+}	1.0	
Cl^-	0.3	
NO^{3-}	50	
^{137}Cs		10^8
^{60}Co		10^6
pH	9–12	
Density	1,200	

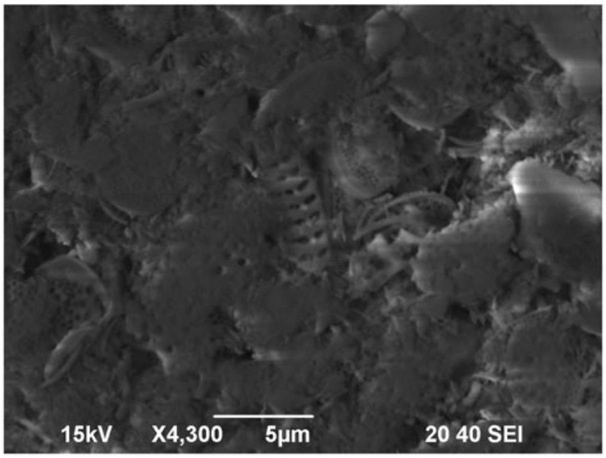

Fig. 1. SEM image of diatomite.

Table 2
Composition of Ordinary Portland Cement (OPC)

Contents	%
CaO	65
SiO_2	20
Al_2O_3	7
Fe_2O_3	2
MgO	3
Alkalis	1
SO_3	2

Laboratory-type mixing machine was used to prepare the cement matrix. Thirty cemented waste mixtures were prepared using different diatomite percentages and used for this study.

The Portland cement is about 80% calcium silicate (mainly Ca3 SiO5). During cementation hydration, process can be defined as:

$$2Ca_3{\cdot}SiO_5 + 6H_2O = [Ca_3{\cdot}Si_2{\cdot}O_7 3H_2O] + 3Ca(OH)_2$$

Cementation solution pH becomes highly alkaline because of the Ca $(OH)_2$. Hydration reaction is highly exothermic. When Portland cement is mixed with water, heat is liberated. This heat is called the heat of hydration, the result of the exothermic chemical reaction between cement and water. The heat generated by the cement's hydration raises the temperature of the concrete. Therefore, internal temperature increases and causes thermal stress, which can lead to cracks [23]. Aggregate is the main constituent of concrete, and the properties of aggregate influence the properties of concrete. Swelling clays increase water demand and decrease the temperature. It can be concluded that most of the authors believe that a significant amount of clay in a cement mixture reduces the amount of water available for the hydration reactions and thereby decreases its workability and also alters the course of the pozzolanic reactions. As a result, hardened cement containing clay minerals expected to have different physical properties from that of cement fabricated without clays [24–26]. In this stage, diatomite works to react with Ca $(OH)_2$. Using the diatomite as an admixture, internal heat was decreased during hydration.

$$3Ca(OH)_2 + 2[SiO_2] = Ca_3{\cdot}Si_2{\cdot}O_7{\cdot}3H_2O$$

Curing represents an important stage for providing moisture to make possible for the process of hydration. The increase in the w/c ratio can be compared to a rather good curing because of the presence of moisture, at least during the first hour after the concrete placing in cylindrical molds (Fig. 2).

For each of leaching and strength tests, thirty cylindrical samples were used in different amounts of diatomite and three different w/c ratios. Specification of each sample is presented in Table 3.

Samples were taken at the end of cementation process and poured into cylindrical molds and remained for curing at laboratory conditions (20˚C and 60% relative humidity). Solidified samples were prepared for mechanical and leaching tests (Fig. 3).

Durability of the concrete is necessary for long-term stability in the waste form. The compressive strength tests were carried out in accordance with ASTM C39/C39M-01 [27] after 28 d for curing of samples. Servo-controlled uniaxial mechanical strength test machine was used to determine the failure value

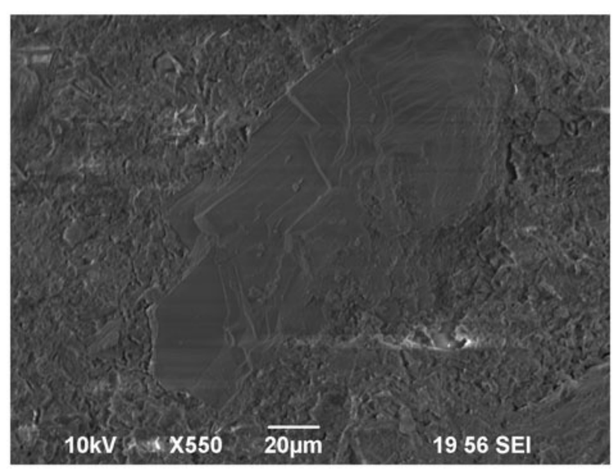

Fig. 2. SEM image of hardened paste.

Table 3
Mixing proportions of the concrete samples

Concrete samples	Water/cement ratio (w/c)	Diatomite amount (%)
C1	0.35–0.45–0.50	0
C2	0.35–0.45–0.50	2
C3	0.35–0.45–0.50	4
C4	0.35–0.45–0.50	7
C5	0.35–0.45–0.50	9
C6	0.35–0.45–0.50	11
C7	0.35–0.45–0.50	13
C8	0.35–0.45–0.50	15
C9	0.35–0.45–0.50	18
C10	0.35–0.45–0.50	20

Fig. 3 Cylindrical samples.

of the sample. The compressive strength tests showed that in case of w/c = 0.35 and 9% diatomite addition, strength of the sample is acceptable. For this reason, 9% diatomite samples were used for leaching tests. The leaching test of radioactive waste immobilized in cement-diatomite matrix was carried out in new dynamic conditions. The experimental setup is depicted in Fig. 4.

Leaching behavior is one of the major critical characteristics for a long-term assessment of the waste matrix prior to disposal process. Main leaching mechanisms are diffusion, dissolution, and ion exchange depending on environmental conditions. Leaching is the process by which radionuclides are released from the cemented waste into the water phase under the influence of mineral dissolution, desorption, and complexation processes as affected by pH. The process itself is universal, as any material exposed to contact with water will leach components

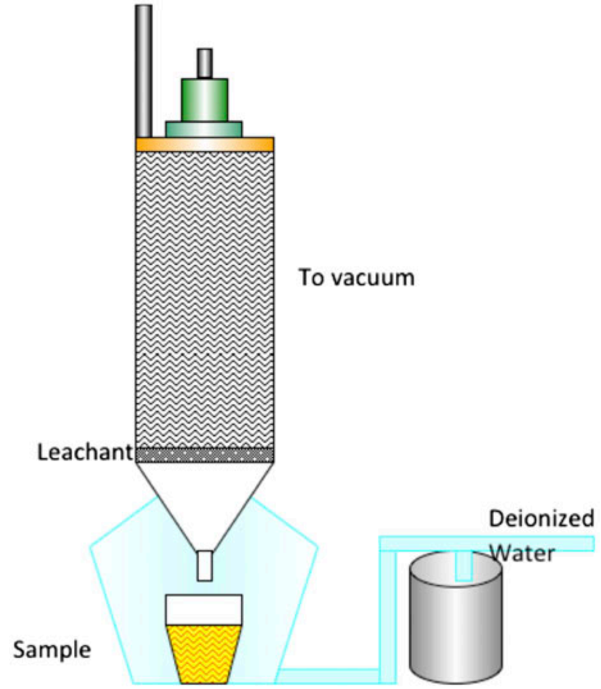

Fig. 4. New dynamic leaching test column.

from its surface or its interior depending on the porosity of the material considered. In this study, a new dynamic leaching test column was designed. Leaching tests were performed using this column and adapted to ASTM C1308-95 [28].

Inner diameter of the test column is 5.4 cm. Cylindrical solidified waste forms were prepared and cut into slices in 5 mm thickness. Solidified waste sample slice was placed at the bottom of the cylindrical test column tightly. The deionized water was introduced to the upper surface of the waste form. Solution in which passed through the sample was taken from the leachate collection jar. It was placed inside a vacuum chamber. The pressure within the chamber was reduced below the atmospheric pressure. The leachate was collected from each sample, and radioactivity content of each leachant was determined. The leachant was periodically withdrawn out of the leachant jar and subjected to spectrometric counting.

The gamma-ray spectrometry system consisted of a HPGe coaxial GCD-80-210 detector with 80% efficiency coupled with a multispectrum hybrid converter, high voltage (5,000 V) with negative polarity. Energy resolutions at 122 keV and 1.33 MeV are 1,000 eV and 2.10, respectively. Peak/Compton's ratio is 77:1; Peak shapes FWHM values at FW1M and FW02M are 2 and 3, respectively. Energy range is 40 keV–10 MeV (GCD). It was mounted on a vertical cryostat, 30 cm in height, connected to Polycold PCC-70K cooling system. The position of the crystal within the shield was fixed at the bottom of the counting chamber. The crystal and its preamplifier electronic component were enclosed in a high-purity copper end cap.

3. Results and discussions

In this study, completely different natural materials were used as an additive into cementation of radioactive borate waste. Long-term leach stability and compressive strength of the cemented borate waste were evaluated by adding of diatomite as an adsorbent admixture. No data have been published, which provide this type study on cement-diatomite matrix for radioactive borate wastes. Cementation is one of the solidification processes in this type of concentrated liquid radioactive borate waste. The typical cementation process includes a mixture of cement, sand and liquid waste in various proportions. In case of adequate arrangements of proportions and suitable conditions, mechanical strength of the product is about 15 MPa after 28 d. However, in existence of the borate waste, mechanical strength of the waste and long-term leachability of the cemented waste form is limited. The compressive strength tests showed that the highest strength value was 12.5 MPa at w/c = 0.35 with 2% diatomite. Although increasing of diatomite from 2 to 9% cause decreasing of strength to 11 MPa, this strength value is acceptable in case of leaching rate is significantly decreased. Compressive strengths vs. diatomite amounts at three different w/c ratios are shown in Fig. 5.

Radioactivity release of sample shows that the sample, which included 9% diatomite and prepared 0.35 w/c, presents the least radioactivity release within the acceptable strength. For all leaching curves, it should be notified that the leaching behavior of radionuclides from the cement–diatomite waste forms revealed three distinguished performances. The first initial period is characterized by a low leachability of radionuclides relative to the second one. This may be explained by the fact that up to nearly 2 d from the starting time, the low release may be attributed to the time requirements for washout of the whole sample. At the second stage, relatively rapid washing process occurred when the sample was completely exposed to the deionized water. This is followed by nearly a steady-state diffusion controlling periods that persist. Leaching solution velocity (v) is defined by the volume (u) of the leachant contacted with solid waste per unit of surface area (S) and unit of time (t) given as:

$$v = u \;/\; (S.t) \tag{1}$$

Leaching rate is dependent to leaching velocity. Using vacuum in dynamic test column ensured high leachant velocity. By this method, ultimate leaching rate was reached within the range of 6–8 d. During the first two days, the flow rate was still very low and there was no significant radioactivity in the leachant. The passed liquid was collected in the leachant jar in a predetermined time interval. During the next four days, the sample was almost filled by deionized water and the sample reached its effective absorption capacity level. After that level, the flow rate and passed radioactivity amounts were relatively constant. This

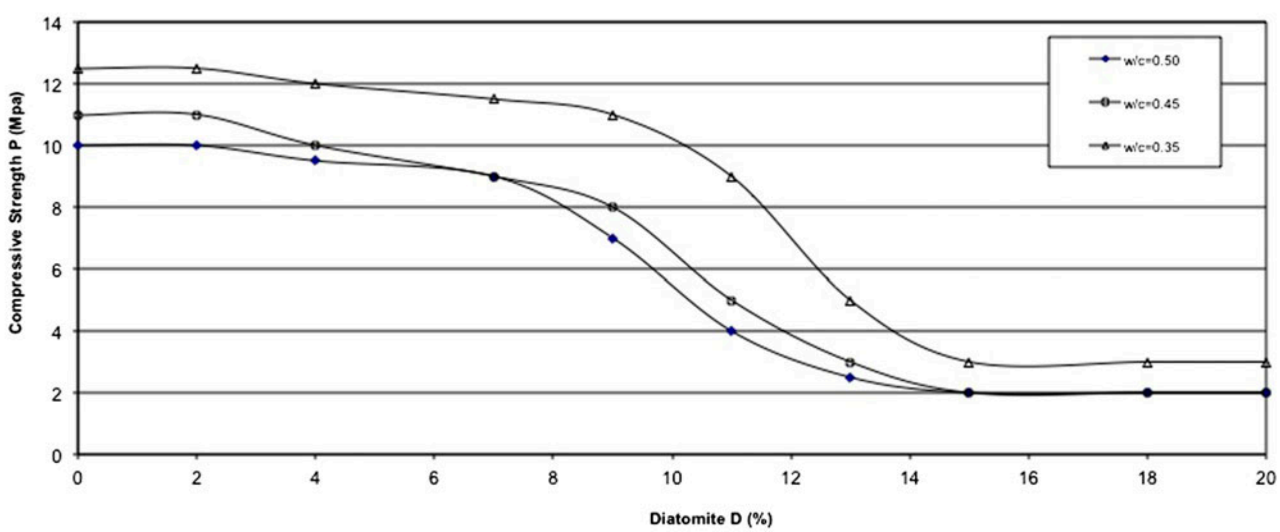

Fig. 5. Compressive strengths vs. diatomite additives at various w/c ratios.

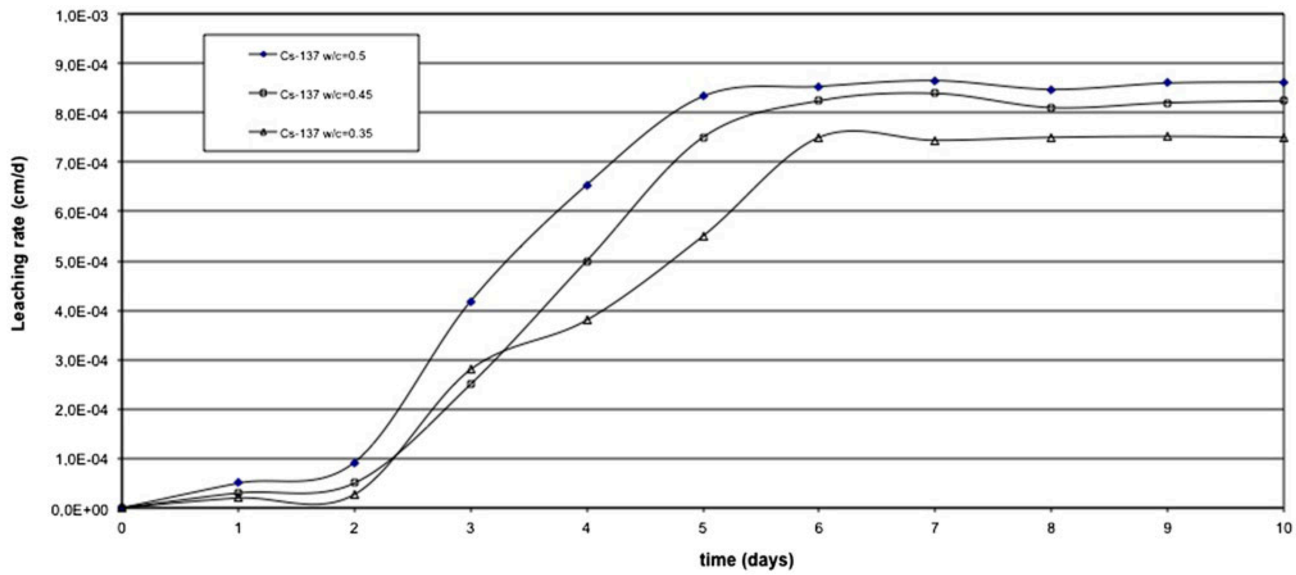

Fig. 6. Leaching rate (^{137}Cs) vs. time.

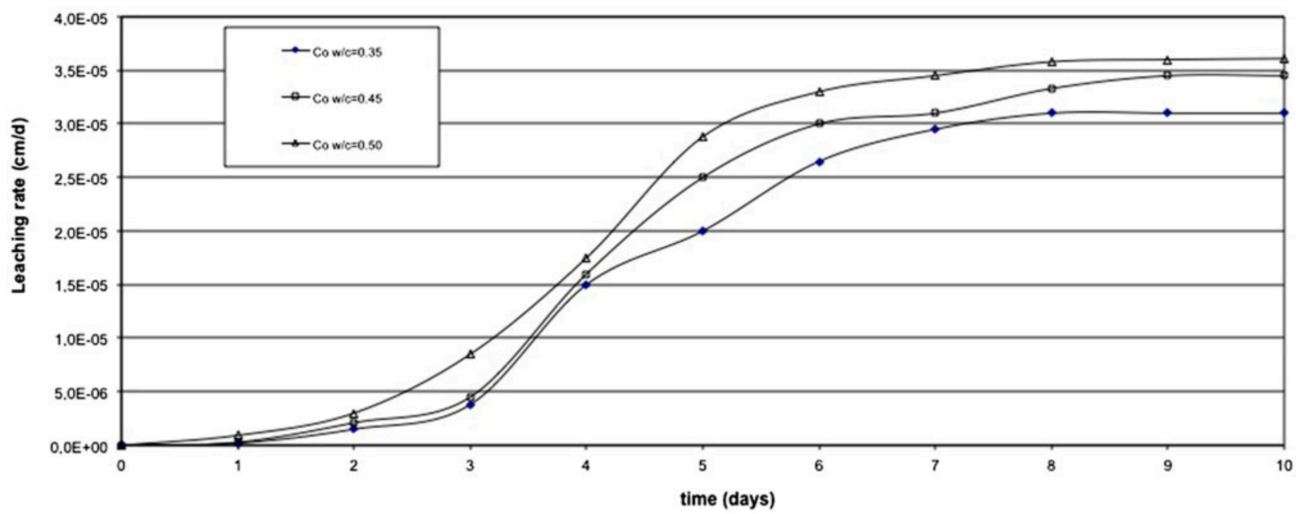

Fig. 7. Leaching rate (^{60}Co) vs. time.

stage can be defined as the filling stage. In the last stage, the samples were completely filled with water. The molecular capacity of the cement-diatomite matrix was filled, and flow through the water was easier than in the previous stages. The leach test results were expressed as leaching rate of a function of the total time of leaching for 137Cs in Fig. 6.

Absorption capacity of the sample was almost filled at the sixth day of the leaching test. After six days, passed solution amount was nearly at leaching rate of 7.5×10^{-4} cm/d for ^{137}Cs.

The leach test results were expressed as leaching rate of a function of the total time of leaching for ^{60}Co in Fig. 7. The sample absorption capacity was almost filled after seventh day of the leaching period. After this time, it stayed nearly constant at leaching rate of 3.2×10^{-5} cm/d for ^{60}Co. Optimum results for leach rate are 7.5×10^{-4} and 3.2×10^{-5} cm/d for ^{137}Cs and ^{60}Co, respectively.

LSRM SpectraLine GP software was used to record the intensity in the incident and transmitted gamma rays. The cumulative radioactivity of ^{137}Cs and ^{60}Co

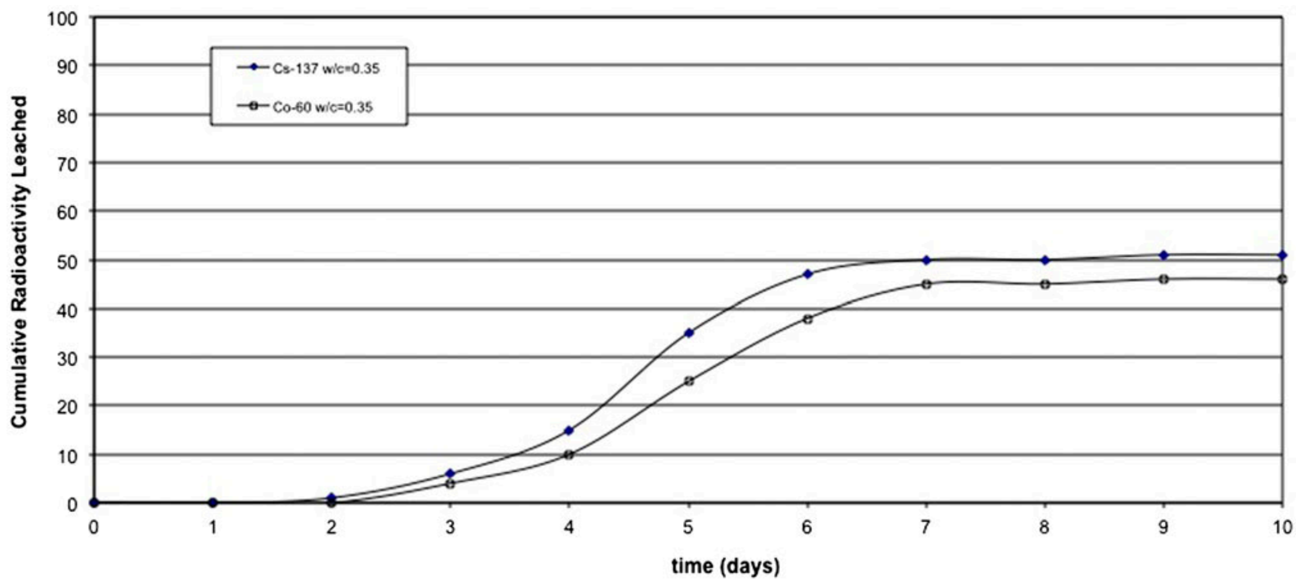

Fig. 8. Release radioactivity vs. time.

radionuclides from the cemented waste form for w/c = 0.35 and 9% diatomite was calculated, and the data were plotted against a function of time in Fig. 8.

4. Conclusions

The most frequent method for solidification of liquid radioactive waste is cementation. Cementation is widely used to encapsulate operational liquid radioactive waste in radioactive waste management. Cementation process has many advantages such as low cost, relatively simple, and provides self-shielding. Liquid radioactive waste becomes a fixed form by application in the cementation process. Fixed forms of waste are easy to handle and store in the radioactive waste management system. In addition, cementation is inexpensive and easily applicable to maintain stable product. After solidification, cement provides a hardened barrier, which resists diffusion of radionuclide, and it is not degraded by radiation. It has low permeability and high surface area for adsorption of species. Previous studies focused on borate concentrates because this type of radioactive waste is always a problem in waste management because of their corrosive, toxic, and radioactive nature [29].

In the cementation process, the highest compressive strength value was measured as 12.5 MPa without diatomite additive. The best strength value was recorded when the water–cement ratio of the sample was 0.35. Diatomite addition into to the cementation process presents a solution to regulate some of the problems of radioactive borate concentrates due to its corrosive nature. The results indicated that using the diatomite as an admixture, internal heat was decreased during hydration. By this way, integrity of the solidified waste is reasonably increased. In addition of diatomite admixture shows that diatomite has a significantly positive effect on leaching rate. Diatomite additive up to 9% of total weight results less than 10% negative effect on the compressive strength of solidified waste form. Optimum diatomite addition amount was determined as 9%. Development of leach resistance of waste forms is a major area of research within the field of radioactive waste management in order to minimize the environmental impact through the back release of the radioactive material. These samples have 11 MPa compressive strength value and of 7.5×10^{-4} and 3.2×10^{-5} cm/d leaching rates for ^{137}Cs and ^{60}Co, respectively. By this way, reasonable leaching rates of the cemented borate waste form within long-term mechanical stability can be achieved. From a practical point of view, these results are of particular interest, which proposes a new dynamic leaching method and efficient cement-diatomite matrix for liquid radioactive borate wastes.

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