

## THE STUDY OF RADIONUCLIDES LEACHING FROM MORTAR MADE WITH NATURAL AGGREGATES AND RECYCLED AGGREGATES ARISING FROM DECOMMISSIONING OF VVR-S RN

R. DEJU<sup>1</sup>, D. GURAU<sup>1</sup>, L. DONE<sup>1,2</sup>, C. MAZILU<sup>3</sup>, I. ROBU<sup>3</sup>

<sup>1</sup>“Horia Hulubei” National Institute for Physics and Nuclear Engineering, POB MG-6,  
Magurele – Bucharest, 077125, Romania

<sup>2</sup>University of Bucharest, Doctoral School on Physics, POB MG-11, Magurele – Bucharest,  
077125, Romania

<sup>3</sup>Technical University of Civil Engineering, 122–124 Lacul Tei Avenue,  
020396, Bucharest, Romania  
E-mail: dejuradu@yahoo.com

*Received November 24, 2015*

*Abstract.* The leach test of radionuclide in cement-solidified waste form was performed. The leaching behavior of  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$  and  $^{152}\text{Eu}$  radionuclides from mortar made with natural aggregates and recycled radioactive concrete into surrounding fluid (demineralized water) was studied. The influence of curing time, type and size distribution of the aggregates was determined. Mercury porosimetry was applied to evaluate the pore volume and surface area. Was found that the migrations of radionuclides in solutions are controlled by a diffusion mechanism through the pores that determine the long-term leaching behavior for the materials.

*Key words:* radionuclides migration, leaching, reuse and recycling of radioactive concrete.

### 1. INTRODUCTION

The radioactive concrete waste resulted from the decommissioning of the VVR-S nuclear research reactor from Magurele represent about 6.5% from the total amount of concrete. The final disposal of these type of materials will decrease the storage capacity. Nowadays, the low level radioactive waste are pre-placed in blocks form in containers and consolidated with mortar made from fine natural aggregate. An innovative solution proposed in this study is the recovery of coarse and fine aggregates from the radioactive concrete waste and their recycling, not as a simple waste, but as filling mortar to stabilize the radioactive waste in specific containers. Plecas and Dimovic [1] have observed that during the interim storage or final disposal of solidified low level radioactive waste, migration/diffusion of radionuclides can occur, when the waste come in contact with water, and so the

radionuclides are transported into the soil/surrounding structure, caused by dissolution or chemical reaction with the chemical components of water. Plecas [2, 3], Moriyama [4] and Geleel [5] and their colleagues demonstrated that in order to prevent widespread dispersion of radionuclides in the environment, radioactive waste must be embedded in an immobilization matrix (cement, asphalt, plastic, glass or ceramic). Plecas [2, 3] showed that radioactive waste immobilization matrix must have leaching resistance and must be mechanically, physically and chemically stable for safe handling, transport and final disposal. If those conditions are fulfilled, the release of radionuclides will be slow in contact with flowing water. Sami and the colleagues [6] showed that the cement is the best known material to solidify and to isolate solid or liquid radioactive waste of low and intermediate activity. Typically, concrete is a mixture of cement, sand, aggregate and water in different proportions, and together determine the structural properties and tightness of the cemented material. Concrete is a porous, continuously hydrated material whose real surface area exceeds by far the specific geometric surface area [7]. As a cementing material, it has the disadvantages of low reduction of volume and a relatively high leachability for a few radionuclides ( $^3\text{H}$ ,  $^{137}\text{Cs}$  and  $^{60}\text{Co}$ ) which, however are quite short-lived. In addition, the concrete has several practical advantages because has good mechanical properties, is cheaper in cost, is easy to handle and has thermal and radiation exposure stability. A number of papers describe the immobilization of radionuclides with cement and cement mixed with various admixture additives (blast furnace slag, silica fume and ilmenite) [8, 9, 10, 11]. Highly effective ingredients were found for cement mortar that can improve the characteristics of the waste matrix towards safety requirements. Therefore, quantitative evaluation of radionuclides that can be leached from the waste package is essential in radioactive waste management. Such leaching behavior must be related to the pore structure and pore solution composition [2, 3, 12, 13, 14]. Some radionuclides are chemically bond to concrete constituents or even incorporated into crystal structures [13].

The aim of this paper is to study the leaching behavior of  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$  and  $^{152}\text{Eu}$  radionuclides in aqueous medium, for the radioactive mortar samples made from recycled aggregates compared to samples made of natural aggregates (river sand). This study is part of a large research project that has as main purpose the minimization of the low level radioactive concrete that should be dispose, in accordance with all the applied legal requirements. Using the radioactive concrete as recycled fine aggregate in the mortar for solidifying the radioactive concrete rubble or blocks inside the disposal containers, can increase the fill ratio of radioactive concrete waste or the total low level waste disposal volume can be reduced. For these analysis, the influence of curing time, type and size distribution of the aggregate on leaching behavior were evaluated.

## 2. EXPERIMENTAL AND MEASUREMENTS

### 2.1. MATERIALS

For this study, three types of mortar samples were used and were marked as N, DR and DP for unique identification. For the preparation of N type mortar, natural aggregates of river sand sort of 0/2.5 mm (Lafarge) were used. For obtaining the fine aggregates necessary for preparing the DR and DP type reference mortar, C25/30 reference concrete [15] was crushed in two steps: (1) cubes with dimensions of  $15 \times 15 \times 15$  cm were crushed in the B 1624J Buffalo Shuttle Jaw crusher, resulting the granulometric fractions  $< 50$  mm; (2) grain size fraction  $> 50$  mm were crushed in the WA-12-H Buffalo Shuttle Hammer crusher using a sieve with 9 mm mesh size, resulting the granulometric fractions  $< 2.5$  mm with particle size distribution presented in Table 1.

*Table 1*

Particle size distribution for recycled aggregate

Particle size [mm]	wt. [%]
2.000–2.500	8
1.000–2.000	9
0.500–1.000	28
0.250–0.500	21
0.125–0.250	18
0.063–0.125	11
0.000–0.063	5

For preparing the DR type mortar, the recycled aggregates were used with a proportion of particle size sorts as resulted from the second stage of C25/30 reference concrete crushing. For DP type mortar preparation, the 0/0.15 mm sort was separated from the fraction  $< 2.5$  mm from the recycled aggregates with a particle size proportion as resulted from the second stage of C25/30 reference concrete crushing. The 0/0.15 mm sort was grounded in a laboratory ball mill with horizontal rotary drum. The specific surface area for 0/0.15 mm particle size fraction, determined with Blaine Permeability meter, has been modified after grinding from  $3000 \text{ cm}^2/\text{g}$  to  $5080 \text{ cm}^2/\text{g}$ . Ground fraction was reincorporated into the base material. All the mortars prepared in the experiments were made with cement type CEM V A(S-V)42.5N (produced by Lafarge, Romania). The compositional data and p-cone time for N, DR and DP type mortar are presented in Table 2.

Table 2

Compositional data and p-cone time through conical funnel for mortar

Sample code	Compositional data [kg]			p-cone time [s]			Density [kg/m <sup>3</sup> ]	Remarks
	Water	Cement	Sand	0	15	30/ 60		
N	0.45	1	0.8	31	48	50/–	–	Plastic, fluid
DR	0.60	1	1.3	31	35	40/ 52	1926	Homogenous, fluid, slight separation
DP	0.65	1	1.7	21	25	28/ 37	1933	Homogenous, fluid, slight separation

The super-plasticizer additive/ highly efficient water reduce quantity – Glenium 27 – was 0.8% for N type mortar and 1.5% for DR and DP type mortars (based on the amount of cement). The Rheomatrix 150 agent was 0.5% for DR and DP type mortar.

## 2.2. SAMPLES MATRIX PREPARATION AND MEASUREMENT

For achieving the leaching experiments, samples were artificially contaminated with <sup>137</sup>Cs, <sup>60</sup>Co and <sup>152</sup>Eu radionuclides. <sup>137</sup>Cs radionuclide was chosen because occurs as a main component of waste streams having a significant radiological risk and its chemical behavior is comparatively simple, being monovalent and soluble, even under the strongly alkaline conditions obtaining in the cement environment. Because of these characteristics, <sup>137</sup>Cs is difficult to immobilize in a cement matrix because of its solubility. Several authors [10, 16, 17] have shown that the cement matrix provide only physical encapsulation for <sup>137</sup>Cs, although the matrix components, especially the amorphous sodium silicate hydrogel have a very high specific surface area (10<sup>4</sup>–10<sup>6</sup> cm<sup>2</sup>/g) (N<sub>2</sub> sorption) and do not display a sorption potential for monovalent ions. <sup>60</sup>Co and <sup>152</sup>Eu were chosen because they are the main activation radionuclides presented in the concrete biological protection of the VVR-S nuclear research reactor from Magurele-Bucharest.

The composition of the samples was realized by 3 minutes manually mixing the dry components of the mortar (fine aggregates sort 0/2.5 mm and cement), then water was added (part of which has been substituted by the radionuclide solutions) and finally the Rheomatrix 150 agent was added. The sample preparation recipe was as follows: 106 ml liquid (44.5 ml distilled water and 61.5 ml solution of <sup>137</sup>CsCl, <sup>60</sup>CoCl<sub>2</sub> and <sup>152</sup>EuCl<sub>3</sub>) for the N samples, 109.5 ml liquid (48 ml distilled water and 61.5 ml solution of <sup>137</sup>CsCl, <sup>60</sup>CoCl<sub>2</sub> and <sup>152</sup>EuCl<sub>3</sub>) for the DR samples and 107.8 ml liquid (45.8 ml distilled water and 62 ml solution <sup>137</sup>CsCl, <sup>60</sup>CoCl<sub>2</sub> and <sup>152</sup>EuCl<sub>3</sub>) for the DP samples. The mixing process continued for 4 minutes, then, the mortar obtained was molded into PVC cylinders with

80 mm diameter and 15 mm height, positioned on a window glass, and finally, the upper surface of each sample was smoothed with a spatula. After 24 hours, the samples were removed from the form, the mass, diameter and height were measured and density was analytically evaluated. N, DR and DP samples were cured at 25 °C for 28 days (Table 3) and respectively at 25 °C for 56 days.

Table 3

Compression resistance of the cured mortar samples, after 28 days

Sample cod	Water/Cement ratio	Sand/Cement ratio	Glenium 27 [%]	MV agent [%]	p-cone (s) at min				$f_c$ [MPa]
					0	15	30	60	
N	0.45	0.8	0.8	–	31	48	50	50	48.1
DR	0.60	1.3	1.5	0.5	31	35	40	52	32.7
DP	0.65	1.7	1.5	0.5	21	25	28	37	30.2

The initial activity,  $\Lambda_i$ , presented in Table 4, of the cured mortar samples was evaluated through gamma-ray spectrometry using a laboratory system with lead castle (from Ortec) consisting of a high purity germanium detector (model GEM60P4-95) and a DSPEC jr. 2.0 Digital Gamma-Ray Spectrometer. The main performance specifications of the detector warranted by the producer are: relative efficiency 60%, resolution (FWHM) 1.95 keV, peak-to-Compton ratio 70:1, peak shape (FWFM/FWHM) 3.0, all evaluated at 1.33 MeV peak of  $^{60}\text{Co}$ . Monte Carlo simulation using GESPECOR code [18] was used for the efficiency evaluation based on a detector characterization process with point sources. To minimize the uncertainties due to matrix inhomogeneity, the initial activities of the cured mortar samples were considered to be the average of the activities evaluated for samples measured on both base sides.

Table 4

Initial activity in the N, DR and DP mortar samples

$\Lambda_i$ [Bq]			$\Lambda_i$ per sample [Bq]
$^{137}\text{Cs}$	$^{60}\text{Co}$	$^{152}\text{Eu}$	
(5.25÷5.68)E+03	(1.25÷1.35)E+04	(8.45÷9.24)E+03	(2.62÷2.84)E+04

Further, each cured mortar sample was introduced into a glass jar with lid of 600 ml volume, placed on a PVC pad, to expose the entire surface of the sample to the leaching agent. In each jar there were poured 400 ml of distilled water. After a period of time previously established (1, 2, 3, 4, 5, 6, 7, 15, 22, 30, 37, 45, 52, 60, 90 days), the water jar was transfused in cylindrical PE containers with sealing lids and then replaced with the same volume of fresh distilled water. Every time was

checked if the water contain concrete residue. For the collected water samples, the pH was determined using a pH meter type WTW Inolab 720, the conductivity using a conductivity meter type WTW Inolab 720 and the activity using a gamma-ray spectrometry system.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. CURING TIME

The leaching fraction value  $\sum \Lambda_n / \Lambda_i$  for concrete samples cured for 28 days was studied for DR and DP samples in comparison with N samples. In Fig. 1 are presented the leach rates of  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  determined for N, DR and DP mortar samples *versus* square root of time.

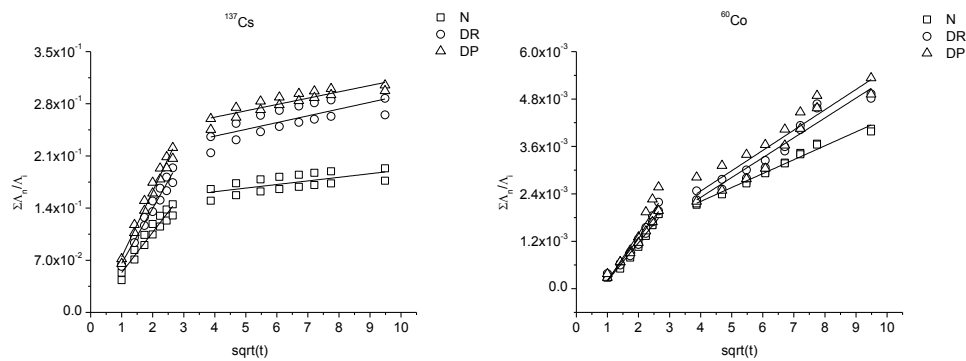


Fig. 1 – Value of  $\sum \Lambda_n / \Lambda_i$  for N, DR and DP concrete samples.

Was observed that after 90 days, in comparison with N samples, the leaching fraction values are higher by up to 34% for DR and 40% for DP in the case of  $^{137}\text{Cs}$  and up to 21% for DR and 29 % for DP in the case of  $^{60}\text{Co}$ . The dissolved  $^{152}\text{Eu}$  radionuclide was not detected in the cementation systems (the Minimum Detectable Activity was aprox. 3.5 Bq for water sample geometry).

The leaching fraction value,  $\sum \Lambda_n / \Lambda_i$ , was analyzed also for the N (river sand in composition), DR and DP (recycled aggregates in composition) mortar samples cured for 56 days in comparison with samples cured for 28 days. In Fig. 2 are represented these values for  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  *versus* square root of time.

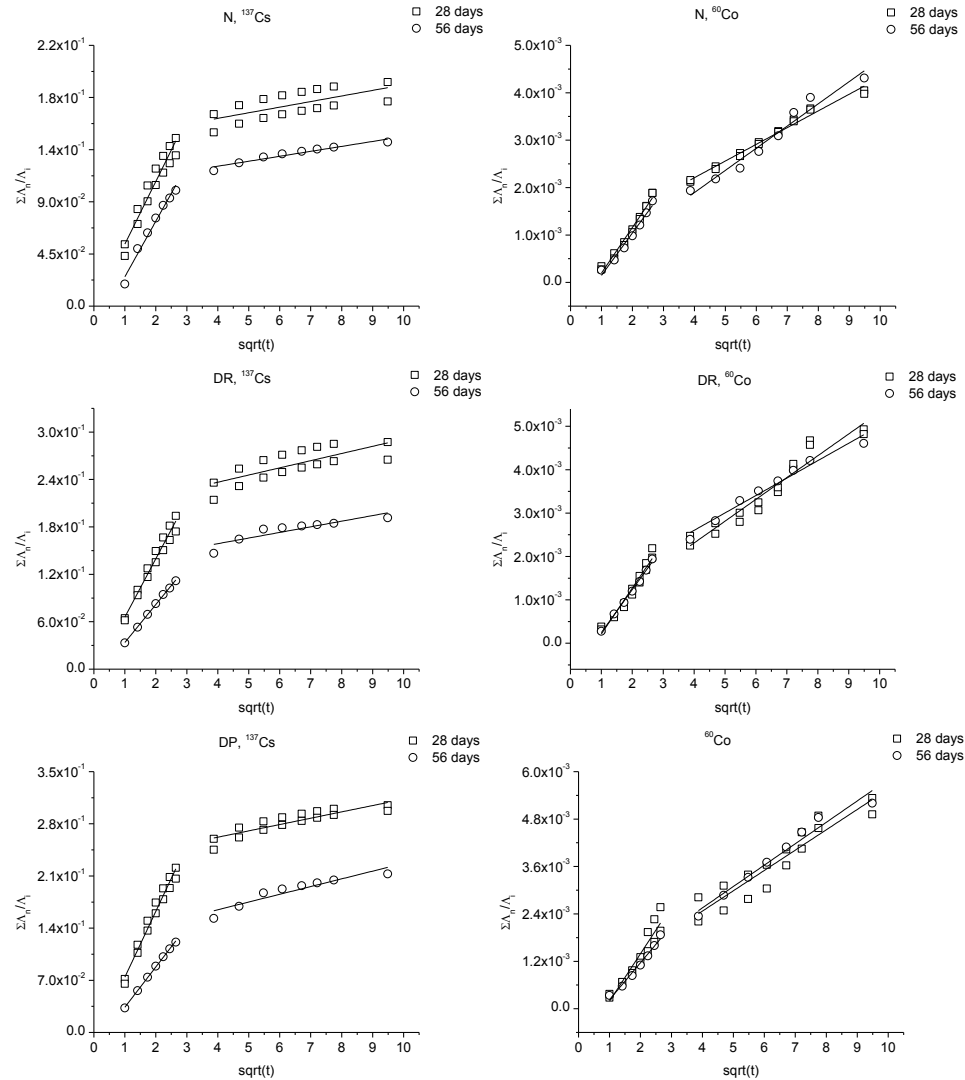


Fig. 2 – Value of  $\sum \Lambda_n / \Lambda_i$  for N, DR and DP concrete samples.

Was observed that the  $\sum \Lambda_n / \Lambda_i$  values for the 56 days cured samples for N, DR and DP cement matrix compared with the 28 days cured samples were lower for  $^{137}\text{Cs}$  and comparable for  $^{60}\text{Co}$ . The leaching curves obtained displays two distinct parts: the initial part of 1÷7 days presents a high leaching rate; the final part of the graph, from 15 to 90 days study period, indicates a low leaching rate. From the analysis of the experimental data's, was observed that the high initial release of  $^{137}\text{Cs}$  radionuclide which, however is quite short-lived, can be attributed

to surface activities that are easily washed when the sample comes in contact with the leaching agent. The size of the cumulative leaching fraction is an index for the release of nuclides from the cement matrix.  $^{137}\text{Cs}$  radionuclide is difficult to be immobilized in a cement matrix due to its solubility. McCulloch, Anderson, Glasser, Friedman and Kelmers and their colleagues [16, 17, 19, 20] have showed that although the matrix components, especially, the hydrogel in amorphous phase of calcium silicate (or close to), have a high specific surface of  $10^4\text{--}10^6\text{ cm}^2/\text{g}$  ( $\text{N}_2$  sorption), do not produce any virtual potential for the sorption of monovalent ions. Thus, the cement matrix produce only physical encapsulation for  $^{137}\text{Cs}$ . However, between the hydroxides of Cs, Co and Eu that have potential of crystallization in mortars, during the curing period, the solubility of Cs hydroxide ( $s_{\text{CsOH}} = 3.0\text{E} + 03\text{ g/l}$  at approx.  $25^\circ\text{C}$ ) in water is much higher than that of Co hydroxide ( $s_{\text{Co(OH)}_2} = 3.2\text{E} - 03\text{ g/l}$  at approx.  $25^\circ\text{C}$ ).  $\text{Eu(OH)}_3$  is the most insoluble between the mentioned hydroxides ( $s_{\text{Eu(OH)}_3} = 1.37\text{E} - 07\text{ g/l}$  at aprox.  $25^\circ\text{C}$ ), fact revealed by the very small value of the solubility product,  $K_{\text{sp}} = 9.38\text{E} - 27$ .

### 3.2. LEACHATE pH AND CONDUCTIVITY

The pH and the conductivity have been measured for fresh demineralized water and for the leaching agent at the end of each leaching period. The initial values for pH and conductivity for fresh demineralized water were 7.70 and 8.38 respectively. From the leaching experiments carried out was observed a variation of pH and conductivity on time (Table 5).

Table 5

pH and conductivity variation for the leaching agent vs. time

<i>t</i> [day]	pH						Conductivity [ $\mu\text{S}/\text{cm}$ ]					
	28 days			56 days			28 days			56 days		
	N	DR	DP	N	DR	DP	N	DR	DP	N	DR	DP
1	10.93	9.49	9.97	10.90	10.89	9.62	917.0	616.0	650.0	541.0	624.0	433.0
2	9.54	8.17	8.90	11.16	8.29	10.07	424.0	292.0	337.0	444.0	198.3	261.0
3	8.08	8.20	8.34	10.20	7.89	8.18	275.0	222.0	246.0	305.0	164.7	187.4
4	9.01	8.04	8.93	10.29	8.43	9.80	202.0	195.4	192.8	303.0	137.3	173.6
6	8.97	7.95	8.22	10.37	7.93	8.07	158.2	176.1	169.9	286.0	125.0	141.7
5	8.02	8.02	7.96	10.08	8.06	8.60	154.3	163.3	162.2	167.4	128.4	107.3
7	7.89	7.96	7.96	8.75	8.17	8.12	149.5	151.7	147.1	125.7	114.5	118.4
15	9.90	9.55	10.53	8.41	8.40	8.38	322.0	352.0	407.0	317.0	331.0	302.0
22	8.96	8.10	8.02	8.08	8.16	8.31	141.1	171.8	152.2	169.4	203.0	211.0
30	8.56	8.12	8.05	8.18	8.22	8.03	89.2	134.4	117.5	157.5	177.3	131.5
37	8.12	8.02	8.17	8.26	8.06	8.17	89.1	120.0	109.1	129.9	143.3	125.7
45	7.86	7.97	7.98	8.14	8.00	7.88	133.3	136.6	129.5	129.0	141.2	136.4
52	7.97	8.02	7.94	7.90	7.94	7.80	129.9	127.8	114.9	133.0	128.5	136.0
60	8.10	8.09	7.61	7.82	8.06	8.03	135.1	135.7	131.6	134.9	160.0	179.0
90	7.96	7.97	7.61	8.02	8.00	9.62	160.4	162.4	139.0	176.5	185.5	433.0



It can be observed that the pH values are higher in the first 30 days of study, then are slightly decreasing to the initial value of 7.70. There were no notable differences in the radionuclides release which can be attributed to the differences between the initial and final values of leaching agent pH. The data showed that the pH and the conductivity have a small effect on the final value of the leaching agent. McIsaac and his colleagues [21] have showed that this is due to the large amount of calcium hydroxide existent in the waste. Initially, the pH and the conductivity of the leaching solution were higher due to the high solubility of the portlandite from the cement matrix, correlated with the radionuclides chlorides solubility. The decreasing of the pH and conductivity in time, can be explained by the formation of hydroxy calcium salts with retention of radionuclides.

### 3.3. LEACHING CONTROL MECHANISM

The main leaching control mechanism of the samples was determined from the return slope ( $n$ ) of the linear regression line through data points in  $\log(CLF)$  and  $\log(t)$ . CLF is the cumulative leache fraction and was evaluated with the following formula:

$$CLF = \frac{\sum \Lambda_n / \Lambda_i}{V/S}, \quad (1)$$

where:  $\Lambda_i$  is the initial sample activity at zero time [Bq];  $\Lambda_n$  is the activity leached out of sample after the leaching time [Bq];  $V$  is the sample volume [ $\text{cm}^3$ ] and  $S$  is the sample surface [ $\text{cm}^2$ ];  $t$  is the renewal period of leaching agent (1, 2, 3, 4, 5, 6, 7, 15, 22, 30, 37, 45, 52, 60, 90 days).

The objective of measuring the cumulative leach fraction (CLF) is to predict the leaching rate of  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$  and  $^{152}\text{Eu}$  radionuclides of potential concern from immobilized waste matrix under continuously saturated condition that represent the worst case.

The slope  $n$  was calculated as a vertical distance divided by the horizontal distance between any two points on the line, which is the rate of change along the regression line, using the next equation:

$$n = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sum (x - \bar{x})^2}, \quad (2)$$

where  $x$  and  $y$  are the sample means of all the  $\log(t)$  values average and  $\log(CLF)$  values average.

If the slope ( $n$ ) takes values  $< 0.35$ , then, the leaching control mechanism of leaching is the surface washing; in the range of  $0.35 \div 0.65$ , the leaching control mechanism is the diffusion; and when the slope takes values  $> 0.65$ , then, the leaching control mechanism is the dissolution. The data obtained for the range of  $1 \div 7$  days were removed from the analysis because this area is characterized by the surface washing and can provide errors. In Table 6 are presented the results for the period from 15 to 90 days.

Table 6

The return slope ( $n$ ) of the linear regression line through data points in LOG(CLF) and  $\log(t)$

Sample	Curing time [days]	$n$	
		$^{137}\text{Cs}$	$^{60}\text{Co}$
		$t = 15, 22, 30, 37, 45, 52, 60, 90$ days	
N	28	9.03E-02	3.70E-01
	56	1.06E-01	4.91E-01
DR	28	1.18E-01	4.49E-01
	56	1.38E-01	3.73E-01
DP	28	9.92E-02	4.41E-01
	56	1.84E-01	4.70E-01

Was observed that the leachate activity increased over 50%, for cement matrix made with recycled fine aggregates than cement matrix made with natural aggregates. The facility of an easier transfer of radionuclides in solution is due to: (a) cracks appeared in the aggregate during the crushing [22]; b) old mortar (with a porous structure) attached to the natural aggregate particles in the recycled aggregate. The surface area and the smoother porosity of cement matrix facilitates the leaching of  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  radionuclides. To study the effect of natural and recycled aggregates concrete properties, mercury porosimetry was investigated. The open and total porosimetry was realized for samples of approximately 1g collected from N, DR and DP mortar type. The mercury intrusion porosimetry (MIP) using Quantachrome PoreMaster was realized to evaluate the pore volume and surface area. In Table 7 are presented the results obtained for pore volume and surface area for N, DR and DP samples.

Table 7

Pore volume and surface area evaluated for N, DR and DP mortar type samples through mercury intrusion porosimetry

Sample	Pore volume [ $\text{cm}^3/\text{g}$ ]	Surface area [ $\text{m}^2/\text{g}$ ]
N	0.1001	3.0331
DR	0.1327	6.1873
DP	0.1134	5.3216

Analyzing the obtained through mercury porosimetry data, was observed that the porosity appreciated through the specific pores volume [ $\text{cm}^3/\text{g}$ ] present a higher value for the DR mortar samples with recycled aggregates in composition, followed by DP samples with recycled aggregated and powder obtained by grinding. The mortar samples with natural aggregates present the lowest porosities. The result are confirmed by the open porosity values evaluated by absorption of water in vacuum. The higher porosity for the samples with recycled aggregates in composition are explained by the increased content of the calcium hydrosilicate. The supplementary quantity of hydrosilicates from the mortar with recycled aggregates compared with mortar with natural aggregates is due to old cement paste attached to granules of natural aggregate from recycled aggregate. The gelic pores proportion in the three types of mortar is revealed by the results obtained through mercury porosimetry for pore diameter content in the range of 0.01–0.10  $\mu\text{m}$  as can be seen in Fig. 3.

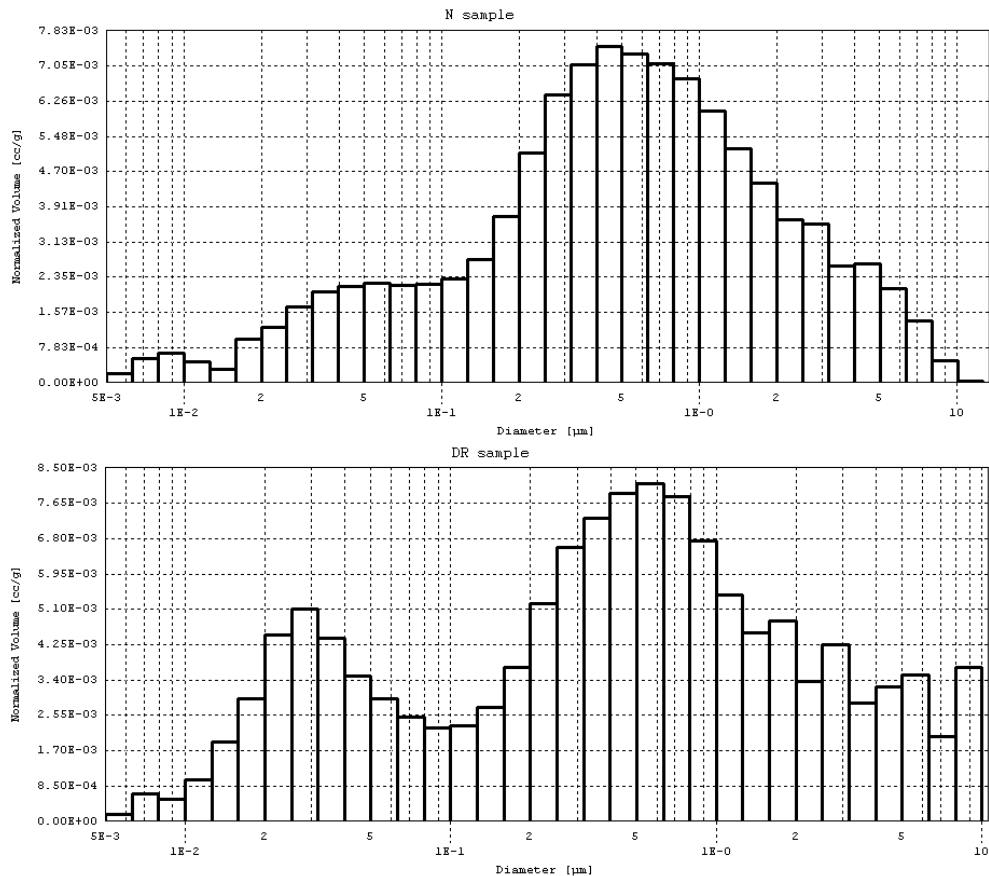


Fig. 3

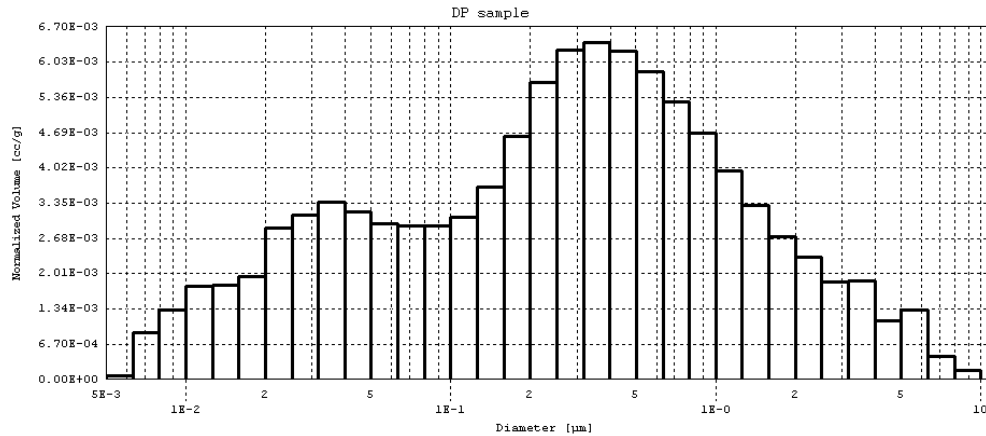


Fig. 3 (continued) – Normalized volume as a function of diameter for N, DR, DP samples obtained from mercury porosimetry technique.

The higher percentage of gelic pores, for samples with recycled aggregate, is highlighted by the total surface area of pores that is significantly higher in mortars with recycled aggregates compared with mortars made with natural aggregates. The presence of a higher content of fine particles in the DP mortar with recycled aggregates makes the contribution of the gelic pores to be lower than in DR mortars with recycled aggregates, due to the fine grinding of 0.10–0.15  $\mu\text{m}$  fraction.

For  $^{60}\text{Co}$  radionuclide, the leaching rate is lower, compared with  $^{137}\text{Cs}$ , and almost constant during the entire time period deemed. As Ochs and his colleagues observed [23],  $^{152}\text{Eu}$  radionuclide displays a limited (decreased) solubility in the cementation systems. The results of the experiments using  $^{152}\text{Eu}$  show that the europium ions are retained almost 100% by the calcium hydrosilicates in the cement matrix; this fact explain the lack of the  $^{152}\text{Eu}$  activity in the solution. The slope values ( $n$ ) indicate that the predominant leaching mechanism is surface washing for  $^{137}\text{Cs}$  and diffusion for  $^{60}\text{Co}$ .

### 3.4. APPARENT DIFFUSION COEFFICIENT

Long-term behavior of the radionuclides in the leaching process from the waste matrix can be evaluated by determining the apparent diffusion coefficient, calculated based on the Fick's second law applied for half-infinite environment. The apparent diffusion coefficient for  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  radionuclides is calculated using the return slope,  $m$ , of the linear regression line through data points in

$\sum \Lambda_n/\Lambda_i$  and  $\text{sqrt}(t)$  (Fig. 2). The formula used for the diffusion coefficient (leach coefficient),  $D$ , is defined as:

$$D = \frac{\pi}{4} m^2 \frac{V^2}{S^2}, \quad (3)$$

where:  $D$  is the diffusion coefficient [ $\text{cm}^2/\text{day}$ ];  $m$  is the slope ( $\sum \Lambda_n/\Lambda_i$ ,  $\text{sqrt}(t)$ ) [ $\text{d}^{-1/2}$ ];  $V$  is the sample volume [ $\text{cm}^3$ ] and  $S$  is the sample surface [ $\text{cm}^2$ ]. In Table 8 are presented the return slope,  $m$ , of the linear regression line through data points in  $\sum \Lambda_n/\Lambda_i$  and  $\text{sqrt}(t)$  for  $^{137}\text{Cs}$  and  $^{60}\text{Co}$ .

Table 8

The return slope ( $m$ ) of the linear regression line through data points in  $\sum \Lambda_n/\Lambda_i$  and  $\text{sqrt}(t)$

Sample	Curing time [days]	$m$	
		$^{137}\text{Cs}$	$^{60}\text{Co}$
		$t = 1, 2, 3, 4, 5, 6, 7$ days	
N	28	5.41E-02	9.37E-04
	56	2.16E-02	4.75E-04
DR	28	7.38E-02	1.06E-03
	56	4.81E-02	9.91E-04
DP	28	8.83E-02	1.20E-03
	56	5.41E-02	9.35E-04
$t = 15, 22, 30, 37, 45, 52, 60, 90$ days			
N	28	4.83E-03	3.52E-04
	56	4.27E-03	4.68E-04
DR	28	9.08E-03	5.03E-04
	56	7.11E-03	4.02E-04
DP	28	8.49E-03	5.14E-04
	56	1.04E-02	5.41E-04

Abdel-Rahman and his colleagues [24] showed that the average apparent diffusion coefficient has values generally in the range of  $10^{-5}$   $\text{cm}^2/\text{s}$  for mobile species, up to  $10^{-15}$   $\text{cm}^2/\text{s}$  for non-mobile species. Based on the average apparent diffusion coefficient, there can be determined the leachability index for the diffusing species. This is a material parameter used to categorize the effectiveness of a matrix material for waste cementation. The formula used for the leachability index,  $L$ , is defined as:

$$L = \log(D). \quad (4)$$

In Table 9 are presented the values of diffusion coefficients and leaching index.

Table 9

Values for diffusion coefficients ( $D$ ) and leaching index ( $L$ )

Sample	Curing time (days)	$D$ [ $\text{cm}^2/\text{day}$ ]		$L$	
		$^{137}\text{Cs}$	$^{60}\text{Co}$	$^{137}\text{Cs}$	$^{60}\text{Co}$
$t = 1, 2, 3, 4, 5, 6, 7$ days					
N	28	8.71E-09	2.61E-12	8.06E+00	1.16E+01
	56	1.42E-09	6.88E-13	8.85E+00	1.22E+01
DR	28	1.52E-08	3.12E-12	7.82E+00	1.15E+01
	56	6.57E-09	2.79E-12	8.18E+00	1.16E+01
DP	28	2.20E-08	4.07E-12	7.66E+00	1.14E+01
	56	8.43E-09	2.52E-12	8.07E+00	1.16E+01
$t = 15, 22, 30, 37, 45, 52, 60, 90$ days					
N	28	6.93E-11	3.69E-13	1.02E+01	1.24E+01
	56	5.57E-11	6.68E-13	1.03E+01	1.22E+01
DR	28	2.31E-10	7.06E-13	9.64E+00	1.22E+01
	56	1.44E-10	4.58E-13	9.84E+00	1.23E+01
DP	28	2.04E-10	7.48E-13	9.69E+00	1.21E+01
	56	3.10E-10	8.45E-13	9.51E+00	1.21E+01

The leaching index must have a minimum value of 6 for the material to be considered suitable for waste immobilization to prevent the radionuclides migration from concrete matrix. From the values obtained for the leaching index ( $L$ ) for all samples was noted that the cement matrix used for mortar preparation present hydraulic and chemical properties (leachability index  $> 6$ ); this make it to be suitable as a matrix material for wastes immobilization, for containers and for engineering barriers. The mortars prepared with natural aggregates and those obtained from recycled concrete (used in the present study) could be considered suitable for radionuclides immobilization in radioactive waste.

#### 4. CONCLUSIONS

The fixation of  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$  and  $^{152}\text{Eu}$  radionuclides for the mortars matrix obtained with natural fine aggregates and recycled fine aggregates was investigated. For the mortar samples cured for 28 days, the highest value of the leaching fraction was for the samples prepared with natural aggregates. Increasing the specific surface area of fine aggregates determine the increase of the leaching fraction value. From the experimental analysis was observed that for the mortar samples, the value of the radionuclides leaching rate varies inversely with the curing time. An increased curing time of mortars decreases the amount of chemically unbound water from the mortar and determine a higher degree of gelic calcium hydrosilicate crystallization. This explain the higher activity of

radionuclides in solutions in which the mortar has 28 days curing time, against those in which the mortar has 56 days of curing. In other words, increasing the time of mortar curing, the leachate activity for  $^{137}\text{Cs}$  radionuclide was decreased. Instead, for  $^{60}\text{Co}$  radionuclide, increasing of the curing time lead to a significant decrease in the amount of leaching function.

The pH and the conductivity have been measured for fresh demineralized water and for the leaching agent at the end of each leaching period. The data showed that the pH and the conductivity have a small effect on the final value of the leaching solution. Analyzing the leaching control mechanism, was established a balance between the ionic species presented in the pores of the mortar samples surfaces and the leached ions in solution. The results obtained for the mercury porosimetry study revealed an increase from N to DP and to DR type of mortar. As expected, the values porosity for mortar made with natural aggregates are low than those made with recycled aggregates. Besides the normal binding of pores in the mortar made with recycled aggregates, the increased porosity for this type of mortar is due to the mechanical cracks. The mercury porosity clearly indicates an increase contribution of gelic pores in mortar with recycled aggregates, but the gelic pores are water-repellent. Further migrations of radionuclides in solutions are controlled by a diffusion mechanism through the pores that determine the long-term leaching behavior for the materials. Long-term behavior of the radionuclides in the leaching process from the waste matrix was evaluated by determining the apparent diffusion coefficient.

Can be concluded that the recycle of radioactive concrete can be an effective solution to reduce the volume of waste, contributing in saving the natural resources and protect the environment.

**Acknowledgments.** This work was supported by the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, in the framework of 145/02.07.2012 project. The authors thank to L. Argatu, C. Mustata, E. Stefanescu, M. Mincu, I. Stoian and M. Stoian for their contributions in realization of this scientific research paper. In addition, the authors offer special thanks to Institute for Nuclear Research (ICN) Pitesti for offering support in evaluation of the pore volume and surface area through mercury porosimetry technique.

#### REFERENCES

1. I.B. Plecas, S.D. Dimovic, *Mathematical Modelling of Immobilization of Radionuclides  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  in Concrete Matrix*, The Open Waste Management Journal **2**, 43-46 (2009).
2. I. Plecas, I., *Leaching Study on the Process of Solidification of Radionuclide  $^{60}\text{Co}$  in Concrete*, Polish Journal of Environmental Studies **14**, 5, 699-701 (2005).
3. I. Plecas, *A Leaching Study in the Process of Solidification of Radionuclide  $^{137}\text{Cs}$  in Concrete*, Facta Universitatis Series: Working and Living Environmental Protection **8**, 1, 1-5 (2011).
4. N. Moriyama, S. Dojiri, H. Matsuzuru, *Leaching of  $^{137}\text{Cs}$  from the Ion-Exchange Resin Incorporated in Polyethylene or Cement Composite*, Health Physics **32**, 6, 549-552 (1977).

5. M.A. Geleel, S.T. Atwa, A.K. Sakr, *Removal of Cr (III) from aqueous waste using Spent Activated Clay*, Journal of American Science **9**, 2, 256-262 (2013).
6. N.M. Sami, A.M. El-Kamash, M.I. El-Dessouky, *Leaching Behaviour of  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  Radionuclides from Stabilized Waste Matrices*, Proceeding of First Environmental Conference, Zagazig Univ., 209-219 (2006).
7. M.A. Geleel, *New trend for incorporation of cobalt and cesium radionuclides in natural and thermal activated bentonite cement blends*, Nature and Science **8**, 10, 311-316 (2010).
8. E.D. Hespe, *Leach Testing of Immobilized Radioactive Waste Solids-A Proposal for a Standard Method*, At. Energy Rev. **9**, 1, 195-207 (1971).
9. R.H. Burns, *Solidification of Low-and Intermediate-Level Wastes*, At. Energy Rev. **9**, 547-599 (1971).
10. H. Matsuzuru, N. Moriyama, *Leaching of Radionuclides from a Cement Composite Incorporating Evaporator Concentrates Generated at a Pressurized Water Reactor Nuclear Power Plant*, Nuclear Science and Engineering **80**, 1, 14-25 (1982).
11. H. Matsuzuru, N. Moriyama, Y. Wadachi, A. Ito, *Leaching of  $^{137}\text{Cs}$  from the Ion-Exchange Resin Incorporated in Polyethylene or Cement Composite*, Health Physics **32**, 6, 529-552 (1977).
12. A.H. Lu, *Modeling of Radionuclide Migration from a low-level Radioactive Waste Burial Site*, Health Physics **34**, 1, 39-44 (1978).
13. I. Plecas, A. Peric, J. Drljaca, S. Glodic, A. Kostadinovic, *Effect of curing time on the fraction of  $^{60}\text{Co}$  and  $^{137}\text{Cs}$  leached from cement matrix*, Cement and Concrete Research **25**, 2, 311-313 (1995).
14. I. Plecas, U. Kozmidis-Luburic, R. Pesic, *Mathematical Modelling of Transport Phenomena in Radioactive Waste-Cement-Bentonite Matrix*, World Academy of Science, Engineering and Technology International Journal of Physical, Natural Science and Engineering **5**, 4, 1-3 (2011).
15. R. Deju, I. Robu, M. Dragusin, C. Mazilu, C. Tuca, *Selection tests for recycled radioactive sand obtaining method*, Rom. Rep. Phys. **67**, 2, 673-692 (2015).
16. K. Anderson, B. Torstenfelt, B. Allard, *Sorption and diffusion studies of Cs and I in concrete*, Technical Report, Chalmers University of Technology, Goteborg, Sweden, 1981.
17. F.P. Glasser, A.A. Rahman, R.W. Crawford, C.E. McCulloch, M.J. Angus, *Immobilization and Leaching Mechanisms of Radwaste in Cement-based Matrices*, CEC/DOE Report, DOE/RW/82.050, 919820 (1982).
18. O. Sima, D. Arnold, C. Dovlete, *GESPECOR: A versatile tool in gamma-ray spectrometry*, J. Radioanal. Nucl. Chem. **248**, 359-364 (2001).
19. C.E. McCulloch, M.J. Angus, R.W. Crawford, A.A. Rahman, F.P. Glasser, *Cements in Radioactive Waste Disposal: Some Mineralogic Considerations*, Mineralogical Magazine **49**, 211-221 (1985).
20. H.A. Friedman, A.D. Kelmers, *Investigation of Leaching of Radionuclides and Hazardous Materials from Low Level Wastes at Oak Ridge National Laboratory*, ORNL/TM-9883 Report (1987).
21. C.V. McIsaac, D.W. Akers, J.W. McConnell, N. Morcos, *Leach Studies on Cement-Solidified Ion Exchange Resins from Decontamination Processes at Operating Nuclear Power Stations, Waste management '92: working towards a cleaner environment: Waste processing, transportation, storage and disposal, technical programs and public education*, Vols. 1 and 2, Technology and programs for radioactive waste management and environmental restoration, IAEA Proceedings, 1643-1650 (1992).
22. A. Konin, D.M. Kouadio, *Influence of Cement Content on Recycled Aggregates Concrete Properties*, Modern Applied Science **5**, 1, 23-31 (2011).
23. M. Ochs, D. Hager, S. Helfer, B. Lothenbach, *Solubility of Radionuclides in Fresh and Leachewd Cementitious Systems at 22 °C and 50 °C*, Mat. Res. Soc. Symp. Proc. **506**, 773-780 (1998).
24. R.O. Abdel Rahman, A.A. Zaki, A.M. El-Kamash, *Modeling the long-term leaching behavior of  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$  and  $^{152,154}\text{Eu}$  radionuclides from cement-clay matrices*, Journal of Hazardous Materials **145**, 372-380 (2007).