

The Long-Term Leaching Behaviour of ^{137}Cs , ^{60}Co and ^{152}Eu Radionuclides Incorporated in Mortar Matrices Made from Natural Aggregates and Recycled Aggregates

R. Deju, M. Mincu, D. Gurau

Abstract—During the interim storage or final disposal of low level waste, migration/diffusion of radionuclides can occur when the waste comes in contact with water. The long-term leaching behaviour into surrounding fluid (demineralized water) of ^{137}Cs , ^{60}Co and ^{152}Eu radionuclides, artificially incorporated in mortar matrices made from natural aggregates (river sand) and recycled radioactive concrete was studied. Results presented in this work are obtained in two years of mortar testing and will be used for the safety increasing in the storage of low level radioactive waste. The study involved the influence of curing time, type and size distribution of the aggregates on leaching behaviour. The mortar samples were immersed in distilled water for 30 days. The leached activity of the mortar samples was measured on samples from the immersing water and analyzed through a gamma-ray spectrometry method using an HPGe detector with a GESPECOR code for efficiency evaluation. The long-term leaching behaviour of the radionuclides was evaluated from the leaching data calculating the apparent diffusion coefficient.

Keywords—Leaching behaviour, recycling of radioactive concrete, waste management, gamma-ray spectrometry.

I. INTRODUCTION

THE VVR-S nuclear research reactor owned by Horia Hulubei National Institute of Physics and Nuclear Engineering (IFIN-HH) from Magurele-Bucharest, is the first major nuclear facility from Romania involved in the decommissioning project. The reactor was open in 1957 and shut down in 1997. The decommissioning project was started in 2010 and is being planned to be finalized in 2020. During the decommissioning project, a large amount of radioactive concrete waste will be generated from the dismantled structures of the VVR-S RN (biological shield of the reactor core and hot cells) [1]. According with the International Atomic Energy Agency (I.A.E.A) Safety Standards of the radioactive waste classification implemented in Romania by National Commission for Nuclear Activities Control (C.N.C.A.N) by Order 156/2005 - NDR-03 (radioactive waste classification norms) the radioactive waste resulted from decommissioning are classified as in [2], [3]: (i) exempt waste

(EW), (ii) very short lived waste (VSLW), (iii) very low level waste (VLLW), (iv) low level waste (LLW), (v) intermediate level waste (ILW), (vi) high level waste (HLW) [2], [3].

The radioactive concrete generated from the decommissioning, represents about 6.5% from the total amount of concrete waste. The final disposal of these types of materials will decrease the final storage capacity having a high cost and a lower economic feasibility. In these times, the LLW are pre-placed in block form in containers and consolidated with mortar made from fine natural aggregates. This method provides a level of filling with the LLW from concrete approximately 50% of the container volume. The concrete solidification of radioactive waste is the most popular method because of the low cost and well-known technology [4]-[6].

The recycling of the radioactive concrete can be a major solution for reducing the volume of waste and can contribute to the saving of the natural resources and environmental protection. This will provide a level of filling with radioactive waste of 75% from the container volume. In this way, the final disposal of the total amount of the radioactive waste will decrease significantly with benefic economic effects [4]-[7].

During the disposal of the radioactive waste, solidified with mortar obtained from recycling of the radioactive concrete, can occur leaching of the radionuclides in contact with water from the environment, thus, the radionuclides are transported into the soil/surrounding structures due to dissolution or chemical reaction with the chemical components of water.

This work presents the continuing research done in more than two years for mortar testing [4]-[7], from 90 days to 840 days, done to increase the safety in the storage of the LLW. A first part of the study, for the period starting from the 1st day until the 90th day, was published by Deju et al. [4].

Following, the leaching rate calculation on short time periods can be estimated for the long-term leaching behaviour of ^{137}Cs , ^{60}Co and ^{152}Eu radionuclides incorporated in mortar matrices made from natural aggregates (river sand) and recycled radioactive concrete.

The recovery of coarse and fine aggregate from radioactive concrete waste and their recycling was studied in the framework of 145/02.07.2012 project, under the Romanian National Authority for Scientific Research.

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II. SAMPLE PREPARATION AND MEASUREMENT

Radioactive mortar samples made from natural and recycled aggregates, marked as N, DR and DP were used for achieving the leaching experiments [4], [5]. Radioactive solution containing ^{137}Cs , ^{60}Co and ^{152}Eu radionuclides were incorporated in the composition of the samples that were cured at 25 °C for 28 days and 56 days [4]-[7]. Each sample was exposed entirely to the leaching agent. Month after month, at exactly 30 days, the agent was transferred in cylindrical PE containers with sealed leads and then replaced with fresh distilled water with identical volume. The leaching activity of the mortar matrices was measured on samples for a period between 90 days to 840 days, from the immersing water. Gamma-ray spectrometry system with HPGe detector (model GEM60P4-95) and a DSPEC jr. 2.0 Digital Gamma-Ray Spectrometer was used for identification and quantification of gamma emitting radionuclides in concrete samples and leaching agent. GESPECOR simulation code was used to evaluate the efficiency for dedicated geometries based on a detector characterization process with point sources [8].

III. RESULTS AND DISCUSSIONS

To assess the safety disposal of radioactive waste material in mortar matrices, the influence of type and size distribution of the aggregates and the curing time on leaching behaviour [9]-[12] was studied.

A. Type and Size Distribution of Aggregates

The leaching fraction was studied for N, DR and DP samples cured for 28 days. Because ^{152}Eu have a decreased solubility in the cementation matrix, the europium ions are retained almost 100% by the calcium hydro-silicates. This was proved by the lack of the ^{152}Eu in the leaching agent.

In Fig. 1 (a) are presented the leach rates for N, DR and DP mortar samples versus square root of time, for ^{137}Cs and ^{60}Co .

After 840 days, was observed that the leaching fraction values are higher for DR and DP samples compared with N samples by up to 33% and 37% for ^{137}Cs and up to 8% and 12%, respectively, in the case of ^{60}Co . The presence of the <150 μm milled fraction in the DP samples increases the leaching fraction compared to DR samples. Also, it was observed that the leaching fraction for ^{137}Cs radionuclide has more a linear dependence versus square root of time in comparison with ^{60}Co radionuclide, where the dependence is more continuous slight increasing. Because there were two sets of samples for each type of matrix and for each radionuclide, the best fit to these data points is the polynomial one. The polynomial model used for fitting was:

$$y = \text{Intercept} + B_1x^1 + B_2x^2 + B_3x^3 + B_4x^4 \quad (1)$$

where: the input x data source are the \sqrt{t} values, the input y data source are the leaching fraction values and *Intercept*, $B_{1..4}$ are the polynomial constants.

Next, in Table I are presented the differences between the leaching fraction values for DR and DP samples compared

with N samples, for ^{137}Cs and ^{60}Co for one to 90 days and 90 to 840 days.

It was observed that after more than two years, the discrepancies between the leaching fraction values for DR and DP samples in comparison with N samples are still big in the case of ^{137}Cs radionuclide than the ^{60}Co situation.

TABLE I
LEACHING FRACTION DIFFERENCES FOR DR AND DP SAMPLES IN COMPARISON WITH N SAMPLES

Period (days)	Leaching fraction difference (%)			
	^{137}Cs		^{60}Co	
	DR	DP	DR	DP
1-90	34	40	21	29
90-840	33	37	8	12

B. Curing Time

In Fig. 1 (b) are presented the leaching fraction values for samples cured for 56 days compared with those cured for 28 days, for N, DR and DP samples, for ^{137}Cs and ^{60}Co .

TABLE II
THE VALUES OF pH FOR THE LEACHING AGENT

t (days)	pH					
	28 days			56 days		
	N	DR	DP	N	DR	DP
90	7.96	7.97	7.61	7.82	8.06	7.80
120	7.86	7.80	7.61	8.02	8.00	8.03
150	7.94	7.77	7.55	7.90	7.68	7.99
180	7.84	7.65	7.67	7.90	7.72	7.63
210	7.77	7.68	7.71	7.91	7.62	7.77
240	7.56	7.74	7.68	7.97	7.97	7.72
270	7.92	7.82	7.91	7.89	7.96	7.72
300	7.68	7.76	7.96	7.76	7.86	7.70
330	7.61	7.84	7.84	7.64	7.83	7.69
360	7.72	7.82	7.74	7.69	7.74	7.71
390	7.68	7.85	7.82	7.66	7.75	7.69
420	7.88	8.11	8.13	7.85	8.10	8.01
450	8.01	8.18	8.18	7.96	8.08	7.99
480	7.82	8.07	8.06	7.89	8.11	7.99
510	7.94	8.10	8.10	8.01	8.08	8.07
540	8.01	8.15	8.17	8.02	8.16	8.14
570	8.07	8.03	8.22	8.02	8.17	8.15
600	8.07	8.22	8.19	8.10	8.18	8.14
630	8.21	8.17	8.20	8.07	8.21	8.18
660	8.18	8.22	8.19	8.08	8.17	8.18
690	8.09	8.15	8.15	8.06	8.12	8.21
720	8.09	8.17	8.09	8.04	8.13	8.06
750	8.12	8.13	8.05	8.06	8.12	8.13
780	8.11	8.11	8.17	8.06	8.13	8.13
810	8.16	8.16	8.12	8.07	8.13	8.14
840	8.13	8.13	8.15	8.04	8.13	8.10

It was observed that in the case of ^{137}Cs , the discrepancies between the samples cured for 28 days and those cured for 56 days are evident with a tendency to become smaller; instead for the case of ^{60}Co , these are comparable.

From the analysis of the experimental data obtained for the leaching fraction vs. \sqrt{t} , for the 90-840 period of time, it

was observed that for ^{137}Cs radionuclide, the leaching fraction has more a linear growth in comparison with the ^{60}Co

radionuclide, where there is more an exponential growth trend.

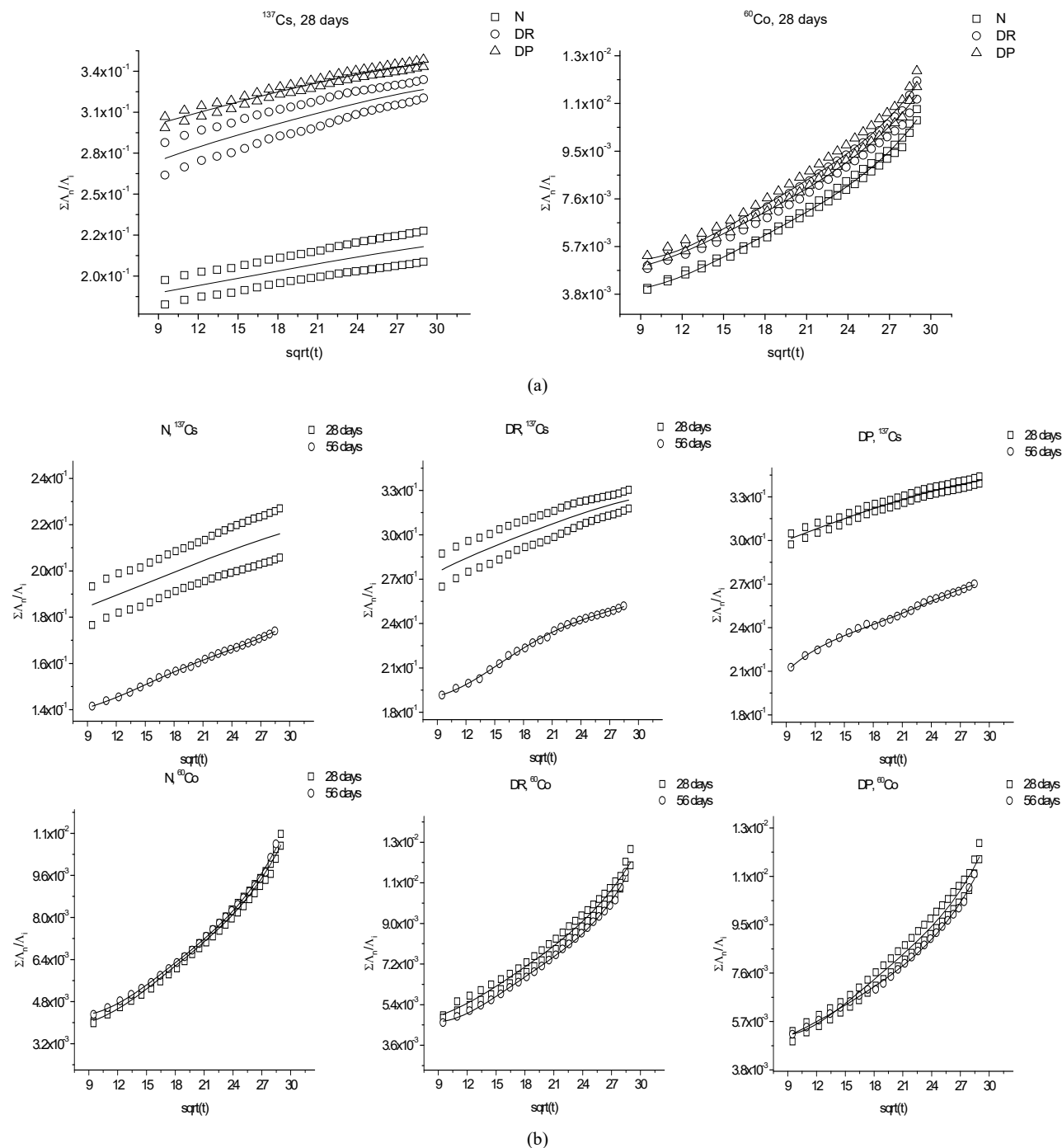


Fig. 1 The leaching vs. \sqrt{t} for 90-840 days, for N, DR and DP samples, (a) cured for 28 days, (b) cured for 28 days in comparison with those cured for 56 days, for ^{137}Cs and ^{60}Co radionuclides

C. Leachate pH and Conductivity

The pH of the leaching agent is very important in determining the radionuclide release process. In Table II, are

presented the values of pH vs. time, for the N, DR and DP samples cured for 28 days and 56 days, respectively.

From the leaching experiments that were carried out, it was observed that the pH values are around 7.80 for 90-390 days,

which is followed by a slight increase to 8.10 for 390-840 days. Because the dissolution of most minerals and also the sorption process are depending on pH, this influences the release process of radionuclides in the leaching agent.

The differences between the studies done for the 1-90 days [4] and 90-840 days periods is that in the first study it was observed that pH values were higher in the first 30 days, then a slight decrease was observed. This was thought to be due to the large amount of calcium hydroxide existent in the waste. The chemical form of a contaminant determines its characteristic leaching behaviour. These contaminants may be in the oxidized or reduced form which is important for their leaching behaviour.

In Table III are presented the values of conductivity vs. time, for the N, DR and DP samples cured for 28 days and 56 days, respectively. The data showed that the conductivity has no effect on the final value of the leaching agent. The decreasing of pH and conductivity values vs. time may be due to the fact that the radionuclides are bound on the hydroxyl calcium salts formed in the matrix of the mortar samples.

TABLE III
THE VALUES OF CONDUCTIVITY FOR THE LEACHING AGENT

t (days)	Conductivity (μS/cm)					
	28 days			56 days		
	N	DR	DP	N	DR	DP
90	160.4	162.4	131.6	134.9	160.0	136.0
120	164.1	155.0	139.0	176.5	185.5	179.0
150	168.8	128.3	130.5	172.6	147.8	193.4
180	170.7	117.7	123.2	149.1	139.4	144.4
210	114.0	105.1	108.5	135.0	109.3	113.6
240	157.3	113.6	106.1	132.3	140.6	124.9
270	127.4	102.2	98.6	130.4	109.6	121.9
300	124.3	118.1	111.7	152.1	122.8	124.4
330	126.8	118.6	112.7	117.2	117.1	118.7
360	115.8	123.5	117.9	120.9	115.2	109.4
390	108.2	120.8	115.8	119.9	127.1	110.7
420	117.1	119.4	120.6	116.6	116.9	111.7
450	115.9	123.4	119.5	122.4	112.1	115.4
480	106.6	115.4	111.8	114.3	134.3	108.9
510	93.2	100.4	96.9	94.3	98.9	91.2
540	94.9	106.0	103.5	93.2	107.9	112.9
570	98.1	108.2	105.0	92.5	106.0	102.7
600	110.4	115.4	111.7	100.1	111.6	108.2
630	106.8	115.6	109.4	100.0	110.7	103.7
660	106.2	114.7	111.0	98.9	108.4	106.0
690	112.0	117.5	112.7	103.7	111.4	107.9
720	105.8	111.8	106.8	100.3	104.7	101.8
750	118.6	111.1	110.2	94.1	107.9	105.9
780	122.0	120.2	118.9	100.2	119.8	114.0
810	122.5	121.8	117.0	107.1	114.8	113.5
840	129.3	121.9	117.8	103.5	117.3	119.3

D. Leaching Control Mechanism

The controlling leaching mechanism was calculated based on the slope (n) of the linear regression of the log(CLF) versus log(t) [4]. The slope was considered to be the vertical distance divided by the horizontal distance between any two points on

the line, which is the rate of change along the regression line. The next equation was used:

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

where: x and y are the sample means of all $\log(t)$ and $\log(CLF)$ value averages.

CLF is the cumulative leach fraction and was evaluated with [4]:

$$CLF = \frac{\sum \Lambda_n / \Lambda_i}{V/S} \quad (3)$$

where: Λ_i is the initial activity of the sample at zero time (Bq); Λ_n is the activity leached out from the sample after the leaching time (Bq); V is the sample volume (cm^3); S is the sample surface (cm^2); and, t is the renewal period of leaching agent; every month, at exactly 30 days.

The cumulative leach fraction (CLF) was measured to find the leaching rate of ^{137}Cs and ^{60}Co radionuclides of potential concern from immobilized matrix under continuously saturated condition.

In Table IV are presented the results obtained for the 90-840 days for the return slope (n).

TABLE IV
THE RETURN SLOPE (n) OF LINEAR REGRESSION LINE THROUGH DATA POINTS IN LOG (CLF) AND LOG (t)

Sample	Curing time (days)	n	
		^{137}Cs	^{60}Co
		t=90÷840 days	
N	28	9.44E-05	5.54E-04
	56	1.17E-04	5.19E-04
DR	28	8.44E-05	4.71E-04
	56	1.57E-04	4.98E-04
DP	28	6.66E-05	4.72E-04
	56	1.24E-04	4.40E-04

The salt concentration of the solution in the product may influence the solubility of other components present in the leaching agent and can cause enhanced leaching due to the complexation, such as metal complexes with chloride or carbonates.

TABLE V
THE RETURN SLOPE (m) OF THE LINEAR REGRESSION LINE THROUGH DATA POINTS IN $\sum \Lambda_n / \Lambda_i$ AND SQRT(t)

Sample	Curing time (days)	m	
		^{137}Cs	^{60}Co
		t=90÷840 days	
N	28	1.59E-03	3.38E-04
	56	1.70E-03	3.29E-04
DR	28	2.39E-03	3.42E-04
	56	3.27E-03	3.30E-04
DP	28	2.03E-03	3.55E-04
	56	2.81E-03	3.11E-04

E. Apparent Diffusion Coefficient

The diffusion is defined as the transport of constituents caused only by the movement of molecules in the absence of flow. This generally plays a role for compacted materials that have a very low permeability and porosity. The release will still occur but on the basis of transport by diffusion. Considering those circumstances, the diffusion can be the limiting transport step before constituents can be taken along due to further advection. The rate of diffusion is dependent on the gradient of the constituent between the product and the contacting water phase, and is time dependent. The long-term behaviour of the ^{137}Cs and ^{60}Co radionuclides in the leaching process from the concrete matrices can be evaluated by determining the apparent diffusion coefficient. This can be calculated using the return slope (m) of the linear regression line through data point in $\sum \Lambda_n/\Lambda_i$ and $\text{sqrt}(t)$ (Fig. 1 (b)).

The values of the return slope (m) are presented in Table V for ^{137}Cs and ^{60}Co for 90-840 days.

The next formula was used to evaluate the diffusion coefficient, D :

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

where: D is the diffusion coefficient (cm^2/day); m is the slope ($\sum \Lambda_n/\Lambda_i$, $\text{sqrt}(t)$) ($\text{d}^{-1/2}$); V is the volume of the sample (cm^3); S is surface of the sample (cm^2). In Table VI are presented the values obtained for the diffusion coefficients for ^{137}Cs and ^{60}Co radionuclides for 90-840 days.

TABLE VI
VALUES FOR DIFFUSION COEFFICIENTS (D)

Sample	Curing time (days)	D (cm^2/day)	
		^{137}Cs	^{60}Co
		$t=90\div840$ days	
N	28	7.53E-12	3.40E-13
	56	8.85E-12	3.29E-13
DR	28	1.59E-11	3.27E-13
	56	3.03E-11	3.10E-13
DP	28	1.16E-11	3.56E-13
	56	2.27E-11	2.80E-13

The diffusion coefficients were calculated for both radionuclides for N, DR and DP samples cured for 28 days and 56 days. The data indicated that ^{137}Cs have largest values of diffusion coefficients in all cement matrices compared to ^{60}Co nuclide.

TABLE VII
VALUES FOR LEACHING INDEX (L)

Sample	Curing time (days)	L	
		^{137}Cs	^{60}Co
		$t=90\div840$ days	
N	28	1.11E+01	1.25E+01
	56	1.11E+01	1.25E+01
DR	28	1.08E+01	1.25E+01
	56	1.05E+01	1.25E+01
DP	28	1.09E+01	1.24E+01
	56	1.06E+01	1.26E+01

F. Leachability Index

Considering the average apparent diffusion coefficient, the leachability index for the diffusing species can be determined. This material parameter is used to categorize the effectiveness of a matrix material for waste cementation. To evaluate the leachability of a diffusing species, a leachability index L can be defined as:

$$L = \log(D) \quad (5)$$

Rahman et al. [13] proposed a uniform scale of the contaminants relative mobility (leaching index value varies from 5, very mobile, to 15, immobile).

Because the leach index is based on a logarithmic relationship, each unit change in the leach index is a change in the effective diffusion coefficient of a factor of 10. The higher the value for the leach index, the better the resistance of the matrix form toward leaching of that matrix species.

In Table VII are presented the values of the leaching index.

IV. CONCLUSION

In this study, the fixation of ^{137}Cs , ^{60}Co and ^{152}Eu radionuclides into the mortar matrix was investigated. The samples were made with natural and recycled fine aggregates and were cured for 28 days and 56 days. The leaching control mechanism was analyzed for the 90-840 day period. In general, the leaching behaviour can be explained as a combination of two processes: The surface wash-off mechanism and the diffusion stage mechanism. A maximum leaching of the ions caused by the surface wash-off process was observed in the first stage of the study, in the 1-90 day period, when a rapid equilibrium was established between the ionic species presented in the pores from the thin external edge of the N, DR and DP samples and the ions from the leaching agent. When each ion leached out from the surface of the sample, it migrates by longer pathways from the bulk through diffusion-controlled stage, which determines the long term leaching behaviour, like in the 90-840 days period study. The leaching process was assumed to be a diffusion controlled process. The mechanism of the diffusion process was very difficult to analyze due to the presence of many variables which can affect the rate of leaching. These can be: the matrix composition, the temperature, the chemical nature of the leaching agent, the chemical nature of the elements that are diffused out, and the radiation effects, etc.

When the concrete samples come in contact with the leaching agent, the movement of soluble materials from the solid sample to the surrounding water was caused by the dissolution or chemical reaction with the chemical component contained in the leaching agent. The ^{137}Cs and ^{60}Co radionuclides and salts form a chemical bondage with the concrete components, or they exist depressively in the state of sole crystals.

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