60

S. D. Dimović.: Influence of Bentonite and Zeolite on Cs$^+$ and Co^{2+} Cement ...
Nuclear Technology & Radiation Protection: Year 2021, Vol. 36, No. 1, pp. 60-65

INFLUENCE OF BENTONITE AND ZEOLITE ON Cs$^+$ AND Co^{2+} CEMENT MATRIX LEACHING PHENOMENA

by

Slavko D. DIMOVIĆ, Ivana V. JELIĆ*, and Marija Z. ŠLJIVIĆ-IVANOVIĆ

Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia,
University of Belgrade, Belgrade, Serbia

The probability of Cs$^+$ and Co^{2+} ions retention by immobilization processes in the cement matrix was determinate as the subject of analyses: matrix design, water/cement ratio, and structure porosity. Comparison of experimental results was accomplished by Hespe standard leaching method. Diffusion and semi-empirical models were used for the assessment of the washing rate as a function of time. The higher value of cement matrix mechanical resistance corresponds to a lower value of Co^{2+} and Cs$^+$ ions leaching. The Co^{2+} leaching level was more than two orders of magnitude less than the leaching level of Cs$^+$. The influence of bentonite and zeolite on Co^{2+} leaching reduction was significantly smaller in comparison with Cs$^+$, while zeolite had a higher Cs$^+$ and Co^{2+} sorption ability than bentonite. Under static leaching conditions, the contribution of diffusion to the total transport of ions in the matrix porous medium was dominant. The contribution of matrix dissolution was insignificant concerning the dominant contribution of diffusion and surface washing. The semi-empirical model showed a better approximation of the Co^{2+} and Cs$^+$ ions laboratory leaching process.

Key words: leaching, immobilization, sorption, radioactive waste

INTRODUCTION

Liquid and solid radioactive waste (RW) is generated in the processes of the nuclear fuel cycle, the industry of exploitation, processing, and enrichment of uranium ore, the activity of reactors of nuclear power plants and research centers, application of radionuclides in research institutes, hospitals and industry [1, 2]. Furthermore, RW pollutants are mainly β/γ emitters that occur in the form of activated corrosive products (^{60}Co and ^{54}Mn) or fission products (^{137}Cs and ^{90}Sr). To facilitate immobilization of the RW, the solidification of the concentrate is achieved by binding to inactive matrices: generally, cement bitumen, polymeric materials, and glass. Cement has several unfavorable characteristics as a solidifying material, *e. g.* low volume reduction and relatively high leachability, but it keeps many practical advantages such as good mechanical characteristics, low cost, easy operation, and thermal and radiation stability.

The probability of radionuclides retention by immobilization processes in the cement matrix was determinate as the subject of analyses: cement matrix formulation, water/cement ratio, and structure porosity. The comparison of the different leaching results could be ac-

complished by the implementation of the standard leaching method by Hespe [3], which was approved by the International Atomic Energy Agency (IAEA).

The diffusion model is used to study the transport phenomenon in order to predict the leaching rate as a function of time, and numerous mathematical analyses are available [4, 5]. The assumptions and boundary conditions that must be implemented for the diffusion model application make sense in the experimental static conditions, if a successive change-renewal of the leaching solution is carried out, where the concentration of Cs$^+$ and Co^{2+} ions in the liquid phase is negligible compared to the solid phase [6, 7]. If the experimental data are obeyed by linear dependence, diffusion is the dominant mechanism in the process of separating the radionuclide from the cement matrix. The corresponding differential equations solution could be presented as the effective diffusion coefficient, D_e, calculated by the slope of the right, m, from the graphics of cumulative leaching fraction of Cs$^+$ and Co^{2+} ions as a time, t, function [4-7]

$$\frac{C_n}{C_0} \quad \frac{V}{S} \quad f(\sqrt{t}) \qquad (1)$$

$$D_e \quad \left(\frac{m}{2}\right)^2 \pi \, [\mathrm{cm^2 d^{-1}}] \qquad (2)$$

---

* Corresponding author; e-mail: ivana.jelic@vin.bg.ac.rs

where C_0 [mgdm^{-3}] – represents the initial concentration of Cs^+ and Co^{2+} ions in the matrix, V [cm^3] – denotes a volume of the sample exposed to distilled water, S [cm^2] – a total surface area exposed to distilled water, and C_n [mg dm^{-3}] represents a concentration of Cs^+ and Co^{2+} ions in the leaching solution according to its nth variation.

Via the leaching cumulative fraction as a time function, it could be differentiated into three mechanisms: diffusion, dissolution, and surface wash off [8]. The mathematical model concerning all three leaching mechanisms is quite complex, while obtained results have very limited practical application. To overwhelm this issue, a semi-empirical model is approved, based on an orthogonal-polynomial equation, which describes leaching waste constituents immobilized in a solid matrix over a long period of time [9]. The leaching cumulative fraction is expressed according to this model

$$\frac{C_n}{C_0} = K_1 + K_2 t^{1/2} + K_3 t \qquad (3)$$

where K_1 is a constant that represents the contribution of surface wash-out to radionuclide transport, K_2 [s$^{-1/2}$] – the contribution of diffusion to the radionuclides transport, K_3 [s^{-1}] – the contribution of a kinetically controlled solution to the radionuclides transport, and the t [s] – the experiment time-span.

EXPERIMENTAL PART

Preparation of cement matrix

The defined composition of the cement matrix (M) with proportion variations of bentonite (MB) or zeolite (MZ), along with the initial Cs^+ and Co^{2+} ions concentration, C_0, of 457 and 819 mg dm^{-3}, respectively, are listed in tab. 1.

Materials of the cement matrix are:
– Portland cement, PC-35 (MPa), manufacturer lafarge,
– Sand *Moravac*, granulate 2 mm,
– Sludge, density ρ_{sludge} = 1.075 gcm^{-3},
– Bentonite, origin Koceljevo mine, Šabac, granulate 200 µm – 250 µm,
– Zeolite, origin Zlatokop mine, Vranjska Banja, granulate 200 µm – 250 µm.

The materials were treated in a planetary mixer to achieve a degree of viscosity that ensures the trans-

fer of the cement matrix to the prepared molds. The duration of mixing after the batch was limited to 15 minutes, generally 5 minutes after achieving the required degree of viscosity. The rotational speed of the mixer was limited to n_1 = 75 rpm while the batch counter was limited to n_2 = 35 rpm.

Investigation of cement matrix mechanical resistance

After cement matrices drying period of 28 days in laboratory conditions, their mechanical resistance was tested by the compressive strength determination. The tested cement matrices samples were cube-shaped with a dimension of 10 cm, while a hydraulic press, in the range 0-140 MPa, was used. The uniaxial compressive strength of these samples was determined following the ASTM standards.

Investigation of leaching in static conditions

Investigation of leaching in static conditions for Co^{2+} and Cs^+ ions immobilized in the cement matrix was performed by the standard Hespe method [3]. The ortho-cylinder, $H = 2r = 4.5$ cm sample was completely immersed in 0.4 L distilled water at temperature $T = 25 \pm 5$ °C. The leaching solution was exchanged after 1st, 2nd, 3rd, 4th, 5th, 6th, 7th, 14th, 21st, 28th, 35th, 42nd, 50th, 63rd, and 93rd day and any change in the leaching solution represented an incremental contribution to the total ions discharge. The concentration of leached metal ions Co^{2+} and Cs^+ was measured by the AAS method using Perkin Elmer Analyst 200.

RESULTS AND DISCUSSION

With the increase of the bentonite and zeolite content, the cement matrix reduced their mechanical resistance, tab. 2, as expected [10, 11]. As a material, zeolite is harder, more compact than bentonite, does not swell in the presence of water, and thus does not negatively affect the structure of the cement matrix. Owing to these properties, the cement matrix containing zeolite has a slightly higher mechanical resistance than the cement matrix with the same bentonite content.

Table 1. Cement matrix composition for the samples V = 1 dm^3 production

Composition [g]	Cement matrix						
	M	MB$_2$	MB$_5$	MB$_{10}$	MZ$_2$	MZ$_5$	MZ$_{10}$
Cement	1000	1000	1000	1000	1000	1000	1000
Sludge	500	500	500	500	500	500	500
Sand	600	580	550	500	580	550	500
Bentonite	0	20	50	100	0	0	0
Zeolite	0	0	0	0	20	50	100

Table 2. Cement matrix mechanical resistance obtained by compressive strength determination

Cement matrix							
	M	MB$_2$	MB$_5$	MB$_{10}$	MZ$_2$	MZ$_5$	MZ$_{10}$
Compressive strength [MPa]	25.3	24.0	23.7	19.2	24.6	22.2	21.7

62

S. D. Dimović.: Influence of Bentonite and Zeolite on Cs$^+$ and Co^{2+} Cement ...
Nuclear Technology & Radiation Protection: Year 2021, Vol. 36, No. 1, pp. 60-65

Leaching and mechanical resistance represent the correlated parameters. The higher value of mechanical resistance corresponds to a lower leaching level [12]. The leaching of Cs$^+$ and Co^{2+} immobilized in all cement matrix types under static conditions is shown in figs. 1-6.

The leaching level of Co^{2+} ions was more than two orders of magnitude lower than the leaching level of Cs$^+$ as expected [13]. As a result of the high cement matrix alkalinity (pH > 10), the Co^{2+} ions react with the hydroxide ions, forming a cobalt-hydroxide that could previously react with CO$_2$ and create soluble cobalt-carbonate [14]. Cobalt also could be exchanged
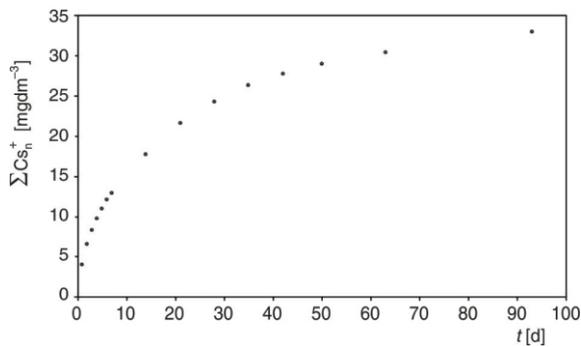
Figure 1. Leaching of Cs$^+$ immobilized in the cement matrix M (○) under static conditions
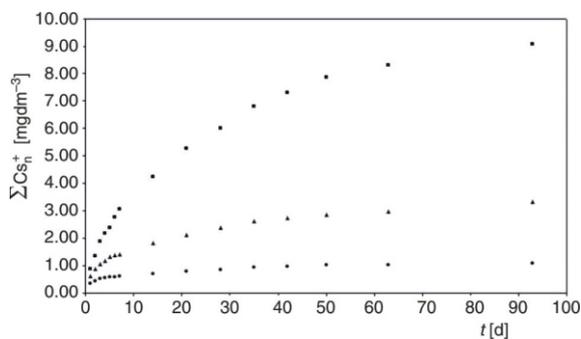
Figure 2. Leaching of Cs$^+$ immobilized in the cement matrix: MB$_2$ (■), MB$_5$ (▲), and MB$_{10}$ (●) under static conditions
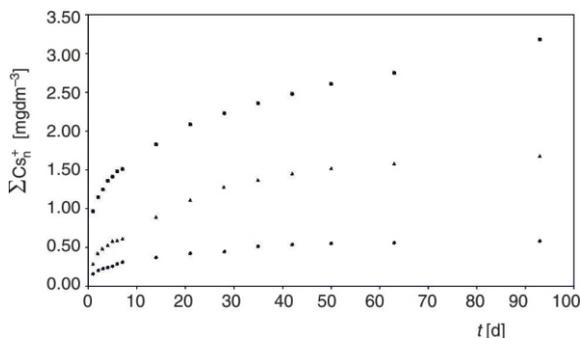
Figure 3. Leaching of Cs$^+$ immobilized in the cement matrix: MZ$_2$ (■), MZ$_5$ (▲), and MZ$_{10}$ (●) under static conditions
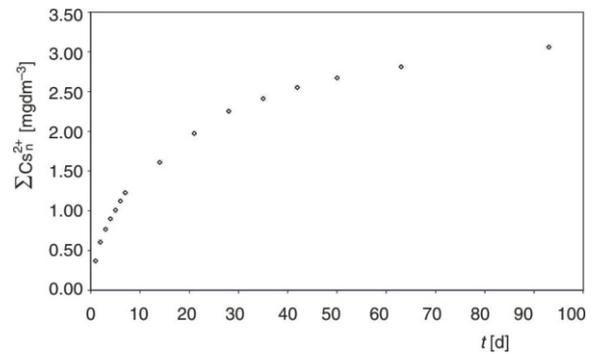
Figure 4. Leaching of Co^{2+} immobilized in the cement matrix M (◇) under static conditions
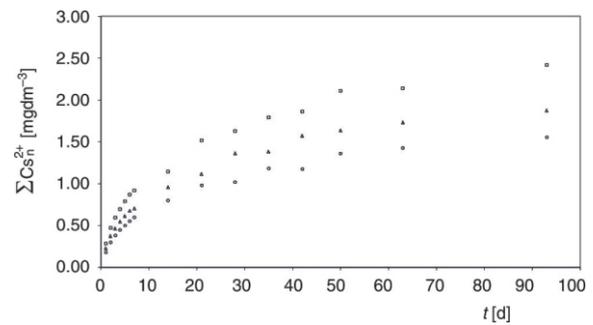
Figure 5. Leaching of Co^{2+} immobilized in the cement matrix: MB$_2$ (□), MB$_5$ (△), and MB$_{10}$ (○) under static conditions
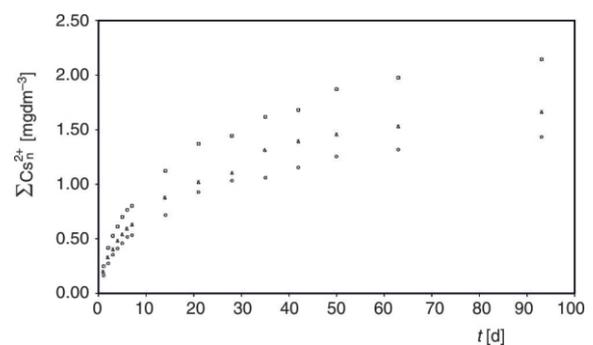
Figure 6. Leaching of Co^{2+} immobilized in the cement matrix: MZ$_2$ (□), MZ$_5$ (△), and MZ$_{10}$ (○) under static conditions

with calcium cations in the C-S-H gel, creating analogous cobalt complex salts and becoming a constituent of the cement matrix structure. On the contrary, since cesium hydrolyzes in solution and is present in the free cationic form at all pH values, its ions retention in the cement matrix is insufficient [15, 16].

The effective diffusion coefficients values, D_e, and the regression coefficients, R, are obtained, by leaching diffusion model of Cs$^+$ and Co^{2+} ions immobilized in the cement matrix under static conditions. The constants K_1, K_2, and K_3 values and the regression coefficients, R, are calculated by a semi-empirical leaching model of Cs$^+$ and Co^{2+} ions bound by the ma-

trix under static conditions. The results are shown in tabs. 3 and 4.

The influence of 2 %, 5 %, and 10 % (in relation to the cement mass) bentonite and zeolite content, as cement matrix constituents, on Co^{2+} and Cs$^+$ ions leaching under static conditions, was investigated. Through analyzing the experimental results, it could be concluded that the increase of the amount of added zeolite and bentonite in the cement matrix significantly reduces the level of leaching of Cs$^+$ ions (diffusion coefficient, D_e, decreased by four orders of magnitude). Furthermore, zeolite has a higher sorption ability of Cs$^+$ ions than bentonite. The influence of bentonite and zeolite on Co^{2+} ions leaching level was significantly smaller, compared to Cs$^+$ (diffusion coefficient, D_e, was reduced five times at most). Once more, a slightly higher sorption ability of Co^{2+} ions on zeolite was observed.

Moreover, bentonite and zeolite selectivity towards Cs$^+$ and Co^{2+} ions and their influence on the leaching reduction degree was confirmed [17-19]. The overall sorption level in porous materials, such as bentonite and zeolite, is controlled by the sorbate mass diffusion transport within their channel and pore network, rather than by the sorption kinetics itself. The diffusion of sorbate ions depends on the sorbent geometric structure (arrangement, size, and irregularity of the pores), hydration energy, ionic radius, and valence [20]. The sorption mechanisms could be ion exchange, surface, and external and internal complexation/precipitation. The nature of the sorbent-sorbate interaction, i. e., the sorption mechanism, is influenced by the hydration of ions and their hydrolysis, thus the mechanism of Cs$^+$ ion sorption on bentonite and zeolite represents ion exchange, while the mechanism of Co^{2+} ion sorption is surface complexation/precipitation.

Linear regression of experimental leaching results under static conditions Co^{2+} and Cs$^+$ showed that the absolute values of the parameters K_3 are one to two orders of magnitude smaller than the absolute values of the parameters K_2 and K_1. This means that the influence of the variable t was negligible, and the influence of the variable $t^{1/2}$ was predominant. Therefore, the contribution of matrix dissolution to the total radionuclides transport was insignificant in relation to the dominant contribution of diffusion and surface washing. Moreover, surface washing could be considered an instantaneous phenomenon ($t = 0$). Even though the diffusion model cannot define the overall leaching process, it is very appropriate for prediction as a result of its simplicity [21]. Based on the regression coefficients values, the semi-empirical model gives a better approximation of the Co^{2+} and Cs$^+$ static leaching process [22].

CONCLUSIONS

By increasing the content of bentonite and zeolite in the cement matrix mechanical resistance to pressure was reduced. The cement matrix containing zeolite showed slightly higher mechanical resistance to pressure than the cement matrix with the same bentonite amount. Furthermore, a higher value of cement matrix mechanical resistance corresponded to a lower leaching level of Co^{2+} and Cs$^+$ ions.

The Co^{2+} leaching level was more than two orders of magnitude lower than the leaching level of Cs$^+$ ions. Moreover, the increased amount of zeolite and benton-

Table 3. Effective diffusion coefficients values and regression coefficients calculated by leaching diffusion model of Cs$^+$ and Co^{2+} ions immobilized in the cement matrix

	Cement matrix						
Diffusion leaching model parameters	M	MB$_2$	MB$_5$	MB$_{10}$	MZ$_2$	MZ$_5$	MZ$_{10}$
D_e(Cs$^+$) [cm^{2}d^{-1}]	8.34 10^{-6}	7.02 10^{-7}	6.78 10^{-8}	5.05 10^{-9}	4.15 10^{-8}	2.11 10^{-8}	1.91 10^{-9}
D_e(Co^{2+}) [cm^{2}d^{-1}]	2.22 10^{-8}	1.33 10^{-8}	8.33 10^{-9}	5.55 10^{-9}	1.07 10^{-8}	6.63 10^{-9}	4.89 10^{-9}
R(Cs$^+$)	0.981	0.989	0.987	0.976	0.996	0.980	0.970
R(Co^{2+})	0.982	0.988	0.986	0.987	0.987	0.985	0.985

Table 4. Constants and regression coefficients calculated by semi-empirical leaching model of Cs$^+$ and Co^{2+} ions immobilized in the cement matrix

	Cement matrix						
Parameters of the semi-empirical leaching model	M	MB$_2$	MB$_5$	MB$_{10}$	MZ$_2$	MZ$_5$	MZ$_{10}$
K_1(Cs$^+$)	−2.65 10^{-3}	−1.05 10^{-3}	2.02 10^{-4}	2.74 10^{-4}	8.57 10^{-4}	−6.21 10^{-5}	6.67 10^{-5}
K_1(Co^{2+})	−1.29 10^{-4}	−4.38 10^{-5}	−5.78 10^{-5}	−3.52 10^{-5}	−6.10 10^{-5}	−5.94 10^{-5}	−5.06 10^{-5}
K_2(Cs$^+$)	8.02 10^{-3}	2.01 10^{-3}	6.51 10^{-4}	1.99 10^{-4}	4.05 10^{-4}	3.90 10^{-4}	1.31 10^{-4}
K_2(Co^{2+})	4.09 10^{-4}	2.77 10^{-4}	2.31 10^{-4}	1.83 10^{-4}	2.60 10^{-4}	2.09 10^{-4}	1.80 10^{-4}
K_3(Cs$^+$)	−3.71 10^{-4}	−7.59 10^{-5}	−2.61 10^{-5}	−9.34 10^{-6}	−9.98 10^{-6}	−1.72 10^{-5}	−6.63 10^{-6}
K_3(Co^{2+})	−1.86 10^{-5}	−1.05 10^{-5}	−9.41 10^{-6}	−7.16 10^{-6}	−1.05 10^{-5}	−8.70 10^{-6}	−7.51 10^{-6}
R(Cs$^+$)	1.000	0.999	0.999	0.995	0.999	0.996	0.997
R(Co^{2+})	0.999	0.998	0.998	0.998	0.999	0.998	0.999

64

S. D. Dimović.: Influence of Bentonite and Zeolite on Cs$^+$ and Co^{2+} Cement ...
Nuclear Technology & Radiation Protection: Year 2021, Vol. 36, No. 1, pp. 60-65

ite in the cement matrix significantly reduced the Cs$^+$ leaching. The influence of bentonite and zeolite on the Co^{2+} leaching reduction was significantly lower in comparison with Cs$^+$, while zeolite showed a higher Cs$^+$ and Co^{2+} sorption ability than bentonite.

Under static leaching conditions, the contribution of diffusion to the total transport of Co^{2+} and Cs$^+$ ions in the cement matrix porous medium was dominant. The contribution of matrix dissolution was insignificant in relation to the dominant contribution of diffusion and surface washing, which could be considered an instantaneous phenomenon. The semi-empirical model gave a better approximation of the Co^{2+} and Cs$^+$ leaching process for the duration of the experiment.

ACKNOWLEDGMENT

AUTHORS' CONTRIBUTIONS

All authors analyzed the results and participated in the preparation of the final version of the manuscript.

REFERENCES

[1] ***, IAEA, Strategy and Mythology for radioactive Waste Characterization, TECDOC No. 1537 IAEA, Vienna, 2007

[2] ***, IAEA, Combined Methods for Liquid Radioactive Waste Treatment, TECDOC No. 1336 IAEA, Vienna, 2003

[3] Hespe, E. D., Leach Testing of Immobilized Radioactive Waste Solids, *Atomic Energy Rev., 9* (1971), 1, pp. 195-207

[4] Plećas, I., Dimović, S. Immobilization of ^{137}Cs and ^{60}Co in Concrete Matrix. Part 2: Mathematical Modeling of Transport Phenomena, *Ann. Nucl. Energy, 32* (2005), 13, pp. 1509-1515

[5] Dimović, S. D., *et al*., Leaching Kinetics of Cs$^+$ and Co^{2+} Under Dynamic Conditions, *Nucl Technol Radiat, 34* (2019), 3, pp. 243-248

[6] Bishop, P. L., Contaminant Leaching from Solidified-Stabilized Wastes, Emerging Technologies in Hazardous Waste Management II, Copyright, ACS Symposium Series, Foreword, American Chemical Society, Washington, 1991

[7] Andre, A., Long-Term Behavior of Toxic Metals in Stabilized Steel Foundry Dust, *J. Hazard. Mater., 40* (1995), 1, pp. 31-42

[8] Abdel Rahman, R. O., *et al*., Modeling the Long-Term Leaching Behavior of ^{137}Cs, ^{60}Co, and ^{152,154}Eu Radionuclides from Cement-Clay Matrices, *J. Hazard. Mater., 145* (2007), pp. 372-380

[9] Cote, P. L., *et al*., An Evaluation of Cement-Based Waste Forms Using the Results of Approximately Two Years of Dynamic Leaching, *Nucl. Chem. Waste Manag., 17* (1987), 2, pp. 129-139

[10] Eskander, S. B., *et al*., Leaching Behavior of Cement-Natural Clay Composite Incorporating Real Spent Radioactive Liquid Scintillator, *Prog. Nucl. Energy, 67* (2013), Aug., pp. 1-6

[11] Plećas, I., *et al*., Influence of Bentonite and Zeolite in Cementation of Dry Radioactive Evaporator Concentrates, *Appl. Clay Sci., 43* (2009), 1, pp. 9-12

[12] Ojovan, M. I., *et al*., Long-Term Field and Laboratory Leaching Tests of Cemented Radioactive Wastes, *J. Hazard. Mater., 187* (2011), 1-3, pp. 296-302

[13] El- Dessouky, M. I., *et al*., Leaching Study in Immobilization of Cesium and Cobalt Radionuclides In Fly Ash- Zeolite Cement, *Arab J. Nucl. Sci. Appl., 46* (2013), 3, pp. 52-62

[14] Dahn, R., *et al*., Soft X-Ray Spectromicroscopy of Cobalt Uptake by Cement, *Environ. Sci. Technol., 45* (2011), 5, pp. 2021-2027

[15] El-Kamash, A. M., *et al*., Immobilization of Cesium and Strontium Radionuclides in Zeolite-Cement Blends, *J. Hazard. Mater., 136* (2006), pp. 310-316

[16] Papadokostaki, K. G., Savidou, A., Study of Leaching Mechanisms of Cesium Ions Incorporated in Ordinary Portland Cement, *J. Hazard. Mater., 171* (2009), 1-3, pp. 1024-1031

[17] Faiz, Z., *et al*., Leaching Study of Cesium from Spent Ion-Exchange Resins and Portland Cement Package, *Int. J. Environ. Sci. Technol., 14* (2017), pp. 1019-1026

[18] El-Dessouky, M. I., *et al*., Leaching and Mechanical Properties of Cement- Polyacrylamide Composite Developed as Matrices for Immobilization of ^{137}Cs and ^{60}Co Radionuclides, *Nature and Science, 10* (2012), 12, pp. 172-177

[19] Plećas, I., Dimović, S., Influence of Natural Sorbents on the Immobilization of Spent Ion Exchange Resins in Cement, *J. Radioanal. Nucl. Chem., 269* (2006), 1, pp. 181-185

[20] Galamboš, M., *et al*., Sorption of Anthropogenic Radionuclides on Natural and Synthetic Inorganic Sorbents, *J. Radioanal. Nucl. Chem., 293* (2012), 2, pp. 613-633

[21] Plećaš, I., Pavlović, R., Pavlović, S., Leaching Behavior of ^{60}Co and ^{137}Cs from Spent Ion Exchange Resins in Cement-Bentonite Clay Matrix, *J. Nucl. Mater., 327* (2004), 2-3, pp. 171-174

[22] Plećas, I., Mathematical Modeling of Immobilization of Radionuclides ^{137}Cs and ^{60}Co in Concrete Matrix, *Prog. Nucl. Energy, 52* (2010), 7, pp. 685-688

S. D. Dimović.: Influence of Bentonite and Zeolite on Cs$^+$ and Co^{2+} Cement ...
Nuclear Technology & Radiation Protection: Year 2021, Vol. 36, No. 1, pp. 60-65

65

Славко Д. ДИМОВИЋ, Ивана В. ЈЕЛИЋ, Марија З. ШЉИВИЋ-ИВАНОВИЋ

УТИЦАЈ БЕНТОНИТА И ЗЕОЛИТА НА ФЕНОМЕН ИЗЛУЖИВАЊА Cs$^+$ И Co^{2+} ИЗ ЦЕМЕНТНОГ МАТРИКСА

Вероватноћа задржавања јона Cs$^+$ и Co^{2+} процесом имобилизације у цементном матриксу одређена је као предмет анализе: дизајна матрикса, односа вода/цемент и његове порозности. Поређење експерименталних резултата извршено је *Hespe*-овом стандардном методом излуживања. Дифузиони и семи-емпиријски модели коришћени су за предвиђања брзине испирања у функцији времена. Виша вредност механичке отпорности цементног матрикса одговара нижој вредности излуживања јона Co^{2+} и Cs$^+$. Степен излуживања Co^{2+} био је више од два реда величине мањи од нивоа излуживања Cs$^+$. Утицај бентонита и зеолита на смањење излуживања Co^{2+} био је значајно мањи у поређењу са Cs$^+$, док је зеолит имао већу сорпциону способност за Cs$^+$ и Co^{2+} јоне од бентонита. У статичким условима излуживања допринос процеса дифузије доминирао је у укупном транспорту јона у порозној средини матрикса. Допринос растварања матрикса био је безначајан у односу на доминантни допринос дифузије и површинског испирања. Семи-емпиријски модел показао је бољу апроксимацију експерименталног процеса испирања јона Co^{2+} и Cs$^+$.

Кључне речи: излуживање, имобилизација, сорпција, радиоактивни отпад