

PRELIMINARY STUDY OF CESIUM IMMOBILIZATION IN A GEOPOLYMER MATRIX

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Geopolymers are modern synthetic materials that have many beneficial characteristics, e.g. excellent mechanical properties, fire- and heat-resistance, minimal shrinkage and can be molded into shape. Given their aforementioned characteristics, geopolymers could be applicable as conditioning materials, e.g. to handle hazardous waste and radioactive materials. However, their long-term applicability needs to be investigated.

The aim of this study is to investigate the mobility of Cs-137 radionuclides in embedding materials. Different geopolymeric matrices - namely kaolinite, bentonite, zeolites and red mud - were tested. The leach test was performed according to the ASTM C1308-08(2017) standard and the activity concentration of Cs-137 isotopes was measured by gamma spectrometry using a high-purity germanium (HPGe) semiconductor detector. According to our preliminary results, the matrices that resulted in the most significant immobilization effect were those in which bentonite, cement, fly ash and 8M NaOH were used, releasing approximately 10% of the cesium.

Keywords: geopolymer, immobilization, radioactive waste, NORMs

1. Introduction

In order to prevent any dispersion of radionuclides from liquid radioactive waste into the environment, this type of waste has been incorporated into various embedding materials. The aim of this process is to make these materials leach-resistant, so that the release of radionuclides is significantly reduced should they come into contact with groundwater. The other reason is to transform these materials into a mechanically, chemically and physically stable form for transport and emplacement [1]. Nowadays, the most commonly used solidifying materials are cement, bitumen and various types of polymers. Of these materials, cement is the most commonly used because it is widely available, cheaper than the other materials and easy to handle. However, it has been shown that cement is not the best material for immobilizing Cs-137 radionuclides. Several studies have shown that the sorption capacity of Cs-137 is low and the diffusion capacity in hydrated cements is high [2]-[3]. The immobilization properties of cement as an embedding material can be enhanced by using different types of additives that have a higher sorption capacity, e.g. bentonite and zeolites [4]-[5]. Given the low hydraulic conductivity and high sorption capacity of cations, bentonite is a promising material with regard to disposing of radioactive waste. Zeolites, particularly clinoptilolite, are used worldwide in ion exchange processes with a great degree of success in the removal

of Cs-137 radionuclides from various types of wastewater. Both are natural materials, which means that their extraction has a huge impact on the environment [6]-[7]. As previously mentioned, since they are mixed with cement to obtain a mixture that has good radionuclide immobilization properties, the mining of zeolites and bentonites is not the only activity with a huge environmental impact. The cement manufacturing process is also known to have a huge environmental impact. The process releases several gases into the air, e.g. CO₂, NO₂, NO₃, SO₂, etc., which have major impacts on global warming [8]-[9]. As a result, research is now being conducted to reduce the amount of raw materials used in the industry and identify replacement materials. Testing NORMs (naturally occurring radioactive materials) - which are available in large quantities worldwide as well as could be used as potential additives in commonly used cement, zeolites and bentonite - could be promising. One of the ways in which radioactive waste solidifies is through geopolymerisation. NORMs, e.g. red mud and fly ash, can be used as additives [10]-[12] and are usually deposited in huge amounts, which has a significant environmental impact due to the heavy metals they contain, moreover, can of course increase the dose rate to passers-by or workers near these deposits [13]. Therefore, a method is needed to reduce the environmental impact of NORMs. However, the following question may be raised: why are they unsuitable as replacements for geopolymers nor as embedding materials for liquid radioactive waste. These

materials are widely used in construction, water treatment and agricultural fertilization, some of which have good adsorption and water-binding capacities. Furthermore, using these materials as additives can reduce the environmental impact of mining and reduce the cost of production.

The solidification of liquid radioactive waste by geopolymerisation is one of the cheapest methods of radioactive waste management. The structure of the resulting final product is stable as well as exhibits extremely good heat- and fire-resistance capabilities, moreover, the concentration of boric acid in liquid radioactive waste does not destroy the structure of geopolymers and the volume of the resulting final product is significantly smaller compared to that of waste conditioned by cementation [14]-[15].

The aim of this study is to investigate the immobilization of Cs-137 in different kinds of geopolymeric materials using NORM additives.

2. Experimental

During the laboratory work, different kinds of geopolymers containing zeolites, bentonite, kaolinite and red mud were prepared, which were mixed in different ratios as presented in *Table 1* below:

Table 1. Mixing ratio of the used materials

Experiment	Used materials	Mixing ratio
I.	Zeolites – Cement	1:1
	Zeolites – Bentonite – Cement	1:1:1
	Zeolites – Kaolinite – Cement	1:1:1
	Bentonite – Cement	1:1
	Bentonite – Kaolinite – Cement	1:1:1
	Kaolinite – Cement	1:1
II.	Cement	1
	Zeolites – Cement	1:1
	Zeolites – Cement	2:1
	Bentonite – Cement	1:2
III.	Red mud – Bentonite – Cement	1:1:1
	Red mud – Zeolites – Cement	1:1:1
	Red mud – Bentonite – Cement	2:1:1
	Red mud – Zeolites – Cement	2:1:1

Cement as a binder as well as an 8M NaOH solution as a wetting agent were added to the mixtures and mixed until a homogeneous mass was obtained. A radioactive Cs-137 solution was mixed with the already moldable mass before being placed in a sample container. The molded samples were then dried for 27 days at room temperature in accordance with the requirements of the

ASTM C 1308-08 standard [16]. After the 27 days, the already solidified samples were placed in a 1L plastic container in such a way that they were attached to the lid of the container by means of a thread to prevent them from dropping to the bottom of the container. 250 ml of distilled water was poured into the vessel used for the dissolution test.

During the leaching tests, the distilled water in the containers was replaced at the time intervals specified by the standard (*Figure 1*) before the amount of leached radionuclides dissolved from the test samples was measured by gamma spectrometry using a high-purity germanium (HPGe) semiconductor detector.

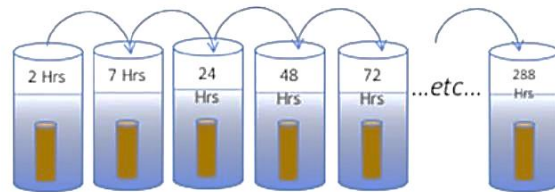


Figure 1. Time intervals according to which the water was changed in accordance with the ASTM C 1308-08 standard [17]

According to the ASTM standard, the Incremental Fraction Leached (IFL) was calculated using the results from gamma spectrometry measurements as follows:

$$IFL = \frac{i a_n}{i A_0} \quad (1)$$

where:

$i a_n$ denotes the quantity of species i measured in the leachate from the n^{th} test interval,

$i A_0$ stands for the quantity of species i in the specimen at the beginning of the test

The cumulative fraction of species i leached over the j^{th} time interval, referred to as the Cumulative Fraction Leached (CFL_j), was also calculated:

$$CFL_j = \frac{\sum_{n=0}^j i a_n}{i A_0} = \sum_{n=0}^j IFL_n \quad (2)$$

In the case of radionuclide i , both terms must be corrected in light of radioactive decay at the beginning of the test.

3. Results and Analysis

During the first part of the experiments, zeolites, bentonite, kaolinite and, of course, cement were used, moreover, the leached amount of radionuclides was measured by gamma spectrometry using a HPGe semiconductor detector. These values were used to calculate the CFL values of each matrix, which are shown in *Figure 2*.

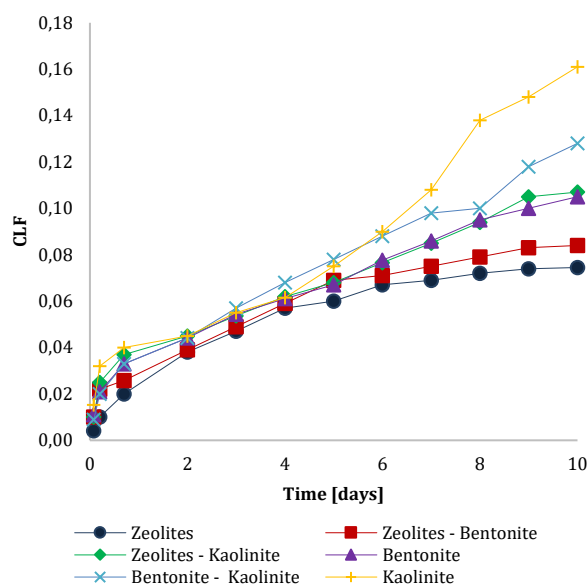


Figure 2. Representation of the change in CFL values obtained during the I. experiment as a function of time

Based on the results obtained, it can be seen that during the 10-day-long dissolution tests, the amount of dissolved Cs-137 was lowest in the case of the geopolymers containing zeolites – cement and zeolites – bentonite – cement in 1:1 and 1:1:1 ratios, respectively. Regarding the sample containing zeolites – cement, the dissolution rate was 9.8%, while for the one consisting of zeolites – bentonite – cement, it was 10.1%. The highest dissolution rate, that is, 17.4%, was measured in the sample containing kaolinite – cement in a ratio of 1:1. The high dissolution rate of kaolinite is due to the structure of kaolin which, like illite, is a layered phyllosilicate in which the absorption of Cs ions is not as high when compared to its montmorillonite counterparts due to its crystal structure. On the basis of the results obtained, it can also be seen that the CFL values of the zeolites – cement and zeolites – bentonite samples constantly increase, moreover, after 7 days, the dissolution rate already increased much more slowly compared to the other samples, where a continuous increase was observed. During the initial phase of the dissolution tests, i.e. in the first few days, not only were the Cs-137 isotopes embedded in the geopolymer dissolved but also those on the surface of the test specimens. As a result, a larger increase in the CFL value was recorded during the initial phase. Once the Cs-137 on the surface has completely dissolved, only the dissolution of Cs-137 inside the geopolymer affects the obtained values.

Of course, the amount of dissolved Cs-137 is also affected by the small microcracks in the samples that may have occurred during their preparation, possibly increasing the amount dissolved.

In the second part of our experiments, ratios resulting in the best CFL values from the previous measurements were used. Cement matrices consisting of zeolites mixed in different ratios were measured and the CFL values obtained can be seen in Figure 3.

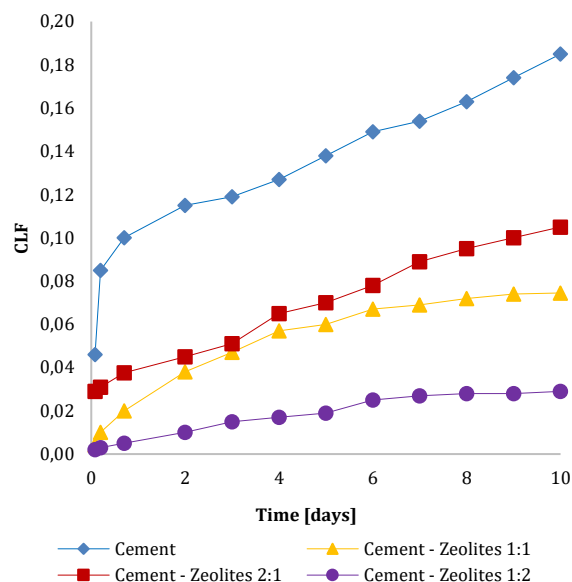


Figure 3. Representation of the change in the CFL values obtained with regard to cement – zeolites matrices in different ratios

It can be seen that the leachability of the Cs-137 radionuclide can be significantly reduced using zeolite additives.

Depending on the quality and quantity of such additives, the dissolution rate may be reduced. As a result of ion exchange processes, the cesium ions absorbed by the zeolites are exchanged for the calcium ions in the cement. The cesium ions are then released from the matrix into the environment by diffusion. The rate at which cesium diffuses away from the matrix is determined by the environment, ion exchange process and rate of diffusion. The ion exchange process can be slowed down by increasing the additive content of the matrices so that the ability of the clay minerals to bind to the calcium hydroxide ions is enhanced, preventing displacement of the cesium ions from the structure of the matrix to such an extent that results in significantly less cesium being released from the matrix. In addition to the calcium ions in the cement, this process can also be influenced by the amount of such ions in the solvent, because if the solvent is rich in calcium, the calcium ions it contains can also displace the cesium ions, thereby increasing the rate at which they escape from the matrix. For this reason, distilled water was chosen as the solvent, as it cannot interfere with the ion exchange processes taking place in the test samples [18].

The results obtained during the dissolution tests were developed in accordance with the aforementioned ion exchange processes. In the case of the cement – zeolites samples in the ratios of 1:1 and 1:2, it can be seen that the amount of dissolved cesium was smaller than in the samples where only cement was present or in larger quantities compared to that of zeolites. In contrast with cement and cement – zeolites specimens, the dissolution rate of Cs-137 dissolved from samples containing zeolites – cement in a ratio of 1:1 was 9.8%, while those containing zeolites – cement in a ratio of 2:1 was only

8.3%. In the case of samples consisting of a ratio of 2:1, the amount of dissolved Cs-137 was 17.5 and 16.2 %.

NORMs containing bentonite and zeolites were also used as additives during leaching tests. Based on recommendations from the literature, red mud was selected as the NORM for the experiment. The leaching rates of Cs-137 from samples containing bentonite and red mud in the ratios of 1:1 and 1:2 were 5.90 and 8.04%, respectively, whereas those of Cs-137 from samples containing zeolites and red mud in the ratios of 1:1 and 1:2 were 10.20 and 11.73%, respectively. The CFL values recorded can be seen in *Figure 4*. Based on the results obtained during the dissolution tests, the specimens containing bentonite proved to have a better immobilization effect on Cs-137.

Based on the results obtained, it can be seen that ion exchange processes can be influenced by some parameters such as the slightly alkaline chemical effect resulting from the composition of bentonite and the Si/Al ratio of the red mud which created favorable conditions for the cesium ions to bind much better in the matrix of the specimens containing bentonite than in those containing zeolites. However, it can also be seen that if the Si/Al ratio of the samples is increased even more by adding additional red mud to the samples, the rate of dissolution increases. This can be explained by the fact that the Al rings in the test specimens become smaller due to the lower Si/Al ratio, so the rate at which cesium ions escape from the structure reduces.

These results are supported by the study written by Quanzhi Tian, Shingo Nakama and Keiko Sasaki in which cesium leaching tests were also carried out on specimens with different compositions and Si/Al ratios [19].

4. Conclusions

The aim of this research was to investigate the applicability of NORMs with regard to the immobilization of radionuclides in liquid radioactive waste. During the experiments, various compositions with different raw materials were investigated in order to determine the basic material whereby the NORM, that is, red mud, is used as an additive.

Based on the results of the laboratory measurements, it can be said that the best CFL value was obtained with a test batch containing a 1:1 mixture of bentonite and red mud. It can also be concluded that the chemical composition of the NORM used as an additive, namely red mud, significantly contributes towards the reduction in ion exchange processes. However, this should be treated with caution as the 1:1 mixture of bentonite and red mud exhibited favorable CFL and diffusion rate values compared to the sample containing twice as much red mud.

All in all, it can be stated that the reuse of NORMs can reduce our impact on the environment. It was observed that NORMs, especially red mud, can be successfully used as additives to manage liquid radioactive waste. This is an opportunity that must be

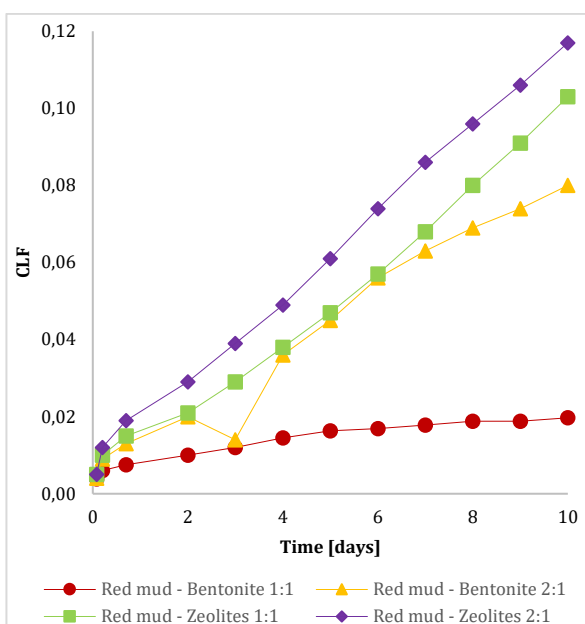


Figure 4. Representation of the change in the CFL values obtained during the II. experiment as a function of time

seized and a field in need of much more thorough research in the future.

REFERENCES

- [1] Plecas, I.: Immobilization of ^{137}Cs and ^{60}Co in concrete matrix, *Ann. Nucl. Energy*, 2003, **30**(18), 1899–1903, DOI: [10.1016/S0306-4549\(03\)00158-0](https://doi.org/10.1016/S0306-4549(03)00158-0)
- [2] Plecas, I.; Dimovic, S.; Smiciklas, I.: Utilization of bentonite and zeolite in cementation of dry radioactive evaporator concentrate, *Prog. Nucl. Energy*, 2006, **48**(6), 495–503, DOI: [10.1016/j.pnucene.2005.12.001](https://doi.org/10.1016/j.pnucene.2005.12.001)
- [3] Glasser, F.P.: Characterisation of the barrier performance of cements, *Proc. Mater. Res. Soc. Symp.*, 2002, **713**, 721–732, DOI: [10.1557/PROC-713-JJ9.1](https://doi.org/10.1557/PROC-713-JJ9.1)
- [4] Plecas, I.; Pavlovic, R.; Pavlovic, S.: Leaching behavior of ^{60}Co and ^{137}Cs from spent ion exchange resins in cement–bentonite clay matrix, *J. Nucl. Mater.*, 2004, **327**(2-3), 171–174, DOI: [10.1016/j.jnucmat.2004.02.001](https://doi.org/10.1016/j.jnucmat.2004.02.001)
- [5] Jock, A. A., Okon, A. N., Offor, U. H., Thomas, F., & Agbanaje, E. O. (2020). Adsorption of Nickel Ions from Petroleum Wastewater onto Calcined Kaolin Clay: Isotherm, Kinetic and Thermodynamic Studies. *Hungarian Journal of Industry and Chemistry*, **48**(2), 45–49. DOI: [10.33927/hjic-2020-26](https://doi.org/10.33927/hjic-2020-26)
- [6] Eisenhour, D.D.; Brown, R.K.: Bentonite and its impact on modern life, *Elements*, 2009, **5**(2), 83–88, DOI: [10.2113/gselements.5.2.83](https://doi.org/10.2113/gselements.5.2.83)
- [7] EPA AP-42, Fifth edition compilation of air pollutant emissions factors, volume I, chapter 11.25: Clay processing, 2005,

- <https://www3.epa.gov/ttnchie1/ap42/ch11/final/c11s25.pdf>
(accessed 17 December 2022)
- [8] Sanjuán, M.Á.; Quintana, B.; Argiz, C.: Coal bottom ash natural radioactivity in building materials, *J. Radioanal. Nucl. Chem.*, 2019, **319**(1), 91–99, DOI: 10.1007/s10967-018-6251-0
- [9] Sanjuán, M.Á.; Suarez-Navarro, J.A.; Argiz, C.; Estévez, E.: Radiation dose calculation of fine and coarse coal fly ash used for building purposes, *J. Radioanal. Nucl. Chem.*, 2021, **327**(2), 1045–1054, DOI: 10.1007/s10967-020-07578-8
- [10] Zákány, I.; Korim, T.: Alkáli aktivált szervesetlen polimerek, mint a kötőanyagok újabb generációja, *Építőanyag*, 2011, **63**(3-4), 74–77, DOI: 10.14382/epitoanyag-jsbcm.2011.14
- [11] Davidovits, J.: Geopolymer chemistry and applications, 4th edition (Institut Géopolymère, Saint-Quentin, France), 2015, pp. 283–315, ISBN: 9782951482098
- [12] Li, Y.; Min, X.; Ke, Y.; Liu, D.; Tang, C.: Preparation of red mud-based geopolymer materials from MSWI fly ash and red mud by mechanical activation, *Waste Manage.*, 2019, **83**, 202–208, DOI: 10.1016/j.wasman.2018.11.019
- [13] Kovács, T.; Horváth, M.; Csordás, A.; Bátor, G.; Tóth-Bodrogi, E.: Tobacco plant as possible biomonitoring tool of red mud dust fallout and increased natural radioactivity, *Heliyon*, 2020, **6**(3), e03455, DOI: 10.1016/j.heliyon.2020.e03455
- [14] Kim, B.; Lee, J.; Kang, J.; Um, W.: Development of geopolymer waste form for immobilization of radioactive borate waste, *J. Hazard. Mater.*, 2021, **419**, 126402, DOI: 10.1016/j.jhazmat.2021.126402
- [15] Xu, H.; Van Deventer, J.S.J.: The geopolymerisation of aluminosilicate minerals, *Int. J. Miner. Process.*, 2000, **59**(3), 247–266, DOI: 10.1016/S0301-7516(99)00074-5
- [16] ASTM, C1308-08 Standard test method for accelerated leach test for diffusive releases from solidified waste and a computer program to model diffusive, fractional leaching from cylindrical waste forms
- [17] Seipel, K.S.; Sheumaker, D.L.; Kirk, L.B.: Kinetic tests of non-amended and cemented paste tailings geochemistry in subaqueous and subaerial settings, *Proc. IMWA 2017 - Mine Water and Circular Economy*, 2017, **2**, 830–835, https://imwa.info/docs/imwa_2017/IMWA2017_Seipel_830.pdf
- [18] Dougherty, D.; Fuhrmann, M.; Colombo, P.: Accelerated leach test(s) program. Annual report (BNL-51955) (Brookhaven National Laboratory, Upton, NY, USA), 1985, pp. 2–3, DOI: 10.2172/5557445
- [19] Tian, Q.; Nakama, S.; Sasaki, K.: Immobilization of cesium in fly ash-silica fume based geopolymers with different Si/Al molar ratios, *Sci. Total Environ.*, 2019, **687**, 1127–1137, DOI: 10.1016/j.scitotenv.2019.06.095