ICCC PRAGUE 2019 • 15ᵀᴴ INTERNATIONAL CONGRESS ON THE CHEMISTRY OF CEMENT

ICCC
PRAGUE
2019

Leaching resistance of alkali-activated binder contaminated with cesium

Gordana Tanasijevic[1,a], Tijana Ivanovic[1,b], John L. Provis[2,c], Miroslav Komljenovic[1,d]

[1]*Institute for Multidisciplinary Research, University of Belgrade, Belgrade, Serbia*
[2]*Department of Materials Science and Engineering, University of Sheffield, Sheffield, United Kingdom*

[a]gordana@imsi.rs
[b]tijana.ivanovic@imsi.rs
[c]j.provis@sheffield.ac.uk
[d]miroslav.komljenovic@imsi.rs

ABSTRACT

Leaching is a phenomenon of fundamental interest in low-level radioactive waste disposal, and the measurement of the leaching resistance of different wasteforms is very important for proper waste management. In general, alkali-activated binders (AABs) can be considered as a sustainable solution for safe immobilization of hazardous wastes containing different toxic or radioactive elements.

In this paper, the leaching resistance of AAB based on blast furnace slag (BFS), contaminated with 2% cesium (i.e., solidified simulated low-level radioactive waste), was investigated according to the ANSI/ANS-16.1-2003 standard procedure.

Based on the leaching results obtained for different elements, in particular for Cs, Si, Al, Ca, Na, and K, it was concluded that the short (up to 5 days) semi-dynamic process of leaching from AAB can be divided into two distinct stages: a) fast leaching of non-bound or loosely bound ions during the initial 24 hours, which occurred mostly between the surface of AAB and the leachant, and b) slower leaching in the later stages of the experiment, which was controlled by diffusion of ions through AAB matrix.

By calculating the diffusion coefficient (D) and the leachability index (L) of cesium, it was also concluded that AAB based on blast furnace slag, synthesized under the given experimental conditions, can be considered as a potentially efficient matrix for immobilizing up to 2% cesium in hazardous wastes.

1. Introduction

Leaching is a phenomenon of fundamental interest in low-level radioactive waste disposal, and the measurement of the leaching resistance of different wasteforms is essential for proper management of these potentially hazardous substances.

Alkali-activated binders (AABs) have frequently been studied for immobilization of different hazardous wastes, such as heavy metals or complex solid and liquid industrial wastes (Lancellotti et al. 2014). However, there are a limited number of studies related to the use of AABs for radioactive waste immobilization (Bernal et al. 2014). in particular when blast furnace slag (BFS) was used either as a sole solid precursor (Qian et al. 2001, Tsutsumi et al. 2014, Vandevenne et al. 2018) or combined with other solid aluminosilicate precursors (Qian et al. 2001, Chen et al. 2010, Kryvenko et al. 2015, Jang et al. 2016, El-Naggar & Amin 2018).

In this paper the leaching resistance of an alkali-activated binder based only on blast furnace slag, contaminated with cesium (i.e., a solidified simulated low-level radioactive waste) by a short-term test procedure (up to 5 days) was investigated according to the ANSI/ANS-16.1-2003 standard test method.

2. Experimental

2.1 Materials

In this work, granulated blast furnace slag from pig iron production at the facility "Železara Smederevo" (Serbia) was used as a solid precursor for the synthesis of the alkali-activated binder. Prior to testing, granulated BFS was ground so that its specific surface area (according to the Blaine test) was ~400 m^2/kg.

Sodium silicate solution (13.60% Na_2O, 26.25% SiO_2, 60.15% H_2O on a mass basis; Galenika-Magmasil, Serbia) was used as an alkali activator; its modulus (n = SiO_2/Na_2O, mass ratio) as supplied was 1.93. The sodium silicate modulus was adjusted to 1.5 for use in alkali-activation by adding sodium hydroxide pellets (98.5 % NaOH, Lach-Ner, Czech Republic), according to the previously optimized procedure (Marjanović et al. 2015).

Cesium chloride (99.5% CsCl, Superlab, Serbia) was used as a Cs source for doping AAB. Concentrated nitric acid (65% HNO_3, Analar Normapur, EC) was used to stabilize the leachate (the solution after the process of leaching and filtration was finished) until instrumental analysis.

2.2 Paste preparation

The preparation of AAB paste was performed by mixing ground BFS, sodium silicate solution, and water or cesium chloride solution (in the case of AAB doped with Cs). The concentration of Na_2O was 4%, while the concentration of Cs was 2.0% with respect to the total mass of BFS. The water/binder ratio (water represents the total amount of water in the system including water from the activator, while binder represents the total mass of BFS and the solid part of the activator) was 0.21. The AAB paste was mixed for two minutes, then poured into a cylindrical plastic mold (ø 60 × 10 mm), after which the air bubbles were removed on a vibrating table. The AAB pastes were cured covered with plastic for 23 h at 95 ºC, and then, also covered, at room temperature until testing.

2.3 Methods of characterization

2.3.1 Chemical composition and particle size distribution of BFS

The chemical composition of BFS was examined by a classical chemical analysis - alkali melting, and the results are given in Table 1, while the particle size distribution of BFS was examined by wet sieving and the results are given in Table 2.

Table 1. Chemical composition of BFS, reported on an oxide basis other than for the reduced S component. LOI is loss on ignition

Comp.	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	SO_3	S	Na_2O	K_2O	LOI
Mass (%)	39.88	6.68	0.97	0.63	39.34	8.61	0.20	0.51	0.42	0.61	1.23

Table 2. Particle size distribution of ground BFS

Particle size	< 45 µm	> 45 µm	> 63 µm	> 100 µm
Mass (%)	85.98	6.50	4.11	3.41

2.3.2 Leaching tests

Semi-dynamic leaching tests of different elements (Si, Al, Ca, Mg, Na, K, Fe, and Cs), both from the reference and Cs-doped AAB, were performed according to the ANSI/ANS-16.1-2003 standard procedure. This test is a semi-dynamic leach experiment that consists of submerging a monolithic sample (with a fixed geometry) in water at a fixed liquid-volume to solid-geometric surface area ratio, and replacing all the leachate at fixed periods of time. The leachates are then analyzed for key constituents.

Demineralized water (<5 µmho/cm at 25 °C) was used as a leachant at a liquid volume to wasteform surface area (L/S) ratio of 10 ± 0.2 cm. The specimens were put in a plastic container with leachant while being supported by a grid plastic holder that does not preclude more than a small fraction of the specimen`s external surface from exposure to the leachant. The standard leaching test was performed without any stirring within a period of 5 days, whereby the leachate was completely replaced by fresh leachant after cumulative leach times of 2, 7, 24, 48, 72, 96, and 120 hours. After the specified period of leaching the leachate was vacuum filtered through a 0.45 µm membrane filter, after which the pH of the leachate was measured with a pH meter (HANNA instruments HI 991001, USA).

An inductively coupled plasma optical emission spectrometer (ICP–OES, Spectro–Genesis EOP II, Spectro Analytical Instruments GmbH, Kleve, Germany) was used to determine the concentration of leached elements present in the leachate. Before testing the leachate was acidified with nitric acid to a pH value less than 2.

3. Results and discussion

3.1 Composition and pH of leachate

The results of the leaching tests for Cs, Si, Al, Ca, Na, and K are given in Figures 1 and 2. The values of Mg and Fe leached were below the detection limit throughout the whole period of testing, i.e. magnesium and iron leached were not detectable; therefore, the results are not given.

In the case of AAB doped with 2% Cs, the concentration of Cs cations leached from AAB has reached its peak after the first 24 hours of testing, probably due to the leaching of non-bound or loosely bound cesium cations present in the pore solution on the surface or close to the surface of specimen, which is also known as the surface wash-off (Abdel Rahman & Zaki 2009). Fast initial leaching of cesium was followed by lower leaching rates between 48 and 120 hours of testing (Figure 1a), which was obviously controlled by the diffusion of Cs through the AAB matrix. Therefore, the surface wash-off mechanisms should also be taken into account while developing models for predicting the long-term behavior of the immobilized waste matrices.

The same leaching pattern was identified for silicon (Figure 1b), potassium (Figure 1f), and to some extent aluminum when the AAB was doped with 2% Cs (Figure 1c). The overall concentration of aluminum leached was quite low, which is in agreement with our previous findings (Komljenović et al. 2012). Relatively high leaching of silicon is probably connected with the excess of sodium silicate present in the pore solution, since it is relatively difficult to remove Si from C–A–S–H gel in AAB by

aqueous leaching. This statement is also supported by quite low silicon leaching when BFS was activated with sodium hydroxide only (Vandevenne et al. 2018). The concentration of sodium leached was relatively high throughout the whole experiment duration (Figure 1e), with a noticeable decline in the final stages of the experiment (72-120 hours) probably due to the depletion of sodium ions present in the pore solution.
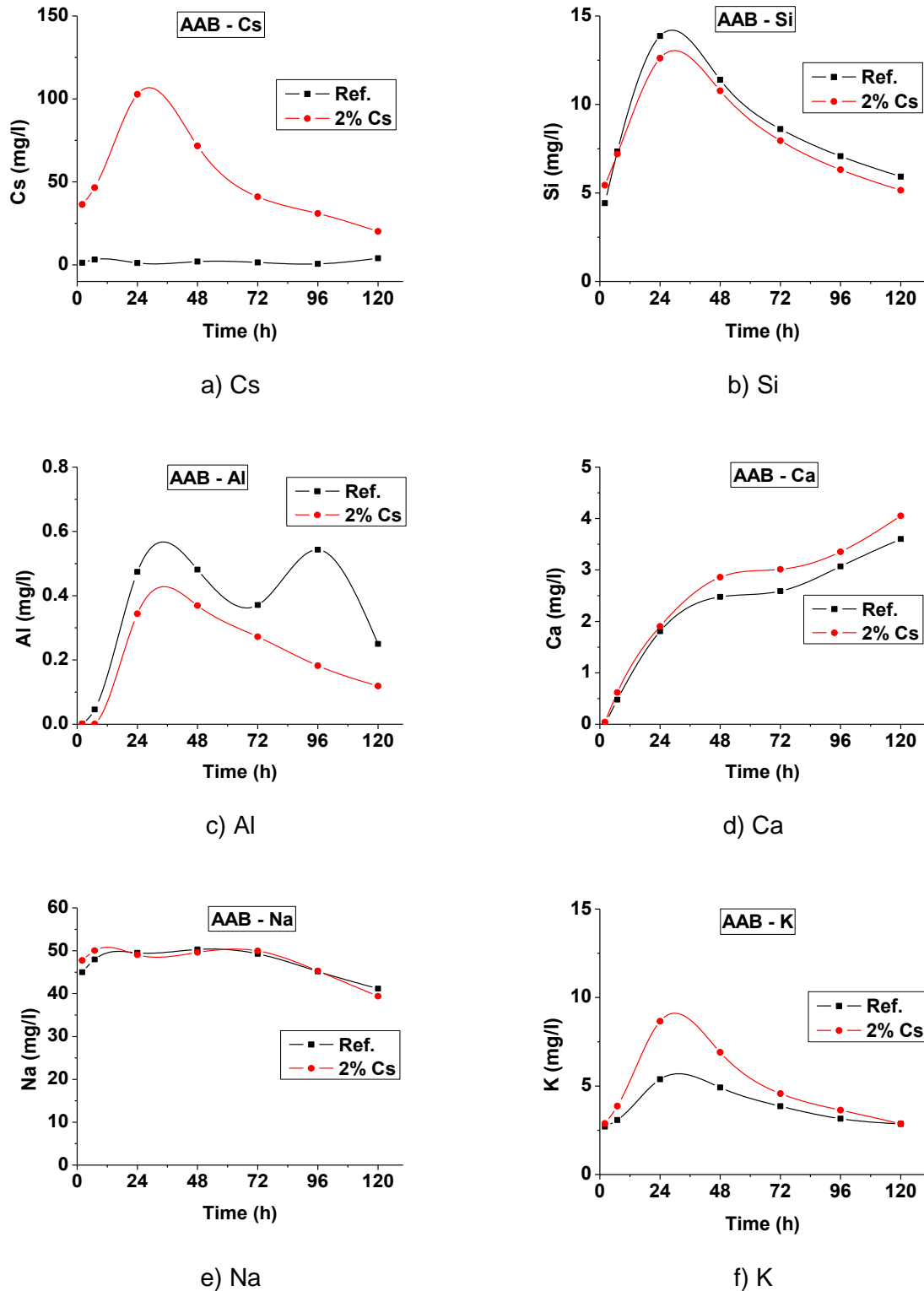
a) Cs

b) Si

c) Al

d) Ca

e) Na

f) K

Figure 1. Incremental leach fractions of main elements from AAB matrix up to 120 hours (reference AAB, and AAB doped with 2% Cs)
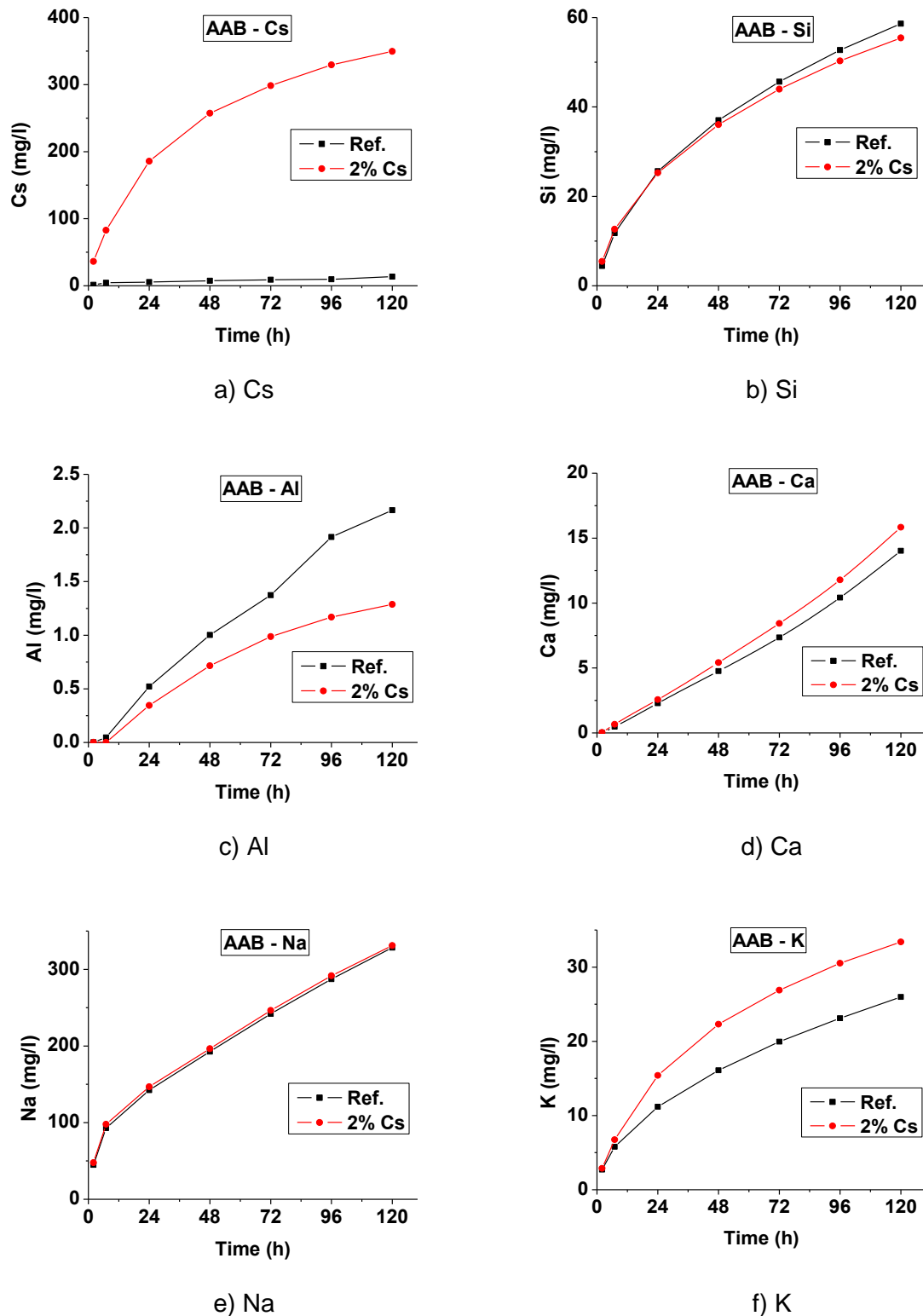
a) Cs

b) Si

c) Al

d) Ca

e) Na

f) K

Figure 2. Cumulative leach fractions of main elements from the AAB matrices up to 120 hours (reference AAB, and AAB doped with 2% Cs)

The presence of Cs cations did not significantly influence the leaching of Si, Ca (Figure 1d), and Na, while some minor influence was noted in the case of Al. The most significant influence of the presence of Cs cations was noticed in potassium leaching, particularly during the first 48 hours (Figure 1f). However, the increased potassium leaching in the mentioned period did not have any significant impact on the pH values of leachate (Table 3), since the concentration of potassium leached was

relatively low, as this was only supplied by the slag and not the activator. On the other hand, sodium leaching had a more pronounced effect on pH value of leachate, particularly after the first 48 hours when the concentration of sodium leached started to decline, followed by a pH decline regardless of the Cs cations present (Table 3). These results are also in good agreement with some recent findings (Vandevenne et al. 2018).

Table 3. pH of leachates up to 120 hours measured at each replacement of the water (reference AAB, and AAB doped with 2% Cs)

Leaching period (h)	2	7	24	48	72	96	120
Ref. AAB	11.02	11.13	11.53	11.42	11.15	11.06	10.93
2% Cs	10.94	11.15	11.51	11.43	11.18	11.05	10.98

Cumulative leaching results for main elements from the AAB matrices are given in Figure 2. These results confirmed the high mobility of alkali cations in the pore system of the AAB matrices based on BFS, particularly of Cs and Na, which might have a negative influence on the efficiency of Cs immobilization. These results are in good agreement with the results of Lloyd et al. (2010) who also suggested that the presence of calcium was important for reducing alkali mobility through reduction of pore volume. This might mean that AAB based on high-calcium containing solid precursors, such as blast furnace slag, could provide a better microstructural environment for safe immobilization of wastes than low-calcium containing solid precursors, such as the ASTM type F fly ash which would generate a more porous binder. However, Cs binding in C-S-H type gels is known to be relatively weak, whereas some low-calcium containing binders could potentially offer specific chemical binding of Cs and/or ion exchange for the other alkalis present (Jang et al. 2016).

It is also worth noticing that the concentration of Ca in the leachate, although relatively low, steadily increased over time. This might be the result either of C-A-S-H decalcification or additional dissolution of unreacted BFS grains, or even both. This phenomenon should not represent a serious threat to the structure stability of AAB since our previous findings showed that the strength of AABs slowly but steadily increases over time even when AABs were exposed to aggressive solutions (Marjanović et al. 2015).

3.2 Diffusion coefficient (D) and leachability index (L)

The diffusion coefficient (D) and the leachability index (L) of cesium leached from AAB can be calculated according to the following equations (ANSI/ANS-16.1–2003):

$$D = \pi \, [(a_n/A_o)/(\Delta t)_n]^2 \cdot [V/S]^2 \cdot T \qquad (1)$$

where D is the effective diffusivity (cm^2/s), a_n is the quantity of cesium released from the specimen during leaching interval n (g), A_o is the total quantity of cesium in the specimen at the beginning of the first leaching interval (g), $(\Delta t)_n = t_n - t_{n-1}$ is the duration of the nth leaching interval (s), V is the volume of the specimen (cm^3), S is the geometric surface area of the specimen in contact with the leachant as calculated from measured dimensions (cm^2), and T is the leaching time representing the "mean time" of the leaching interval (s) as follows:

$$T = [1/2(t_n^{1/2} + t_{n-1}^{1/2})]^2 \qquad (2)$$

The non-dimensional leachability index is defined by:

$$L_i = 1/7 \, \Sigma_1^7 [\log(\beta/D_i)]_n \qquad (3)$$

where β is a defined constant (1.0 cm^2/s).

Based on the results of cesium leaching tests (given in Figure 1a) and the equations (1), (2), and (3), the diffusion coefficient (D) and leachability index (L) of cesium leached from alkali-activated BFS doped with 2% Cs were calculated, and are given in Figure 3.
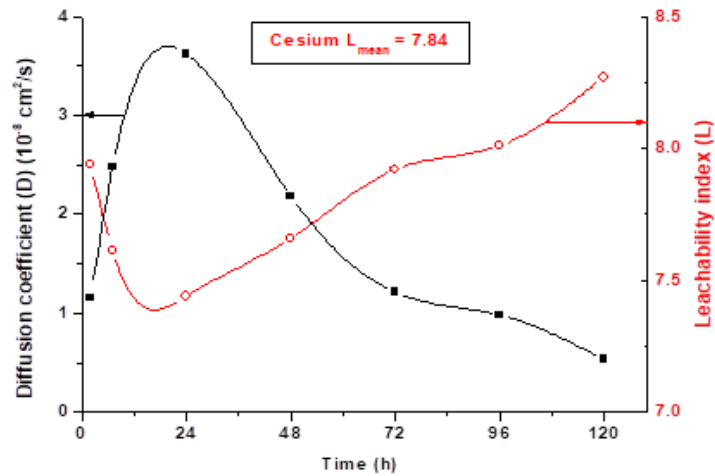
Figure 3. Diffusion coefficient (D) and non-dimensional leachability index (L) of cesium leached from alkali-activated BFS doped with 2% Cs versus time

The leachability index (L) is a parameter which characterizes the leaching resistance of an element of interest, and can be used to estimate the applicability of a certain material or matrix for safe immobilization of hazardous waste. Obviously, the mean leachability index of cesium leached from alkali-activated BFS doped with 2% Cs (7.84, Figure 3) exceeded the minimum required value of 6, since the value of 6 is considered as the threshold for a given matrix to be accepted as adequate for the immobilization of radioactive wastes (Abdel Rahman et al. 2007). The results presented here are comparable with the results for cesium immobilized in Portland cement matrix obtained under same experimental conditions (ANSI/ANS-16.1), where after 5 days of leaching the mean cesium diffusion coefficient and leachability index were $1.2 \cdot 10^{-7}$ cm^2/s and 6.9, respectively (Jang et al. 2016). Consequently, an AAB based on BFS, synthesized under given experimental conditions, can be considered as a potentially efficient matrix for immobilizing cesium from radioactive wastes.

It also seems resonable to expect that by the addition of some other material with high sorption capacity, such as clay or zeolite, the leachability index of cesium immobilized in alkali-activated BFS might be additionally improved.

4. Conclusions

In this paper the leaching resistance of alkali-activated binder (AAB) based on blast furnace slag (BFS), contaminated with 2% cesium (i.e., a solidified simulated low-level radioactive waste), was investigated according to the ANSI/ANS-16.1-2003 standard procedure.

Based on the leaching results obtained for different elements, in particular for Cs, Si, Al, Ca, Na, and K, it was concluded that the short (up to 5 days) semi-dynamic process of leaching from AAB can be divided into two distinct stages: a) fast leaching of non-bound or loosely bound ions in the initial 24 hours which occurred mostly between the surface of AAB and the leachant, and b) slower leaching in the later stages of experiment which was controlled by diffusion of ions through the AAB matrix.

By calculating the diffusion coefficient (D) and the leachability index (L) of cesium it was estimated that AAB based on blast furnace slag, synthesized under the given experimental conditions, can be considered as a potentially efficient matrix for immobilizing up to 2% cesium in hazardous wastes.

5. Acknowledgements

6. References

Abdel Rahman RO, Zaki AA, & El-Kamash AM, (2007). *Modeling the long-term leaching behavior of ^{137}Cs, ^{60}Co, and $^{152,154}Eu$ radionuclides from cement–clay matrices*, Journal of Hazardous Materials, Volume 145, pp 372–380.

Abdel Rahman RO, & Zaki AA, (2009). *Assessment of the leaching characteristics of incineration ashes in cement matrix.* Chemical Engineering Journal, Volume 155, pp 698–708.

ANSI/ANS-16.1–2003 (R2017). *Measurement of the leachability of solidified low-level radioactive wastes by a short-term test procedure.* American Nuclear Society.

Bernal SA, Krivenko PV, Provis JL, Puertas F, Rickard WDA, Shi C, & van Riessen A, (2014). *Other Potential Applications for Alkali-Activated Materials.* Chapter 12 in Alkali Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM, Provis JL, & van Deventer JSJ (eds.), RILEM, pp 339-381.

Chen S, Wu M, & Zhang S, (2010). *Mineral phases and properties of alkali-activated metakaolin-slag hydroceramics for a disposal of simulated highly-alkaline wastes.* Journal of Nuclear Materials, Volume 402, pp 173–178.

El-Naggar MR, & Amin M, (2018). *Impact of alkali cations on properties of metakaolin and metakaolin/slag geopolymers: Microstructures in relation to sorption of ^{134}Cs radionuclide*, Journal of Hazardous Materials Volume 344, pp 913–924.

Jang JG, Park SM, & Lee HK, (2016). *Physical barrier effect of geopolymeric waste form on diffusivity of cesium and strontium.* Journal of Hazardous Materials, Volume 318, pp 339–346.

Komljenović M, Baščarević Z, Marjanović N, & Nikolić V (2012). *Decalcification resistance of alkali-activated slag.* Journal of Hazardous Materials, Volume 233-234, pp 112-121.

Kryvenko P, Cao H, Petropavlovskyi O, Weng L, & Kovalchuk O, (2015). *Applicability of alkali-activated cement for immobilization of low-level radioactive waste in ion-exchange resins.* Восточно-Европейский журнал передовых технологий, Issue 1/6, Volume 79, pp 40-45.

Lancellotti I, Barbieri I, & Leonelli C, (2014). *Use of alkali-activated concrete binders for toxic waste immobilization.* Chapter 20 in Handbook of Alkali-activated Cements, Mortars and Concretes, Pacheco-Torgal F, Labrincha JA, Leonelli C, Palomo A, & Chindaprasirt P, (eds.), Woodhead Publishing, pp 539-604.

Lloyd RR, Provis JL, & van Deventer JSJ, (2010). *Pore solution composition and alkali diffusion in inorganic polymer cement.* Cement and Concrete Research, Volume 40, pp 1386–1392.

Marjanović N, Komljenović M, Baščarević Z, Nikolić V, & Petrović R, (2015). *Physical–mechanical and microstructural properties of alkali-activated fly ash–blast furnace slag blends.* Ceramics International, Volume 41, pp 1421–1435.

Qian G, Sun DD, & Tay JH, (2001). *New aluminium-rich alkali slag matrix with clay minerals for immobilizing simulated radioactive Sr and Cs waste.* Journal of Nuclear Materials, Volume 299, pp 199-204.

Tsutsumi T, Nishimoto S, Kameshima Y, & Miyake M, (2014). *Hydrothermal preparation of tobermorite from blast furnace slag for Cs⁺ and Sr²⁺ sorption*, Journal of Hazardous Materials, Volume 266, pp 174–181.

Vandevenne N, Iacobescu RI, Pontikes Y, Carleer R, Thijssen E, Gijbels K, Schreurs S, & Schroeyers W, (2018). *Incorporating Cs and Sr into blast furnace slag inorganic polymers and their effect on matrix properties.* Journal of Nuclear Materials, Volume 503, pp 1-12.