

PAPER • OPEN ACCESS

The influence of alkaline activator on immobilization of metals in alkali-activated blast furnace slag

To cite this article: E Bystrianska and J Koplík 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1039** 012013

View the [article online](#) for updates and enhancements.



240th ECS Meeting ORLANDO, FL

Orange County Convention Center **Oct 10-14, 2021**

Abstract submission deadline extended: April 23rd

SUBMIT NOW

The influence of alkaline activator on immobilization of metals in alkali-activated blast furnace slag

E Bystrianska¹ and J Koplík¹

¹ Brno University of Technology, Faculty of Chemistry, Purkyňova 118, 612 00 Brno, Czech Republic

Email: emilia.bystrianska@vut.cz

Abstract. In this work the influence of alkaline activator on immobilization of lead and copper in alkali-activated blast furnace slag was investigated. A total of five alkali activators were used; sodium waterglass, potassium waterglass, sodium hydroxide, potassium hydroxide and sodium carbonate. The leaching test according to ČSN EN 12457-4 was used to evaluate the level of immobilization of heavy metals, the leached solutions were analyzed by ICP-OES. For a better understanding of immobilization process, the selected samples were characterized by analytical methods (SEM, XPS). It was found that the degree of immobilization of Pb²⁺ and Cu²⁺ in AAS was very high regardless of the type of alkaline activator used. The high degree of immobilization is caused by formation of insoluble or poorly soluble lead and copper compounds in an alkaline environment while the insoluble compounds have been confirmed by SEM and XPS.

1. Introduction

Solidification/stabilization (S/S) is one of the most important techniques for treating wastes containing heavy metal contaminants. The purpose of S/S technology is physically as well as chemically fix heavy metals (or polluted waste) in the solid matrix to reduce their mobility and therefore minimize the threat to the environment. This technology is widely used to dispose of low-level radioactive waste, hazardous and mixed waste. Ordinary Portland cement (OPC) has been the most common solidification material because of its availability and low cost. However, OPC binders are not very effective in stabilizing some heavy metals [1–2].

The efficiency of the heavy metal immobilization is strongly related to the microstructure of hardened paste and total porosity. Hardened alkali-activated slag (AAS) binders have less porosity than OPC binder. Therefore, the mitigation of solution into the AAS binder is limited which results in a lower leachability of toxic waste. Except for total porosity of binders, pH values of pastes play an important role in the process of S/S and type of C-A-S-H gel forming in paste too. In a high alkaline environment, most of the heavy metals precipitate into less soluble or insoluble compounds. Besides low permeability and alkaline pore solution, AAS binders present other important properties including high mechanical strength and high resistance to acid or chloride attack. Due to all these physical and chemical advantages, alkali-activated slag binders are considered to be more effective for waste immobilization than OPC [3–5].

The ability of alkali-activated slag to immobilize heavy metals or other hazardous materials in its structure has been investigated in various studies [6–8]. The efficiency of heavy metal immobilization in alkali-activated slag binders depends on many factors including nature and concentration of alkaline activator used or type of immobilized material and its dosage. Heavy metals addition (Zn²⁺, Pb²⁺, Cd²⁺ a Cr⁶⁺) up to 2% of slag weight can be well stabilized in NaOH, Na₂CO₃, and sodium silicate-activated



slag binder [9]. Solidification/stabilization of Pb^{2+} and Cu^{2+} were mostly investigated in fly ash-based geopolymers with high immobilization efficiency [10–13].

The aim of this work is to compare the ability of AAS binders activated by different types of alkaline activators to immobilize Pb and Cu in their structure. In the present work, we have also tried to determine if the heavy metals are stabilized by chemical converting into their less soluble or insoluble forms.

2. Experimental procedure

2.1. Materials

2.1.1. Ground granulated blast furnace slag. Ground granulated blast furnace slag (GGBFS) was obtained from Kotouč Štramberk, Ltd. having a Blaine specific surface area of $400 \text{ m}^2 \cdot \text{kg}^{-1}$. The GBFS was mostly amorphous but it also contained crystalline phases such as åkermanite, calcite, merwinite, and quartz (measured by X-ray powder diffraction). The chemical composition of GGBFS measured by the X-ray fluorescence technique used for alkali activation is given in table 1.

Table 1. Chemical composition of ground granulated blast furnace slag.

GGBFS Kotouč Štramberk [wt. %]									
CaO	SiO ₂	MgO	Al ₂ O ₃	SO ₃	TiO ₂	K ₂ O	MnO	Na ₂ O	Fe ₂ O ₃
41.1	34.7	10.5	9.1	1.4	1.0	0.9	0.6	0.4	0.3

2.1.2. Alkaline activators. For this work five alkaline activators were used: Liquid sodium waterglass (S-WG) – Silicate modulus $M_s = 1.96$; Liquid potassium waterglass (P-WG) – Silicate modulus $M_s = 1.67$; Sodium hydroxide (SH); Potassium hydroxide (PH) and Sodium carbonate (SC). Sodium and potassium hydroxide were used as 50% solution. Sodium carbonate was dissolved in water and cooled to ambient temperature before alkali activation. The Na_2O/K_2O dosage of the alkaline activator was kept the same.

2.1.3. Heavy metals. The heavy metal-containing compounds $Pb(NO_3)_2$ p.a. and $Cu(NO_3)_2 \cdot 3H_2O$ p.a. have been used in sample preparation. The amounts of heavy metals (Pb^{2+} , Cu^{2+}) adding to the hydrating samples were on level 1% of slag weight.

2.2. Tests and methods

2.2.1. Sample preparation. The pastes were prepared at the water to binder ratio equal to 0.38 (w/b was kept the same for each activator used). The concentration of alkaline activator in the slag binder was 6% of Na_2O/K_2O of the slag content for each activator used. The alkaline activators were fully dissolved in water and after that mixed with slag. The pastes were mixed in a standard laboratory mixer for 180 s, cast into moulds ($20 \times 20 \times 100$ mm) and vibrated for 30 s to remove large air bubbles. All the samples were matured in the moulds for the first 24 h at 20 C and 100% relative humidity. After that samples were open-air cured at ambient conditions.

2.2.2. Mechanical properties testing. Specimens with dimensions $20 \times 20 \times 100$ mm were used for compressive strength determination using the Desttest 4310 Compact A (Beton System, Ltd.). The compressive strength of the alkali-activated slag was measured after 1, 7, and 28 days on three samples.

2.2.3. Leaching test. The leaching tests were performed using an adaptation of standard ČSN EN 12457–4:2002. After 28 days of curing, specimens of dimensions $20 \times 20 \times 100$ mm were placed into the PET bottle with distilled water at a liquid/solid ratio 10:1 and rotated at 10 rpm for 24 h.

The leachates were analysed on ICP-OES spectroscope (Inductively coupled plasma optical emission spectrometry).

2.2.4. Characterization of materials, hydration products and microstructure analysis. The GGBFS was characterized by XRD and XRF methods. XRD measurement was performed using a PANanalytical Empyrean X-ray diffractometer. The tube voltage and current were 40 kV and 30 mA, respectively. The tube anode was $\text{CuK}\alpha_1$ (1.54 Å). The sample was step-scanned from 5° to 90° 2θ using vertical high-resolution goniometer with a step size of 0.01313 2θ . Times per step were 96 s.

The chemical composition of GGBFS was determined with the Xenometrics EX-6600 XRF spectrometer. Measurement of GGBS powder was performed in vacuum using accelerated voltage 30 kV.

Hydration products and microstructure investigations of AAS with and without heavy metals addition were carried out by SEM and XPS (X-ray photoelectron spectroscopy). These investigations were performed on samples after 28 days of curing.

The SEM analysis was performed on ZEISS EVO LS 10 with the energy dispersive X-ray spectroscopy (EDS) detector. Accelerated voltage was set to 15 kV and the working distance was 12 mm. All samples were sputtered by gold to obtain good surface conductivity.

The XPS analyses were conducted with Kratos Axis Ultra DLD spectrometer using a monochromatic $\text{Al K}\alpha$ ($h\nu = 1486.7$ eV) X-ray source operating at 150 W (10 mA, 15 kV). The high-resolution spectra were measured with a step size of 0.1 eV and 20 eV pass energy. The instrument base pressure was 2×10^{-8} Pa.

3. Results and discussion

3.1. Compressive strength

As can be seen from data obtained (table 2) the type of the alkaline activator used strongly influenced the compressive strength of AAS pastes. Without heavy metals addition the highest 28-day compressive strengths were obtained from AAS samples activated by sodium and potassium waterglass. Effect of cations (Na^+ , K^+) from silicate activators cannot be described because of different silicate modulus of waterglass activators used. However, in sodium and potassium hydroxide activation with same dosage, KOH-activated samples formed denser microstructure [14]. Sodium carbonate-activated slag pastes required a prolonged setting time so they were kept in moulds for 3 days. The longer hardening process is related to the slow development of the alkalinity required for initializing slag dissolution. Although, after 28 days of curing, the sodium carbonate-activated samples gained relatively high compressive strengths (56.9 MPa) [15].

The influence of 1% Pb^{2+} addition on the compressive strength of alkali-activated slag is not very significant. In waterglass-activated samples the measured 1-, 7- and 28-day compressive strengths were very comparable to the reference samples. Samples with Pb^{2+} addition activated by sodium or potassium hydroxide exhibited strength loss up to 30% after 28 days of curing. The addition of 1% Cu^{2+} influenced the compressive strength more significantly regardless of alkaline activator used. Sodium carbonate-activated samples were most affected by Cu^{2+} addition and the 28-day compressive strengths reached only half the strength compared to the reference samples.

The nature of alkaline activator plays an important role in compressive strength development. The highest compressive strengths were obtained by sodium and potassium waterglass and the lowest compressive strength were measured on the samples activated by sodium or potassium hydroxide. Similar results were found in other studies [9, 16].

Table 2. Compressive strength of AAS samples with different alkali activator used.

Sample	Compressive strength [MPa]		
	1 day	7 days	28 days
Na-WG	19.4	69.2	102.1
Na-WG (1% Pb)	18.6	68.0	94.9
Na-WG (1% Cu)	11.2	39.6	77.5
NH	10.4	22.0	37.4
NH (1% Pb)	4.6	16.3	24.6
NH (1% Cu)	4.3	9.3	22.6
K-WG	20.6*	50.6	76.5
K-WG (1% Pb)	20.1*	44.9	78.1
K-WG (1% Cu)	10.5*	17.0	59.4
KH	10.2	30.2	44.3
KH (1% Pb)	5.2	19.1	36.3
KH (1% Cu)	4.4	12.7	31.5
NC	-	51.1	56.9
NC (1% Pb)	-	13.1	45.8
NC (1% Cu)	-	10.1	28.4

*samples measured after 3 days of curing

3.2. Leaching tests

Leaching tests were performed based on the ČSN EN 12457-4:2002. Three specimens from each sample were subjected to a leaching test in distilled water for 24 hours. Results from heavy metal leaching are given in table 3 and table 4. The results showed that the immobilization efficiency of both heavy metals (Cu and Pb) is very high. The highest Pb release occurred in sodium waterglass-activated samples which could be a result of microcracks observed in these samples. The leaching rate of Pb^{2+} corresponds to the findings obtained by Deja et al who reported that amounts of Pb^{2+} ions leached from waterglass-activated mortars are higher than from Na_2CO_3 -activated mortars [9].

Samples with Cu^{2+} addition also showed a low concentration of heavy metal in leachates. From the data obtained the best copper and lead stabilization is achieved by potassium waterglass-activated slag binder. It should be noted that concentrations of both heavy metals in all samples are low and all types of alkaline activators provide safe heavy metals immobilization. High immobilization efficiency of Pb^{2+} and Cu^{2+} in alkali-activated GGBFS was presented in the work of Giergiczny et al [12].

Table 3. Concentration of Pb^{2+} in leachate.

sample	Na-WG (1 % Pb)	NH (1 % Pb)	K-WG (1 % Pb)	KH (1 % Pb)	NC (1 % Pb)
c(Pb^{2+}) [mg/l]	3.070 ±1.146	0.870 ±0.345	0.413 ±0.039	2.797 ±0.050	1.240 ±0.388

Table 4. Concentration of Cu^{2+} in leachate.

sample	Na-WG (1 % Cu)	NH (1 % Cu)	K-WG (1 % Cu)	KH (1 % Cu)	NC (1 % Cu)
c(Cu^{2+}) [mg/l]	0.950 ±0.138	0.930 ±0.043	0.443 ±0.072	0.980 ±0.024	0.470 ±0.076

3.3. Microstructure of pastes

The microstructure of hardened alkali-activated pastes with heavy metals addition was investigated by SEM analysis. All the AAS samples (regardless of alkaline activator used) had a very dense structure with C-(A)-S-H gel as the main component. The significant differences between the samples doped with heavy metals and reference samples were not observed. The samples with sodium waterglass activation showed higher amounts of microcracks than any other samples (figure 1). Heavy metal compounds (lead and copper) were rather cumulated in some regions than dispersed through the structure. The precipitated lead compound can be seen in figure2 and hollow compound containing copper is

shown in figure 3. From EDS analysis taken in areas with high heavy metal concentration (table 5, table 6) can be seen that lead and copper are primary cumulated with oxygen.

Table 5. EDS analysis of the area with high Pb concentration from figure 2.

Element	O	Na	Mg	Al	Si	Ca	Pb
Atom. %	41.21	3.29	0.37	0.33	7.35	1.13	15.73

Table 6. EDS analysis of the hollow particle containing copper from figure 3.

Element	O	Na	Si	Cl	Ca	Cu
Atom. %	61.89	9.54	0.72	5.31	1.22	20.34

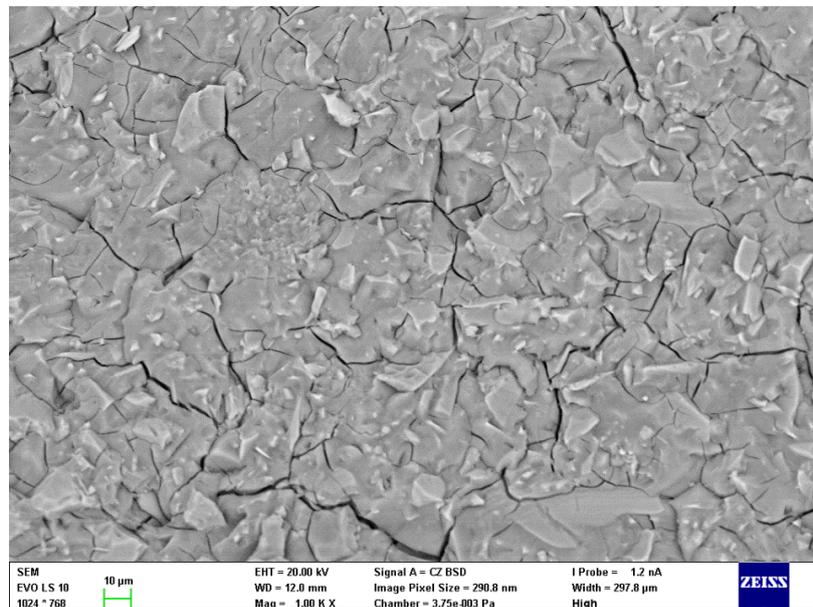


Figure 1. Sodium waterglass AAS binder doped with Pb^{2+} .

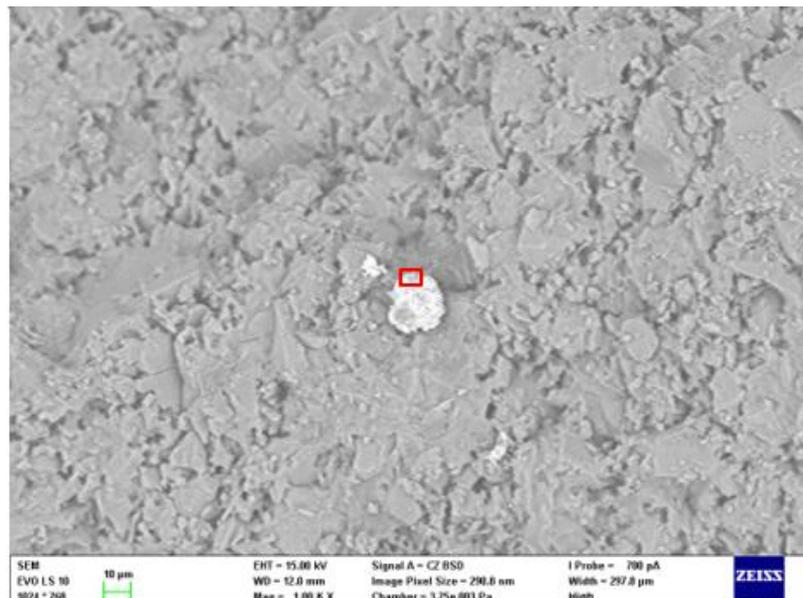


Figure 2. Sodium carbonate AAS binder doped with Pb^{2+} .

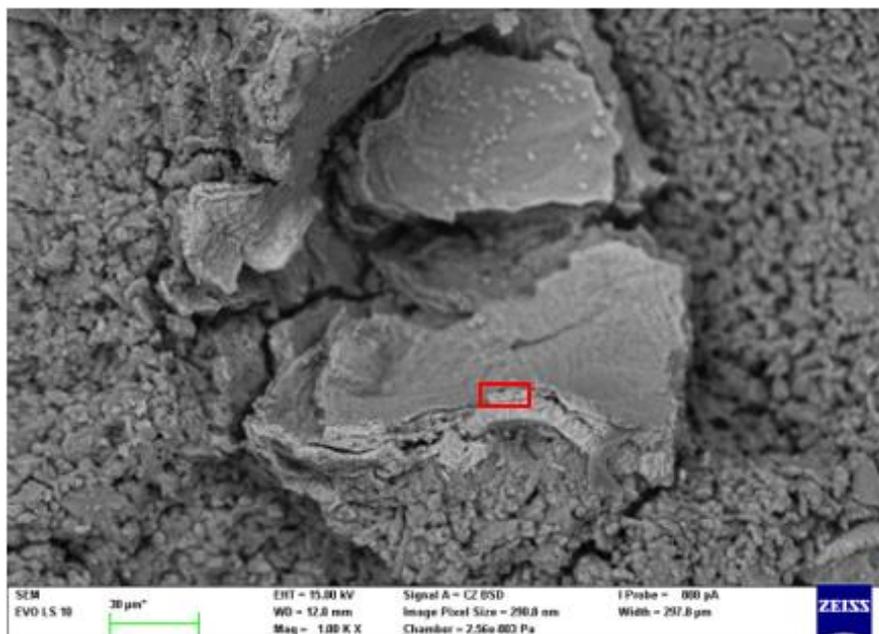


Figure 3. Sodium hydroxide AAS binder doped with Cu^{2+} .

3.4. XPS analysis

The XPS spectra of Pb of sample Na-WG (1% Pb) is shown in figure 4. The binding energies of Pb $4f_{7/2}$ and Pb $4f_{5/2}$ are 138.6 eV and 143.3 eV. These values are typical for $\text{Pb}(\text{OH})_2$. The highly soluble primary phase $\text{Pb}(\text{NO}_3)_2$ dissolves during sample preparation and Pb^{2+} ions in an alkaline solution precipitate into an insoluble hydroxide.

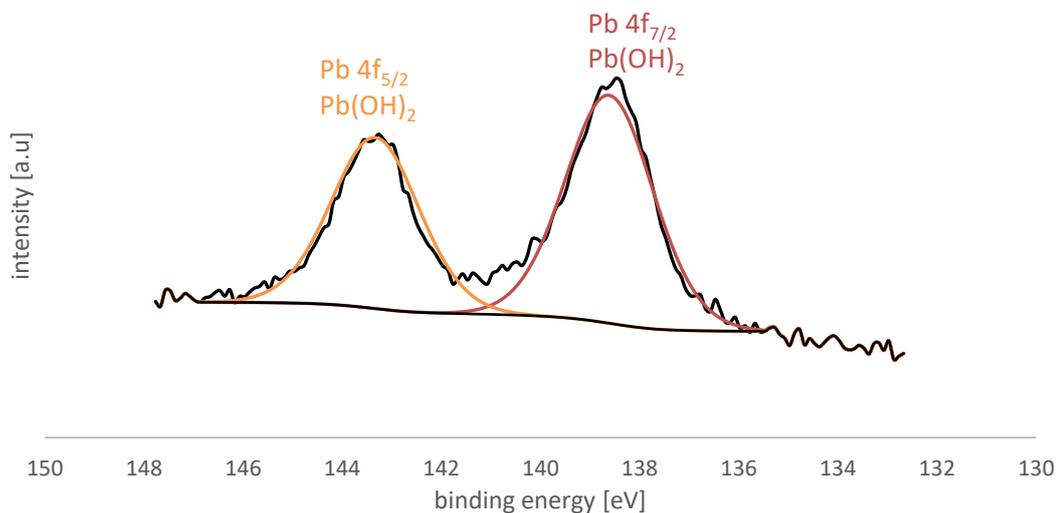


Figure 4. XPS spectra of Pb in sample activated by sodium waterglass.

In XPS spectra (figure 5) of a sample containing copper and activated by 50% solution of sodium hydroxide (1% Cu) are shown two different chemical states. The first, Cu $2p_{3/2}$ component with binding energy 935.35 eV with strong shake-up satellites belongs to $\text{Cu}(\text{OH})_2$. Shake-up satellites occur when an outgoing electron interacts with a valence electron and excites it (shakes it up) to a higher energy level. As a consequence, the energy core electron is reduced and a satellite structure appears a few eV below (KE scale) the core level position. The second peak, Cu $2p_{3/2}$ with binding energy 933.50 eV, represents the bond between Cu and O. That can be interpreted as the formation of copper oxide or

the formation of the bond with the matrix. Both copper compounds (CuO and $\text{Cu}(\text{OH})_2$) are insoluble in distilled water [17, 18].

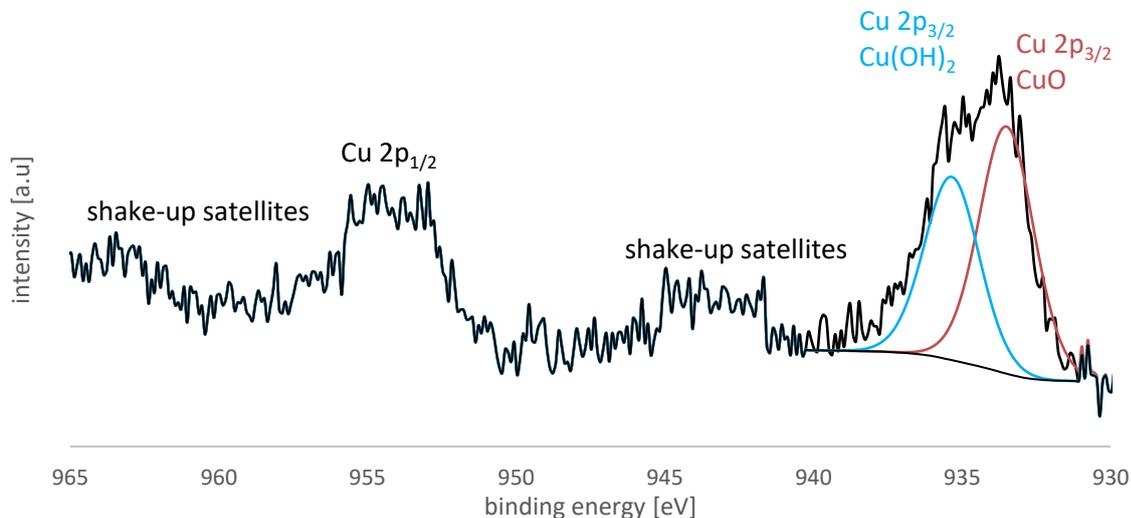


Figure 5. XPS spectra of Cu in sample activated by sodium hydroxide.

4. Conclusion

The influence of alkaline activator type on heavy metals (Pb and Cu) immobilization was investigated. Five alkaline activators were used: sodium waterglass, potassium waterglass, sodium hydroxide, potassium hydroxide and sodium carbonate. From the results obtained by leaching tests (ČSN EN 12457-4:2002) can be seen that the immobilization efficiency of heavy metals (Pb^{2+} and Cu^{2+}) is very high for all types of alkaline activator used. Slightly higher concentrations of heavy metals in leachates were observed when the samples were activated by sodium waterglass. It was probably caused by presence of microcracks which allowed leaching out heavy metals from samples. From SEM observation can be seen that both heavy metals – lead and copper, were rather cumulated in some areas than disperse through the whole structure. Finally, XPS analysis confirmed that Pb and Cu formed insoluble salts in alkali-activated slag binders.

References

- [1] Yilma O, Ünlü K and Cokca E 2003 Solidification/Stabilization of Hazardous Wastes Containing Metals and Organic Contaminants *Journal of Environmental Engineering* **129**(4) pp 366–376
- [2] Al-kindī G, Provis J L, Myers R J, San Nicolas R and Van Deventer J S J 2019 Evaluation the Solidification/Stabilization of Heavy Metals by Portland Cement: Alternative matrices for the immobilisation of hazardous wastes *Journal of Ecological Engineering* **20**(3) pp 91–100
- [3] Shi C, Fernández-Jiménez A, Rekha P, Bindhu V H and Anjaneyulu Y 2006 Stabilization/solidification of hazardous and radioactive wastes with alkali-activated cements *Journal of Hazardous Materials* **137**(3) pp 1656–1663
- [4] Provis J L and Van Deventer J S J 2014 Alkali Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM.
- [5] Palomo A, López Dela Fuente J I, Rekha P, Bindhu V H and Anjaneyulu Y 2003 Alkali-activated cementitious materials: Alternative matrices for the immobilisation of hazardous wastes *Cement and Concrete Research* **33**(2) pp 281–288
- [6] Qian G, Delai Sun D, Hwa Tay J and Sun G 2003 Characterization of mercury- and zinc-doped alkali-activated slag matrix *Cement and Concrete Research* **33**(8) pp 1251–1256
- [7] Shi C, Fernández-Jiménez A, Zhao M, Yang K, Shen R and Zheng Y 2006 Stabilization/solidification of hazardous and radioactive wastes with alkali-activated cements

- Journal of Hazardous Materials* **137**(3) pp 1656–1663
- [8] Zhang M, Yang C, Zhao M, Yang K, Shen R and Zheng Y 2017 Immobilization potential of Cr(VI) in sodium hydroxide activated slag pastes *Journal of Hazardous Materials* **321**(8) pp 281–289
- [9] Deja J, Sun W, She W and Sun G 2002 Immobilization of Cr⁶⁺, Cd²⁺, Zn²⁺ and Pb²⁺ in alkali-activated slag binders *Cement and Concrete Research* **32**(12) pp 1971–1979
- [10] Zhang Y, Sun W, She W and Sun G 2009 Synthesis and heavy metal immobilization behaviors of fly ash based geopolymer *Journal of Wuhan University of Technology-Mater. Sci. Ed.* **24**(5) pp 819–825
- [11] Wang Y, Han F, Mu J and Sun G 2018 Solidification/stabilization mechanism of Pb(II), Cd(II), Mn(II) and Cr(III) in fly ash based geopolymers *Construction and Building Materials* **160**(8) pp 818–827
- [12] Giergiczny Z, Król A, Zhao M, Yang K, Shen R and Zheng Y 2008 Immobilization of heavy metals (Pb, Cu, Cr, Zn, Cd, Mn) in the mineral additions containing concrete composites *Journal of Hazardous Materials* **160**(2–3) pp 247–255
- [13] Zheng L, Wang W, Qiao W, Shi Y, Liu X and Zheng Y 2015 Immobilization of Cu²⁺, Zn²⁺, Pb²⁺ and Cd²⁺ during geopolymerization *Journal of Hazardous Materials* **9**(4) pp 642–648
- [14] Tänzer R, Jin Y and Stephan D 2017 Alkali activated slag binder: effect of cations from silicate activators *Materials and Structures* **50**(1)
- [15] Bernal S A., Provis J L, Myers R Y, San Nicolas R and Van Deventer J S J 2015 Role of carbonates in the chemical evolution of sodium carbonate-activated slag binders: Alternative matrices for the immobilisation of hazardous wastes *Materials and Structures* **48**(3) pp 517–529
- [16] Fernandez-Jimenez A, Palomo J and Puertas F 1999 Alkali-activated slag mortars-Mechanical strength behaviour
- [17] Watts J F and Wolstenholme J 2005 *An Introduction to Surface Analysis by XPS and AES* (John Wiley & Sons)
- [18] Biesinger M C, Provis J L, Myers R Y, San Nicolas R and Van Deventer J S J 2017 Advanced analysis of copper X-ray photoelectron spectra: Alternative matrices for the immobilisation of hazardous wastes *Surface and Interface Analysis* **49**(13) pp 1325–1334