Immobilization of heavy metals (Cd, Ni or Pb) using aluminate geopolymers

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Abstract

In the present study, a waste aluminate solution from the anodizing industry was used to synthesize coal fly ash- and blast furnace slag-based geopolymers as metal-immobilizing matrixes. Different alkali-activating agents such as NaOH and sodium silicate have also been used in order to achieve a defined Si/Al ratio in the mixtures. Mixtures of simulated waste containing hazardous metals such as Pb, Cd, or Ni with the geopolymer materials have been processed to study the potential of geopolymers as waste immobilizing agents. The effects of composition on the compressive strength and metals leachability were assessed. Of the two aluminate geopolymers studied, those containing slag exhibited better mechanical performance. Concentrations of the metals leached from the stabilized products were strongly pH dependent, showing that the leachate pH was an important variable for the immobilization of metals.

Keywords: Slag, geopolymer, fly ash, aluminum waste, compressive strength, hazardous metals, leachability

1. Introduction

In this paper, geopolymerization technology has been proposed to stabilize and solidify a simulated residue containing hazardous metals such as Pb, Cd or Ni. Geopolymers are commonly obtained by the reaction between a solid aluminosilicate and a highly concentrated aqueous alkali hydroxide or silicate solution [1]. The raw materials mainly used in geopolymerization are clays or pozzolanic materials such as kaolin, calcined kaolin, different fly ashes (FA) and blast furnace slag (BFS) that partially dissolve in the alkali solution.

The alkali solution dissolves alumina and silica precursors and maybe for this reason alkaline silicates or aluminates have been proposed as activating solutions. The use of aluminates as geopolymer activators has been described in the literature using different sources such as sodium aluminate [2-3], calcium aluminum cements [4] or Bayer-process liquors as a primary source of caustic sodium aluminate [5].

Geopolymers have found application as a binder in metals waste Stabilization/Solidification (S/S) systems since their discovery. When geopolymers are used in S/S systems to immobilize hazardous metals they function similarly to cement binders in terms of encapsulation, however, they can manifest the improved chemical and physical properties shown by geopolymers in construction [1]. The mechanism of heavy metals immobilization is believed to be either physical or chemical.

The use of aluminate containing geopolymer matrixes for heavy metals solidification and immobilization is very limited. Due to the $[AlO_4^-]$ negative charge in geopolymer, some attraction had been focused on the immobilization of metal cations by charge neutralization in recent years.

Ogundiran et al. [6] have evaluated the Pb immobilization of the metal coming from a lead smelting slag in a coal fly ash-aluminate mixture. A spent aluminum etching solution, which contains sodium aluminate, similar to the one described in the present work, was employed. Lead immobilization using aluminate AES-geopolymers was compared with a potassium silicate KS-geopolymer immobilizing matrix. AES performed slightly better than KS. According to the authors, the difference might be due to enhanced chemical bonding of Pb in the more negatively charged AES-based geopolymers that, therefore, could accommodate more cations for charge balancing.

Lee et al. [7] have also evaluated the effect of alkaline activator type (commercial silicate versus aluminate) on the stability of the immobilization of lead (added as lead nitrate) in a FA-

geopolymer. The authors suggest that the Si:Al ratio in the geopolymeric matrix (lower in the aluminate-activated geopolymers) is a critical factor governing the lead immobilization efficiency.

Aluminate-geopolymers were also applied to the stabilization of the metals contained in a Municipal Solid Waste Incineration (MSWI) FA [8]. A series of samples was designed to investigate the effect of aluminate or silicate addition on the strength, microstructure and heavy metal immobilization capability of MSWI FA-based geopolymers. The main conclusion was that heavy metal cations cannot be immobilized as counter cations through exchange with Na^+. Moreover, heavy metal immobilization can be improved by aluminate by isomorphous substitution of heavy metals in the geopolymer.

In this study, a waste sodium aluminate solution from the alkaline etching step in the anodizing industry was used to synthesize FA-based and BFS-based geopolymers as metal-immobilizing matrixes. Different alkali-activating agents such as NaOH and sodium silicate have also been used. Mixtures of simulated waste (containing Cd, Ni or Pb) with this kind of geopolymer materials have been processed to study the potential of those geopolymers as waste-immobilizing matrixes.

2. Materials and methods

BFS was used as aluminosilicate source. SiO_2, CaO and Al_2O_3 percentages in BFS were 15.9, 38.2 and 5.97 wt%, respectively. Class F FA was also used. SiO_2, CaO and Al_2O_3 percentages in FA were 63.9, 3.94 and 21.5 wt%, respectively. An aqueous waste sodium aluminate (ALU) from the anodizing aluminum industry (Laminex Granada SA, Spain) was used as activating solution. Sodium aluminate contains Al: 60 g/L, Na: 42 g /L, total S: 4,2 g/L and water: 85 wt%. To increase Na/Al ratio it has been necessary to add NaOH to ALU solution (ALUNa). 5.6 g-NaOH/100 g-ALU for FA-geopolymers and 30.3 g-NaOH/100 g-ALU for BFS-geopolymers Solid sodium silicate was also used in the manufacture of FA-geopolymers. Pb as $Pb(NO_3)_2$, Ni as $Ni(NO_3)_2 \cdot 6H_2O$ or Cd as $Cd(NO_3)_2 \cdot 4H_2O$ were added to the mix in order to study the S/S of

Pb, Ni and Cd. Percentages of Pb, Ni and Cd in geopolymers were 1, 0.75 and 1 wt%, respectively. Cylindrical plastic molds (30 mm-diameter and 30 mm-height) were filled and vibrated for 5 minutes to release entrapped gas bubbles. Samples were cured at room temperature. After 28 days of curing samples were subjected to compressive strength test (EN 196-1) [9] and US-EPA LEAF 1313 leaching test [10]. LEAF 1313 consists in 9 parallel extractions with different pH fluids (pH 2-13). After the tests, samples were filtered through Whatman membrane filters (pore size 0.45 μm). When the procedures were completed, the metal contents in the solutions were determined using ICP-OES techniques. Compositions of the S/S-geopolymer are detailed in Table 1.

Table 1. Compositions of S/S-geopolymer and compressive strength results

S/S geopolymer		FA	BFS
		wt%	wt%
Raw material		61.5	69.3
NaSil		3.10	-
ALUNa		21.3	15.4
Metal-solution	Pb-nitrate	1.0	1.1
	Cd-nitrate	1.8	1.9
	Ni-nitrate	2.4	2.6
	Water	8.9	9.7
Total solid		64.6	69.3
Total liquid		35.4	30.7
Compressive strength (MPa)		0.25 (0.57)	3.11

3. Results and discussion

3.1. Compressive strength

Table 1 shows the compressive strength (CS) values after 28 curing days. FA-geopolymers CS was 0.25 MPa, below the USEPA limit for stabilized wastes (0.35 MPa) [11], although the CS of these samples increased over the time, reaching 0.57 MPa at 45 days. BFS-geopolymers CS was 3.11 MPa. When slag is activated with alkali (sodium) solutions not only sodium aluminum

silicate hydrate (NASH)-gel is formed but mainly a calcium aluminum silicate hydrate (CASH)-gel is also formed which can enhance the geopolymers mechanical properties [1].

3.3. LEAF 1313 results

Figure 1 shows the acid neutralization capacity (ANC) curves (pH versus acid-equivalents/g-dry solid) of FA- and BFS-geopolymers. The ANC curves show the acid buffering capacity of matrices, which is an important variable to evaluate the efficacy of a S/S process of metal-bearing wastes, since this depends on the ability of the matrix to maintain alkaline conditions and the metal solubility greatly depends on pH conditions [12]. As can be seen, the buffering capacity of BFS-geopolymers was higher than that of FA-geopolymers. CASH-gel from BFS-geopolymers, which is probably responsible for this, seems to exert its buffering capacity in the pH-range of 9-12.5. FA-geopolymers, which develop NASH-gel instead of CASH-gel, present low buffering capacity. The matrix acid buffering capacity is going to affect the metal immobilization. ANC curves can also supply information regarding leaching of solids in different leaching agents, for example in an acetic acid solution, as the USEPA TCLP test [13] which corresponds to 2 eq/g-dry and is used for classifying wastes as hazardous.

Figure 1. ANC curves of FA- and BFS-geopolymers

Figure 2 shows the Pb leachate concentrations at different pHs and the TCLP limit (hazardous waste) for Pb. As can be seen, the most effective geopolymers to immobilize lead seems to be those prepared with BFS. Lead leachate concentrations were lower in BFS-geopolymers than in FA-geopolymers over the pH-range studied. A possible reason for this could be the higher buffering capacity of BFS-geopolymers. Other possible reason could be related to solid permeability and porosity, which are linked to mechanical strength (stronger matrices shows less permeability and lower leachability) [1]. Figure 2 also highlights the strong dependence of Pb with pH, which emphasizes the amphoteric behavior of Pb. Finally, as can be seen the TCLP limit was fulfilled by both geopolymers in neutral-basic media (pH 6-12.5).

Figure 2. Pb Leachability vs leachate pH

Figure 3 shows the Cd and Ni leachate concentrations at different pHs. The TCLP limit for Cd is also detailed (there is no TCLP limit for Ni). Data again show the relationship of Cd and Ni concentrations with pH, revealing a step curve (between pH 6-10) with a high leachability at lower pH values and a low leachability at high pH values. Once again, BFS-geopolymers were more effective immobilizing cadmium than FA-geopolymers. However, Ni immobilization does not depend on the type of geopolymer precursor (BFS or FA), which could indicate that probably its immobilization was controlled by the solubility of a Ni hydroxide solid phase. For leachate pHs > 9, Cd concentrations were always below TCLP limit.

Figure 3. Cd and Ni Leachability vs leachate pH

4. Conclusions

The aluminate geopolymers studied have demonstrated great metal immobilization efficiency. Of the two aluminate-geopolymers studied, those containing BFS exhibited better performance than FA-geopolymers. Compressive strength values in the range 1–5 MPa were obtained at 28 days only in the case of the BFS-geopolymers. In addition, BFS-geopolymers were the only mixtures that met the USEPA limits for hazardous wastes. In summary, aluminate geopolymers seem a promising matrix for metal immobilization and can also provide an economical and environmental advantage when a waste aluminate is used instead of a commercial product in a "geopolymer waste matrix for immobilizing hazardous wastes".

4. References

[1] J.A. Pacheco-Torgal, J. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasirt, Handbook of Alkali-activated Cements, Mortars and Concretes. Woodhead Publishing, Cambridge, UK. 2015.

[2] J.W. Phair, J.S.J. Van Deventer, Characterization of fly-ash-based geopolymeric binders activated with sodium aluminate, Ind. Eng. Chem. Res. 41 (17) (2002) 4242-4251.

[3] A. Hajimohammadi, J.L. Provis, J.S.J. Van Deventer, One-part geopolymer mixes from geothermal silica and sodium aluminate Ind. Eng. Chem. Res. 47 (23) (2008) 9396-9405.

[4] M. Vafaei, A. Allahverdi, Influence of calcium aluminate cement on geopolymerization of natural pozzolan, Construc. Build. Mater. 114 (2016) 290-296.

[5] A. Van Riessen, E. Jamieson, C.S. Kealley, R.D. Hart, R.P. Williams, Bayer-geopolymers: An exploration of synergy between the alumina and geopolymer industries, Cement. Concrete. Comp. 41 (2013) 29-33.

[6] M.B. Ogundiran, H.W. Nugteren, G.J. Witkamp, Immobilisation of lead smelting slag within spent aluminate-fly ash based geopolymers, J. Hazard. Mater. 248-249 (1) (2013) 29-36.

[7] S. Lee, A. Van Riessen, C-M. Chon, N-H. Kang, H-T. Jou, Y-J. Kim, Impact of activator type on the immobilisation of lead in fly ash-based geopolymer, J. Hazard. Mater. 305 (2016) 59-66.

[8] L. Zheng, W. Wang, X. Gao, Solidification and immobilization of MSWI fly ash through aluminate geopolymerization: Based on partial charge model analysis. Waste. Manage. 58 (2016) 270–279.

[9] EN 196-1: 2006. Methods of testing cement-Part 1: Determination of strength. European Committee for Standarisation. Brussels, Belgium.

[10] Background Information for the Leaching Environmental Assessment (LEAF) Methods - EPA/ 600/R-10/170, November 2010. Method 1313.

[11] Y. Luna-Galiano, C. Fernández-Pereira, J. Vale, Stabilization/solidification of a municipal solid waste incineration residue using flyash-based geopolymers. J. Hazard. Mater. 185 (2011) 373–381.

[12] C. Fernández-Pereira, Y. Luna-Galiano, M.A. Rodríguez-Piñero, J.F. Vale, X. Querol, Utilization of Zeolitised Coal Fly Ash As Immobilising Agent of a Metallurgical Waste, J. Chem. Technol. Biot. 77 (2002) 305-310

[13] TCLP. US-EPA, 1986. Test methods for evaluating solid wastes, Toxicity Characteristic Leaching Procedure, Method 1311 SW-846.