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Scientific paper

Mechanisms of Heavy Metal Immobilisation using Geopolymerisation Techniques – A review

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Abstract

Every year, substantial amount of waste materials containing toxic substances is produced throughout the world, which causes serious damage to the environment and poses threat to human health. Among available techniques of immobilisation of toxic elements in harmful by-products, geopolymerisation is considered as an effective approach to deal with many environmental issues. Geopolymer binders have long been recognised to have great potential in immobilisation of hazardous wastes due to its advantages over Portland cement based binders. A profound knowledge of how hazardous elements are immobilised by geopolymer binders is necessary for achieving effective waste management strategies. This paper provides some important aspects of geopolymer materials regarding the immobilisation mechanisms and factors influencing the immobilisation efficiency, which are necessary to carry out further research on addressing the hazardous waste immobilisation.

1. Introduction

The rapid industrialisation of many countries, including Vietnam, gives rise to generation of millions of tons of industrial wastes every year and releases undesirable contaminants to the environment. Toxic heavy metal contaminants may be the most dangerous wastes because of their recalcitrant nature (Tchounwou *et al.* 2012) and the severe damage they cause to human health (Science Communication Unit of University of the West of England 2013). Just a very small proportion of harmful wastes produced is reused while most of it is often disposed of at hazardous landfills. In some cases, stabilisation/solidification methods are applied to immobilise toxic elements in harmful wastes and then the subsequent product is disposed of at non-hazardous landfills, which is very useful to minimize environmental threat. If not stabilised, it may become an issue because hazardous waste disposal on land may lead to serious groundwater pollution problems (Bishop 1988). Apart from industrial waste, heavy metals can also be released from several other sources in the environment, as shown in **Fig. 1**.

In the immobilisation of heavy metals, binders obviously have a key role to play and Portland cement is,

often, widely used as the cementitious material in stabilisation/solidification systems because it has low processing costs and the ability to meet stringent processing and performance requirements (Portland Cement Association 1991; Glasser 1997). However, the production of Portland cement not only consumes a large quantity of natural resources and energy but also releases a significant amount of greenhouse gases into the atmosphere (Davidovits 1991, 1994; Neupane 2016). Producing one ton of cement clinker consumes about 3000 MJ of heat energy (although the theoretical value is considered to be about 1750 MJ per ton of clinker) and is very much dependent on the process used. Production of one ton of cement releases nearly one ton of CO₂. Thus, stabilisation/solidification methods using Portland cement could probably be viewed as half measures and new types of binder are required, in terms of the protection of the environment.

Geopolymer, an amorphous inorganic polymer composed of [SiO₄] and [AlO₄]-tetrahedrons linked alternately by sharing all the oxygen (Davidovits 1991), a solid and stable aluminosilicate material formed by alkali hydroxide or alkali silicate activation of a precursor (Duxson *et al.* 2007a), has been valued as a viable alternative to Portland cement in the concrete industry (Davidovits 2005; Duxson *et al.* 2007b; Lloyd and Rangan 2009; Neupane 2016). Since the production of geopolymer materials could enable the reuse of a considerable amount of by-products such as fly ash and slag, generated by industrial activities and reduce the CO₂ emission generated by the production of cement by about 80-90%, geopolymers are ideal materials for immobilisation of toxic wastes.

It was reported that geopolymers have the properties such as high early strength, low shrinkage and improved resistance to alkali-silica reaction, freeze-thaw, sulfate attack and reinforcement corrosion and thus make them

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ideal for the construction of many structural components including floor slabs of containment disposal facilities (Davidovits 1994). Portland cement based materials are unsuitable for stabilisation of various toxic wastes (especially those containing sodium salts of arsenate, borate, phosphate, iodate and sulfides, salts of magnesium, tin, zinc, copper, and lead), and are also unsuitable for solidification of end-product residues with high sulfide contents (Davidovits 2002). This view was shared by Palomo and de la Fuente (2003) who suggested that excellent performances of geopolymers could be achieved in the immobilisation of certain chemical species. This is because geopolymers exhibit superior properties such as having a favourable pore structure with the abundance of the very small pores, low permeability, very high alkalinity, good chemical stability, and a three-dimensional microstructure. A considerable amount of recent researches on geopolymers reported on the degree of toxic waste immobilisation of geopolymers but only a few have attempted to explain how heavy metals are immobilised in geopolymer matrices. This review paper focuses on the immobilisation mechanisms and possible effects of some important factors such as characteristics of source materials, type and dosage of alkali activator, characteristics of the heavy metal forms, and the microstructure of geopolymers on the metal immobilisation of geopolymer binders.

2. Background

2.1 Geopolymerisation / Activation

Geopolymers can be produced from waste and natural aluminosilicate materials such as fly ash, slag, kaolinite, metakaolinite and red mud, through a process called geopolymerisation, or activation procedure. The chemistry of geopolymerisation, or activation procedure of different types of source materials was detailed in RILEM State of the Art Reports (Bernal *et al.* 2014; Provis and Bernal 2014a; Provis *et al.* 2014). There are some noticeable models for geopolymerisation processes. Firstly, Glukhovsky (1959) described that the alkali activation of materials containing silica and reactive alumina consists of a series of processes, namely, destruction, coagulation, condensation and crystallisation. Many researchers then further developed the Glukhovsky theory and proposed different models for geopolymerisation processes. Palomo and de la Fuente (2003) claimed that the geopolymerisation of raw materials might be related to a set of destruction-condensation reactions that could be divided into three stages: Firstly, bonds such as Si-O-Si, Al-O-Al and Al-O-Si of the raw materials are broken. This process needs a stimulus, for example, the variation of the ion force of the medium when adding ions with electro-donor properties (alkaline metals). It is needed in order to redistribute the electronic density over the silicon atoms and stimulate the Si-O-Si bond to break. The negative electrical load of these anions is balanced by cations of alkali

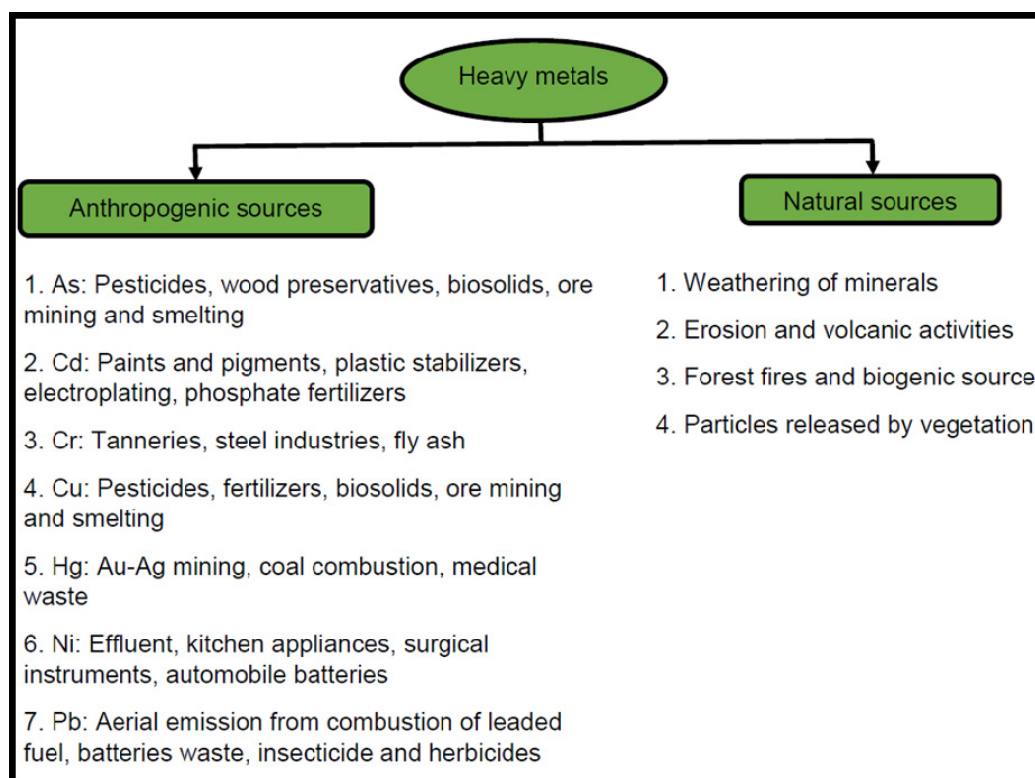


Fig. 1 Sources of heavy metals in the environment (Dixit *et al.* 2015).

Table 1 The simplification of the source materials and reaction products of alkaline activation processes, based on previous studies (Provis and Bernal 2014b; Palomo *et al.* 2014; Provis 2014).

Type	Alkaline activated materials		
	I	II	III
Precursor	High calcium and silicon contents (blast furnace slag BFS)	Low CaO contents (metakaolin, type F fly ash)	A combination of the type I + II (such as a blend of blast furnace slag and type F fly ash)
The main reaction product	A calcium silicate hydrate C-S-H gel, similar to the gel obtained during OPC hydration, with a small percentage of Al in its structure C-A-S-H gel	A three- dimensional inorganic alkaline polymer, a sodium aluminosilicate hydrate N-A-S-H gel that is considered as geopolymer gel	A mix of C-A-S-H and N-A-S-H gels

line metals, generating alkaline silicates. In addition, these alkaline silicates may react with divalent ions, forming Si-O-Ca-OH type complexes. The Al-O-Si bonds are influenced in the same way, and depending on the pH, complexes of the type $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$ will be formed. Secondly, de-segregated products accumulate, generating a coagulation structure in which polycondensation processes take place. The final stage of geopolymerisation is the precipitation of products. Duxson *et al.* (2007) described geopolymeri-

sation process as the multiple gel stages (see Fig. 2).

In Fig. 2, the first stage of the process starts with dissolution of the vitreous component of solid aluminosilicate source by alkaline hydrolysis, and produces aluminate and silicate species. This stage is followed by incorporation of aluminate and silicate species into the aqueous phase. After gelation, a massive precipitation of a rich Al gel (gel 1) occurs. Following that, gel 1 is transformed into a new and more stable gel (gel 2) that is Si-rich. After polymerization and hardening, a synthetic alkali aluminosilicate with three-dimensional network is formed.

According to a recent perspective, geopolymer is deemed as a low calcium subset of the alkaline activated materials (AAMs). AAMs are solid and stable aluminosilicate materials formed by alkali hydroxide or/and alkali silicate activation of a precursor (Provis and Bernal 2014b). There are three types of AAMs, as shown in Table 1, primarily depending on the nature of the source materials or precursors, and geopolymer is considered as the type II of AAMs.

Type I and type II have distinct activation procedures and produce different reaction products. The right-hand pathway in Fig. 3 describes the geopolymerisation of low calcium content precursors (type II), while the left-hand pathway shows the activation of high calcium source materials (type I).

The main reaction product of type I activation is a C-A-S-H (calcium-silicate-hydrate) gel (see Fig. 4), while that of type II is a three dimensional inorganic alkaline polymer (zeolite framework) which can be regarded as a zeolite precursor N-A-S-H (sodium aluminosilicate hydrate) (see Fig. 5) or K-A-S-H (potassium aluminosilicate hydrate). Type III is a mix of these two mentioned types, in which C-A-S-H gels co-exist with zeolite precursor N-A-S-H or K-A-S-H under some conditions (Garcia-lodeiro *et al.* 2011). Due to the zeolite framework within the geopolymeric matrix (see Fig. 5), heavy metals could be locked and the matrix could possess superior mechanical properties and durability.

Red mud is a toxic by-product of the industrial process that refines bauxite, raw aluminum ore, into aluminum oxide, or alumina (Power *et al.* 2011). Bauxite is a mixture of minerals. In addition to aluminum compounds, it contains iron oxides, sand, clay and small amounts of a form of titanium oxide called anatase; it

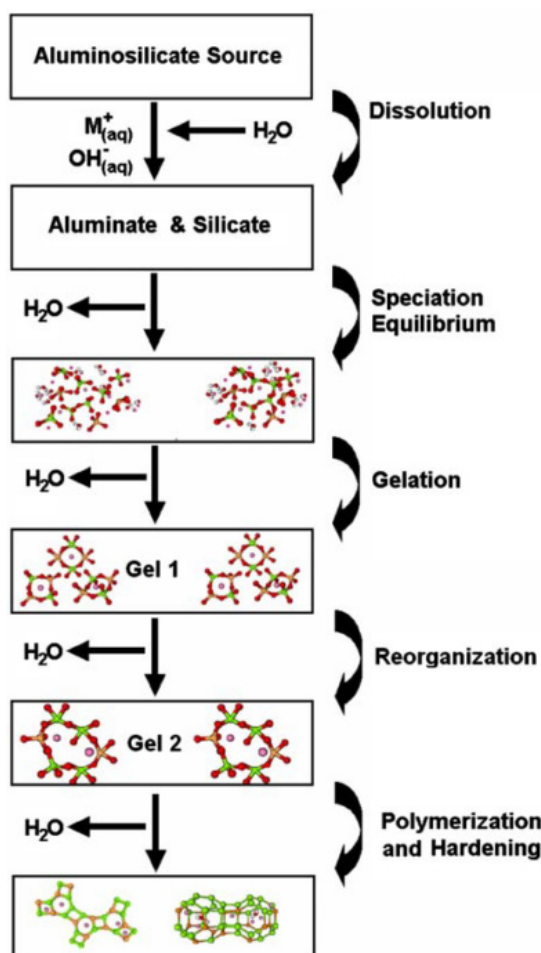


Fig. 2 Conceptual model for geopolymerisation (Duxson *et al.* 2007). [Reprinted by permission of Springer, Journal of Materials Science, © 2007]

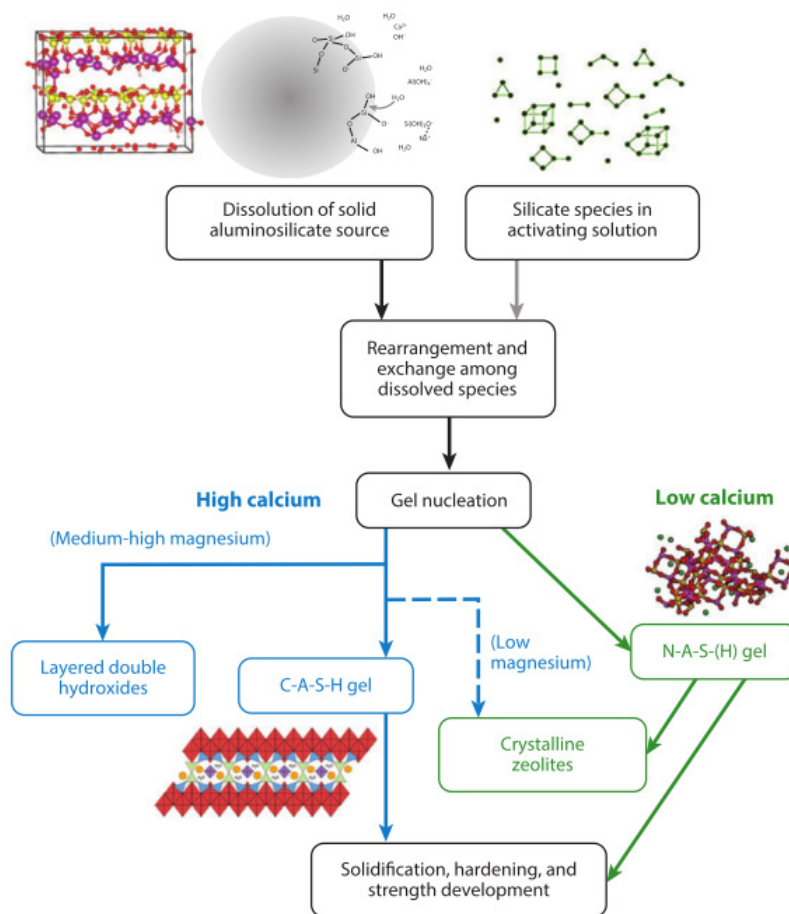


Fig. 3 Process and reaction products of alkaline activation of a solid aluminosilicate precursor (Provis and Bernal 2014b). [Republished with permission of the Annual Reviews,©2014]

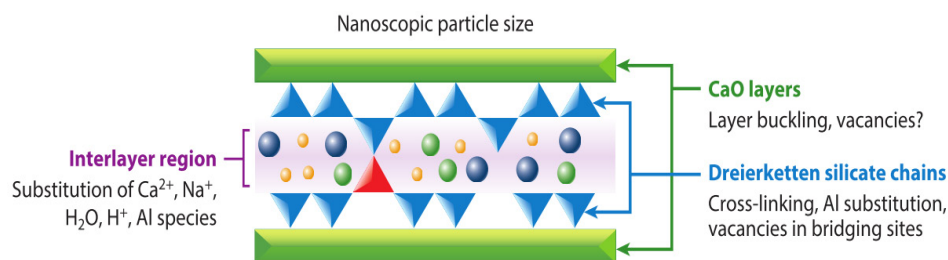


Fig. 4 Tobermorite like C-A-S-H gel structure (Provis and Bernal, 2014b). [Republished with permission of the Annual Reviews,©2014]

can also hold traces of radioactive minerals, such as uranium or thorium compounds (Gu *et al.* 2017). This raw material is bathed in a solution of a strong base such as sodium hydroxide (lye or caustic soda) at a high temperature and pressure. The aluminum compounds in the bauxite dissolve in the hot caustic solution while the other components remain behind. Everything that does not get dissolved in the process is called red mud, its rusty colour is derived from the iron compounds. The mud also has a high pH because of the sodium hydroxide solution used in the refining process. Apart from some limited use to produce a pigment in the manufacture of bricks (Pera *et al.* 1997) and cement (Singh *et al.* 1996; Singh *et al.* 1997), the red mud is a waste mate-

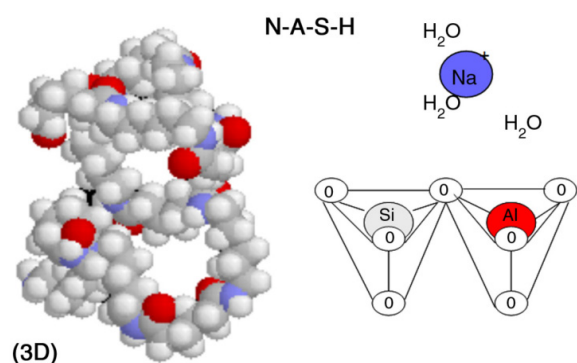


Fig. 5 The three-dimensional structure of a N-A-S-H gel (Palomo *et al.* 2014).

rial. Although it contains useful elements, such as iron, titanium and residual aluminum, there is no economically viable way to extract them from the mud. Most refineries collect the mud in open ponds to allow some of the water to evaporate. Once it is dry, after several years, the red mud is buried or mixed with soil. Some refineries use powerful presses to squeeze the water out of the mud and evaporators to dry most of the rest. Red mud is also used as a source material for geopolymers (He and Zhang 2011). It will be useful to study red mud based geopolymer systems to immobilise toxic wastes.

2.2 Method of evaluation of immobilisation efficiency - Leaching test

The efficiency of heavy metal immobilisation is defined basically by strength and the leach resistance (Malviya and Chaudhary 2006). While the strength development is considered as an indicator of solidification, leaching test is probably the most important measure to assess the degree of heavy metal stabilisation. Many leaching methods have been commonly used to acquire useful information for environmental decision-making. Yet, there is no a single leaching test that can assess the leaching behavior of a wide variety of waste materials. Selecting an appropriate leachate test was summarized in the guide of Environmental Protection Agency (Environmental Protection Agency 2011). Palacios and Palomo (2004) studied on three different leaching tests including Modified Static Leaching Test (MCC1-P), Leaching test of the matrices by means of the American National Standard (ANSI/ANS 16.1), and Toxicity Characteristic Leaching Procedure (TCLP) in order to determine the amount of lead fixed by activated fly ash systems. They concluded that the different results obtained from the various leaching tests can be justified according to the nature of each individual test. Each test is found to have advantages and disadvantages regarding evaluating the results, and the major mechanism responsible for lead leaching is diffusion. According to Fernández Pereira *et al.* (2009), the best results of stabilisation were observed with geopolymers when using the EN 12457 test, whilst the TCLP test showed the best results in OPC samples. Mercury immobilisation efficiencies are consistently higher in TCLP tests than EN 12457 tests (Donatello *et al.* 2012). This is probably due to the fact that the test material used in TCLP tests are coarser than that in EN 12457, and that the high leachate pH value used in EN 12457 tests possibly increases the solubility of mercury precipitates. Thus, choosing the leaching test method should be taken into account when evaluating the efficiency of heavy metal immobilisation of geopolymer materials. Using more than one leaching test method is strongly recommended.

3. Mechanisms for heavy metal immobilisation

In traditional stabilisation and solidification systems,

heavy metals are generally converted to low solubility precipitates such as carbonates, hydroxides, silicates, or sulfides, and then formed as a solid with solidification reagents (Portland Cement Association 1991). According to Shi and Spence (2004), there are three aspects in the stabilisation and solidification by cements. The first two aspects rely on the nature of the hydration products, including chemical fixation of contaminants and physical adsorption of the contaminants on the surface of hydration products of the cements (see Fig. 6). The third aspect is the physical encapsulation of contaminated waste (due to low permeability of the hardened pastes), which is governed by both the nature of the hydration products and the density and physical structure of the pastes.

In stabilisation and solidification systems using geopolymer binders, geopolymer cements might capture hazardous elements within the three dimensional framework of the geopolymeric matrix and convert semi-solid waste into an adhesive solid (Davidovits 1994). It was also stated that heavy metals might be immobilised through three general steps (Zheng *et al.* 2010):

- (1) metal ions are taken into the geopolymer network;
- (2) metal ions are bound into the structure for charge balancing roles and
- (3) a precipitate containing heavy metals is physically encapsulated.

To date, the exact mechanism of heavy metal immobilisation in geopolymer materials has not been fully understood, though in principle most of the heavy metal cations are easily attracted and combined with $[\text{AlO}_4]$ tetrahedrons due to larger mass, smaller radius and higher valence (van Jaarsveld *et al.* 1999). Future studies on the current topic are therefore recommended.

A study on the immobilisation of Cu and Pb in geopolymers derived from fly ash, carried out by van Jaarsveld *et al.* (1998), reported that these metals may be immobilised in geopolymeric matrices by physical encapsulation, chemical bonding and adsorption. van Jaarsveld *et al.* (1998) found that there were some dif-

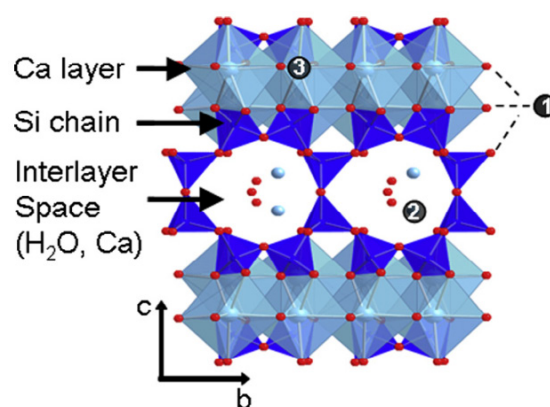


Fig. 6 Possible positions of heavy metals in the tobermorite structure. [Reprinted from (Vespa *et al.* 2014) with permission from Elsevier, ©2014]

ferences in infrared spectra and no apparent major differences in X-ray diffraction between the geopolymer matrix containing Cu and the matrix containing Pb, while these matrices exhibited different compressive strengths and leaching behaviour. These results implied that these metals might be taken into the geopolymer network and possibly bound into the structure for charge balancing roles, and that these metals are bound into the amorphous regions of the product matrices.

One question that needs to be asked, however, is whether physical encapsulation, chemical bonding and adsorption are equally effective. van Jaarsveld *et al.* (1998) concluded that, in geopolymers, physical micro-encapsulation is deemed to be more important than chemical bonding in influencing the efficiency of immobilisation, and adsorption is not thought to play a major role. Geopolymeric matrices with smaller pore openings as well as higher compressive strength, which is related to solidification, often, exhibited better immobilisation efficiency.

The dominance of physical encapsulation was also observed in several other studies (Palacios and Palomo 2004; Phair and van Deventer 2001). Findings of Phair and van Deventer (2001) showed that increasing the dissolution of Al and Si from the aluminosilicate sources (by raising pH of alkali silicate activation) leads to a greater amount of monomeric and/or oligomeric species of both aluminate and silicate available, which is essential for insolubilising polycondensation reactions. This resulted in better reactive conditions for the immobilisation of Pb. Therefore, the immobilisation of Pb within geopolymer matrices was believed to be an encapsulation process of precipitates and gels, and the contribution of the adsorption process might be negligible. Palacios and Palomo (2004) also found that the Pb compound formed in the fly ash matrix is a highly insoluble silicate Pb_3SiO_5 , identified by XRD, implying that the immobilisation of Pb in fly ash based geopolymers is mainly by encapsulation of Pb_3SiO_5 .

In contrast, the predominance of chemical immobilisation was proven by Fernandez-Jimenez *et al.* (2005), in which As was supposed to be chemically bound rather than physically encapsulated. To be more specific, As was found to be associated with amorphous Fe-rich regions within fly ash based geopolymers through EDX data.

In a recent study about the mechanism of immobilisation of Pb(II), Cu(II), Cd(II) and Cr(III) in geopolymers derived from kaolin/zeolite, conducted by El-Eswed *et al.* (2015), heavy metals were believed to balance the negative charge of tetrahedral Al in unreacted zeolite and geopolymer frameworks, and the emphasis was not placed on physical encapsulation process. They stated that the mechanical strength and XRD results were not influenced by incorporation of heavy metals. Therefore physical encapsulation, formation of metal hydroxides or carbonates and silicates were not probably mechanisms for immobilisation of metals. This is because

there is no evidence for participation of heavy metals in new reactions of geopolymerisation process. It appears that this area requires further investigation.

4. Factors influencing immobilisation efficiency

Conner (1990) reported that the immobilisation of heavy metals depends not only on the solubility of the metal precipitate, but also on the permeability of the monolith which is a function of pore structure and the amount of water present in the waste. As a consequence, all factors that can change the solubility of the metal precipitate and the permeability of geopolymeric matrix can probably have a bearing on the final immobilisation efficiency of heavy metals, as shown in **Fig. 7**. These factors and their effects are described in detail below.

4.1 The characteristics of the source materials

Raw materials are generally used as the primary reagents in generating the geopolymeric binders that serve as a medium for the immobilisation of metals. It is a fact that fly ash is commonly used as a source material in generating geopolymer binders, though chemical composition of fly ashes varies a lot with the coal source and burning conditions (Rickard *et al.* 2011; Rickard *et al.* 2012). This results in inconsistent geopolymer products. Regarding hazardous waste management, metakaolin may be a better raw material as it has more consistent chemical compositions than fly ash (Zhang *et al.* 2016). However, metakaolin is a thermally treated product from kaolin, which is energy intensive, therefore using geopolymers obtained from metakaolin would not be a cost effective solution.

In some cases, hazardous wastes which need to be treated also play a role in the choice of the source material for producing geopolymer binders. Red mud generally serves as the filler in geopolymeric matrix because of its poor dissolubility in the alkaline solution (Dimas *et al.* 2009). After experiencing thermal pre-treatment, the red mud dissolves better in alkaline solution and hence functions as a source of alumina and silica for geopolymerisation process, with a higher solubility of calcined red mud resulting in a higher strength of the binders (Ye *et al.* 2014). Municipal solid waste incineration residue, a hazardous waste (because of high content of heavy metals), was used as an aluminosilicate source for producing geopolymer binder that could successfully stabilise and solidify heavy metals (Zheng *et al.* 2010). After being calcined at 800°C for 1 hour and ground to have a suitable particle size, water treatment residue that contains heavy metals was valued as an alternative waste material for the synthesis of geopolymers due to its suitable chemical composition (Waijarean *et al.* 2014).

The structure and properties of the geopolymer materials obtained strongly depend on the particle size, the vitreous phase content and SiO_2/Al_2O_3 ratio of raw ma-

terials (Fernández-Jiménez and Palomo 2003; Jang and Lee 2016), implying that the immobilisation capacity of hazardous elements is strongly dependent on the properties of source materials. The increasing Al, Si species liberated from raw materials would provide better environment to form a new phase that would adequately bind and encapsulate heavy metals into a more insoluble form. In addition, the geopolymeric matrix with the highest immobilisation efficiency seems to have the smaller pore openings as well as the higher compressive strength. van Jaarsveld *et al.* (1998) stated that the source materials appear to have the greatest impact on the eventual ability of the matrix to immobilising metals, since the source materials had an effect on the structure formation at an intratetrahedral scale. The matrices produced from a six-coordinated aluminum source, for example kaolinite, seem to be more stable under leaching conditions than those synthesised from a four-coordinated aluminum source, for example metakaolinite, probably because the six coordinated aluminum is easier to complete the process of geopolymerisation than its four coordinated counterpart (van Jaarsveld *et al.* 1998). Palacios and Palomo (2004) compared the capacity of fixation of Pb in two types of fly ash activated in a highly alkaline medium. They pointed out that the nature of the fly ash has a significant impact on the effectiveness of Pb fixation in these systems. In other words, fly ash with a higher proportion of reactive silica and fine particles (greater specific area) would result in greater containment capacity of geopolymeric matrix.

These factors will make a better Pb immobilisation system, since Pb might be mainly immobilised in geopolymeric matrix by physical encapsulation. This view was shared by Nikolić *et al.* (2017) and he concluded that fly ash reactivity was a deciding factor for the immobilisation property. An other investigation conducted by Phair *et al.* (2004) on the effect of the Al sources on the Pb and Cu stabilisation showed that the immobilisation of Pb is linked with the total extractable cation concentration of the Al source. It is difficult to explain this result, but it may be related to the fact that Pb precipitates are more susceptible to subsequent reactions than Cu precipitates, so they tend to be affected by the available amount of cations released from Al source, which can transform Pb precipitates into more stable forms, amorphous aluminosilicate phases. In contrast, the immobilisation of Cu was observed to be mainly associated with the physical characteristics of the source of Al (Phair *et al.* 2004). This is possibly because precipitates of Cu may be more stable than that of Pb. Thus, compressive strength of the matrix and the suspension viscosity of the Al source have a considerable effect on the Cu immobilisation efficiency.

4.2 The pH and type of alkali activator

In general, the pH of alkali activator is strongly affected by the type of activator and its concentration. The pH of alkali activator was deemed to be a major contributing factor for the final immobilisation efficiency, since increasing pH would lead to the reduction of the pore size,

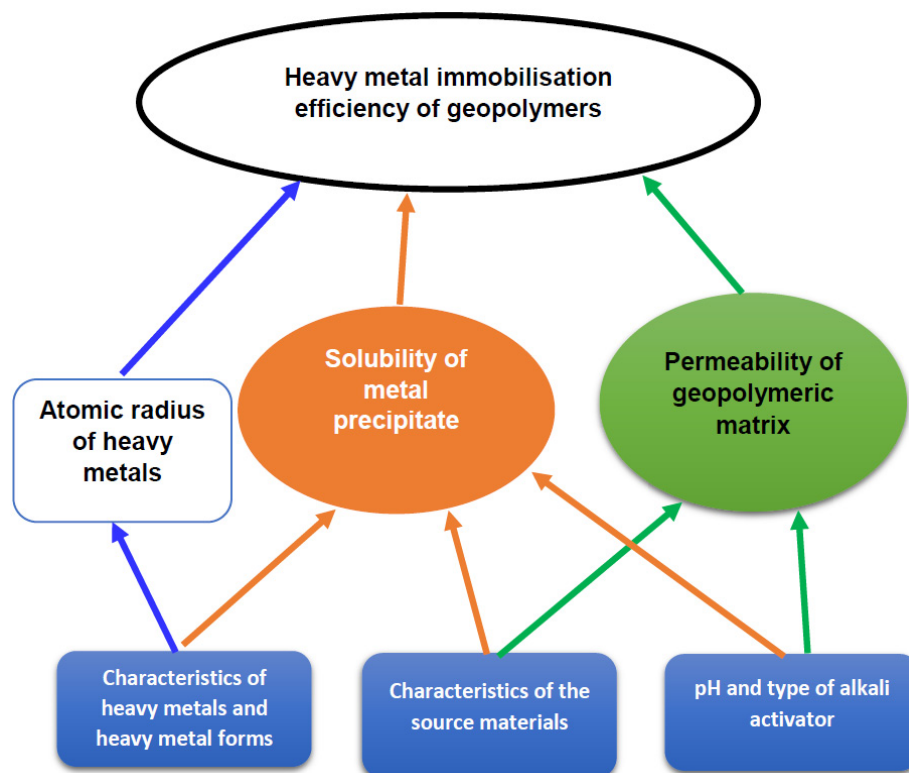


Fig. 7 Possible factors affecting the capacity of geopolymer materials for immobilising heavy metals.

Table 2 Atomic radii of some toxic heavy metals.

Atomic Number	Element	Empirical (pm)	Calculated (pm)	Van der Waals (pm)	Covalent (Single bond) (pm)	Covalent (Triple bond) (pm)	Metallic (pm)
24	Cr	140	166	no data	127	103	128
27	Co	135	152	no data	126	96	125
28	Ni	135	149	163	121	101	124
29	Cu	135	145	140	138	120	128
30	Zn	135	142	139	131	no data	134
33	As	115	114	185	119	106	
34	Se	115	103	190	116	107	
48	Cd	155	161	158	148	no data	151
80	Hg	150	171	155	149	no data	151
82	Pb	180	154	202	147	137	
92	U	175	no data	186	no data	118	156

and therefore matrix permeability (Davis *et al.* 1994). Depending on the relative proportions of silicate and hydroxide available in the alkali silicate environment, heavy metal precipitates formed in geopolymeric matrices could be either metal hydroxide and/or metal silicate species. Therefore, the metal immobilisation within geopolymers was thought to be strongly dependent on the pH of the alkali activator used (Phair and van Deventer 2001). For instance, at pH 12 the amount of silicate ions would be large enough to preferentially combine with the cations in considerable amounts, while at pH 14 there would be a tendency for cations to combine with hydroxide than at pH 12. Further, the precipitates formed at pH 12 is more insoluble than the precipitates at pH 14, so the immobilisation efficiency at pH 12 is expected to be higher than at pH 14. Notwithstanding, the matrix produced at pH 12 was found to be more porous and subsequently more permeable, and therefore reduced the efficiency of metal immobilisation (Phair and van Deventer 2001). Thus, it could be concluded that the increase of immobilisation efficiency and the increasing pH are directly linked. In another study of Cheng *et al.* (2012), the amount of heavy metals adsorbed on the geopolymers increased with increasing pH of the solution. It was explained that when the concentration of H^+ in the solution is higher, geopolymer tends to adsorb H^+ . As a result, the adsorption capability of heavy metals increases in a higher pH environment. A similar result was seen by Nikolić *et al.* (2013). Increasing pH of alkali solution resulted in better Zn immobilisation from metallurgical waste.

As for the impact of alkali activator type on the stabilisation of heavy metal, Phair and van Deventer (2001) reported that Cu or Pb are stabilised better in sodium silicate solutions than potassium silicate solutions. It may be probably because sodium silicate is less polymerised at high pH than potassium silicate because of the larger hydration sphere of the sodium ion. In addition, the hydration spheres of sodium silicate, Cu and Pb are relatively similar, so Cu and Pb interchange with sodium silicate more easily than with potassium silicate, resulting in the better immobilisation efficiency (Phair and van Deventer 2001). Similarly, using sodium hydroxide in the activating solution led to the higher ca-

capacity of Cr immobilisation compared to using potassium hydroxide (Galiano *et al.* 2011). Moreover, the characteristic pore size of geopolymers was demonstrated to be closely related to the type of the alkali cation Na^+ or K^+ used in activation (Kriven *et al.* 2008; Steins *et al.* 2014), implying that the heavy metal stabilisation is possibly influenced by the choice of alkali.

4.3 The characteristics of heavy metals and heavy metal forms

Atomic radius of metal has been an important factor for the heavy metal immobilisation. The atomic radius of an element is the distance from the centre of the nucleus to the outermost shell of the electron. Since the boundary is not a well-defined physical entity, there are various non-equivalent definitions of atomic radius. Depending on the definition, the term may apply only to isolated atoms, or also to atoms in condensed matter, in covalent bond in molecules, or in ionised state. Atomic radii of some toxic heavy metals are shown in **Table 2**.

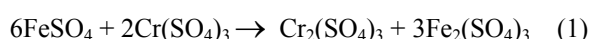
The immobilisation of Cu in geopolymeric matrices is generally less effective compared to Pb, since the atomic radius of Cu is smaller than that of Pb (see **Table 2**), which makes diffusion, translocation and leaching of Cu much easier although the electrical charges on both Cu and Pb are the same (Phair and van Deventer 2001). Slag based geopolymeric matrix showed a better immobilisation efficiency for Pb than for Cu in the case of large dosages of heavy metals, probably because ionic radius of Pb and Cu are different. Hence, Cu and Pb are immobilised in different ways in the slag based geopolymeric matrix (Yunsheng *et al.* 2007).

The size of the hydrated ions which bears on the attraction force between hydrated ion and metal, free energy of hydration (the higher the level of free energy of hydration, the smaller is the possibility for heavy metal ions to enter the adsorbent structure), and activity of metal ions were thought to be responsible for the adsorption of the heavy metal ions on the geopolymeric matrix (Cheng *et al.* 2012). On the other hand, Xu *et al.* (2006) investigated the leaching behaviour of Cd, Cu, Pb and Cr in fly ash based geopolymer and stated that the leaching behaviour of heavy metals could be influenced by other heavy metals in a complex system as

well. However, this study was unable to explain how this occurred and led to many unanswered questions which need further investigation.

Apart from size, the nature of heavy metals is also important. The stabilisation of metals in geopolymeric matrices could be affected by the chemical properties of the metal compounds. This was proved in the case of Pb (Guo *et al.* 2017) and Cr (Zhang *et al.* 2008b; Chen *et al.* 2016). Three types of the Pb contaminants PbO, PbSO₄ and PbS, common in the environment, were added in the fly ash based geopolymer matrices. Pb was proved to be dispersed throughout the geopolymeric matrix in the case of PbO addition, forming leaded geopolymer via Pb-O-Al or/and Pb-O-Si. By contrast, PbS was observed to be segregated from the bulk of the binder (Guo *et al.* 2017). It was concluded that when Pb compounds were supplied in the form soluble in sodium hydroxide solution, the Pb ions would participate in the formation of geopolymer network, stimulating both chemical bonding and physical encapsulation. In the case of the Pb compounds that are inert to alkali, the immobilisation may be mainly by the physical encapsulation in the geopolymeric matrices. As a result, the upper limit of the Pb content, which can be immobilised in the geopolymer, varies with the form of Pb (Guo *et al.* 2017).

In nature, common oxidation states of Cr are 3⁺ and 6⁺ states. Cr(VI) is particularly toxic, soluble, and relatively mobile in the environment (Kresic 2006). The immobilisation of Cr(VI) was found problematic (Palomo and Palacios 2003; Zhang *et al.* 2008a). The matrix of alkali-activated fly ash was found to be unable to stabilise 2.6% Cr(VI) in the form of CrO₃, because Cr(VI) acted on the activation of fly ash due to the formation of a highly soluble compound Na₂CrO₄·4H₂O (observed through XRD and FTIR) (Palomo and Palacios 2003). Even with a smaller dosage of Cr(VI) 0.5% as Na₂CrO₄ added in fly ash based geopolymers, long-term leaching tests in different media showed that more than 75% Cr extraction was observed (Zhang *et al.* 2008a). On the contrary, Cr(III) is less toxic, less mobile, and relatively insoluble as Cr(OH)₃ as well as mixed hydroxide phases containing some Ca (Omotoso *et al.*, 1996). Reduction from Cr(VI) to Cr(III) was recommended as pre-treatment before immobilisation of chromium wastes in several previous studies (Eary and Rai 1988; Portland Cement Association 1991; Lan *et al.* 2007). The most common chemical reductants for converting Cr(VI) to Cr(III) are ferrous iron Fe(II) compounds (shown in Eq.1) and sulfur compounds.



In a study carried out by Zhang *et al.* (2008b), sulfur compound (Na₂S·9H₂O) was added to fly ash based geopolymer, which reduced Cr(VI) (Na₂CrO₄, PbCrO₄) to Cr(III), enabling precipitation in highly insoluble forms and resulting in the increasing the immobilisation

efficiency. In another case, a mixture of FeCl₂·4H₂O and K₂Cr₂O₇ was used to convert Cr (VI) to Cr (III) (Chen *et al.*, 2016). Cr³⁺ was then attracted by [AlO₄] due to the electrostatic attraction and stabilised in metakaolin-based geopolymeric matrices, leading to a relatively high immobilisation efficiency of Cr (Chen *et al.* 2016).

5. Conclusions

From the literature reviewed above, the following conclusions can be reached:

Heavy metal immobilisation in a geopolymer binder is mainly conditional upon the nature of heavy metal, the characteristics of the raw materials of the geopolymer, the pH and type of activator and the resulting pore structure of the geopolymer.

The mechanisms of immobilisation of different heavy metals in geopolymer matrices could be physical encapsulation or chemical bonding. However, most often it is a combination of the two mechanisms and the combination varies considerably, depending on the nature of heavy metals and metal compounds which needs to be safely disposed. It is essential that the correct combination of the physical and chemical mechanisms is identified and developed for safe disposal of a particular heavy metal waste.

For efficient immobilisation of toxic metals, the synthesis and curing conditions of geopolymers and the long term stability of the products are important considerations. These areas are avenues available for obtaining an effective stabilisation/solidification system of harmful metals.

Different raw materials and their reactivity in the presence of different activators also need to be investigated further for a certain hazardous metal immobilisation.

In addition to this, the role of interfacial transition zone of geopolymers materials with particular reference to physical encapsulation process of heavy metal immobilisation should be further investigated.

References

- Bernal, S. A., Provis, J. L., Fernández-Jiménez, A., Krivenko, P. V., Kavalerova, E., Palacios, M. and Shi, C., (2014). "Binder chemistry - High calcium alkali activated materials." In: J. L. Provis and J. S. J. van Deventer Eds. *Alkali Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM*. Dordrecht: Springer Netherlands, 59-91.
- Bishop, P. L., (1988). "Leaching of inorganic hazardous constituents from stabilized/solidified hazardous wastes." *Hazardous Waste and Hazardous Materials*, 5(2), 129-143.
- Chen, J., Wang, Y., Wang, H., Zhou, S., Wu, H. and Lei, X., (2016). "Detoxification/immobilization of hexavalent chromium using metakaolin-based geopolymer coupled with ferrous chloride." *Journal of Environmental Chemical Engineering*, 4(2), 2084-2089.

- Cheng, T. W., Lee, M. L., Ko, M. S., Ueng, T. H. and Yang, S. F., (2012). "The heavy metal adsorption characteristics on metakaolin-based geopolymer." *Applied Clay Science*, 56, 90-96.
- Conner, J. R., (1990). "Chemical fixation and solidification of hazardous wastes". Van Nostrand Reinhold, New York, 692, f5.
- Davidovits, J., (1991). "Geopolymers: Inorganic polymeric new materials." *Journal of Thermal Analysis*, 37(8), 1633-1656.
- Davidovits, J., (1994). "Properties of geopolymer cements." *First International Conference on Alkaline Cements and Concretes*, 131-149. (in Kiev, Ukraine)
- Davidovits, J., (2002). "Environmentally driven geopolymer cement applications". *Geopolymer 2002 Conference*, 1-9. (in Melbourne, Australia)
- Davidovits, J., (2005). "Geopolymer chemistry and sustainable development. The poly (sialate) terminology: a very useful and simple model for the promotion and understanding of green-chemistry." *2005 Geopolymer Conference*, 9-15. (in Saint-Quentin, France)
- Davis, P. J., Deshpande, R., Smith, D. M., Brinker, C. J. and Assink, R. A., (1994). "Pore structure evolution in silica gel during aging/drying. IV. Varying pore fluid pH." *Journal of Non-Crystalline Solids*, 167(3), 295-306.
- Dimas, D. D., Giannopoulou, I. P. and Papias, D., (2009). "Utilization of alumina red mud for synthesis of inorganic polymeric materials." *Mineral Processing and Extractive Metallurgy Review*, 30(3), 211-239.
- Dixit, R., Wasiullah, Malaviya, D., Pandiyan, K., Singh, U. B., Sahu, A. and Paul, D., (2015). "Bioremediation of heavy metals from soil and aquatic environment: An overview of principles and criteria of fundamental processes." *Sustainability*, 7(2), 2189-2212.
- Donatello, S., Fernández-Jiménez, A. and Palomo, A., (2012). "An assessment of Mercury immobilisation in alkali activated fly ash (AAFA) cements." *Journal of Hazardous Materials*, 213-214, 207-215.
- Duxson, P., Fernández-Jiménez, A., Provis, J. L., Lukey, G. C., Palomo, A. and van Deventer, J. S. J., (2007). "Geopolymer technology: the current state of the art." *Journal of Materials Science*, 42, 2917-2933.
- Duxson, P., Provis, J. L., Lukey, G. C. and van Deventer, J. S. J., (2007). "The role of inorganic polymer technology in the development of green concrete." *Cement and Concrete Research*, 37(12), 1590-1597.
- Eary, L. E. and Rai, D., (1988). "Chromate removal from aqueous wastes by reduction with ferrous ion." *Environmental Science & Technology*, 22(8), 972-977.
- El-Eswed, B. I., Yousef, R. I., Alshaaer, M., Hamadneh, I., Al-Gharabli, S. I. and Khalili, F., (2015). "Stabilization/solidification of heavy metals in kaolin/zeolite based geopolymers." *International Journal of Mineral Processing*, 137, 34-42.
- Environmental Protection Agency, (2011). "Background information for the Leaching environmental Assessment Framework (LEAF) test methods." Washington, D.C., USA.: Environmental Protection Agency, EPA/600/R-10/170.
- Fernandez-Jimenez, A., MacPhee, D. E., Lachowski, E. E. and Palomo, A., (2005). "Immobilization of cesium in alkaline activated fly ash matrix." *Journal of Nuclear Materials*, 346(2-3), 185-193.
- Fernández-Jiménez, A. and Palomo, A., (2003). "Characterisation of fly ashes. Potential reactivity as alkaline cements." *Fuel*, 82, 2259-2265.
- Fernández Pereira, C., Luna, Y., Querol, X., Antenucci, D. and Vale, J., (2009). "Waste stabilization/solidification of an electric arc furnace dust using fly ash-based geopolymers." *Fuel*, 88, 1185-1193.
- Galiano, Y. L., Salihoglu, G., Pereira, C. F. and Parapar, J. V., (2011). "Study on the Immobilization of Cr (VI) and Cr (III) in geopolymers based on coal combustion fly ash." *World of Coal Ash (WOCA) Conference*, 12. (in Denver, CO, USA).
- Garcia-lodeiro, I., Palomo, A., Fernández-jiménez, A. and Macphee, D. E., (2011). "Compatibility studies between N-A-S-H and C-A-S-H gels. Study in the ternary diagram $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$." *Cement and Concrete Research*, 41, 923-931.
- Glasser, F. P., (1997). "Fundamental aspect of cement solidification and stabilization." *Journal of Hazardous Material*, 52, 151-170.
- Glukhovskiy, V. D., (1959). "Soil silicates". *Gosstroyizdat, Kiev*, 154-157.
- Gu, H., Wang, N., Yang, Y., Zhao, C. and Cui, S., (2017). "Features of distribution of uranium and thorium in red mud." *Physicochemical Problems of Mineral Processing*, 53(1), 110-120.
- Guo, B., Pan, D., Liu, B., Volinsky, A. A., Fincan, M., Du, J. and Zhang, S., (2017). "Immobilization mechanism of Pb in fly ash-based geopolymer." *Construction and Building Materials*, 134, 123-130.
- He, J. and Zhang, G., (2011). "Geopolymerization of red mud and fly ash for civil infrastructure applications." *Geo-Frontiers Congress 2011*. (in Dallas, Texas, USA)
- Jang, J. G. and Lee, H. K., (2016). "Effect of fly ash characteristics on delayed high-strength development of geopolymers." *Construction and Building Materials*, 102, 260-269.
- Kresic, N., (2006). "Hydrogeology and groundwater modeling." CRC press.
- Kriven, W. M., Bell, J. L. and Gordon, M., (2008). "Microstructure and nanoporosity of asset geopolymers." *Ceramic Engineering and Science Proceedings*, 27, 491-503.
- Lan, Y., Deng, B., Kim, C. and Thornton, E. C., (2007). "Influence of soil minerals on chromium(VI) reduction by sulfide under anoxic conditions." *Geochemical Transactions*, 8, 4.
- Lloyd, N. and Rangan, V., (2009). "Geopolymer concrete - Sustainable cementless concrete." *Tenth ACI International Conference ACI International Conference*, 33-53. (in Seville, Spain)

- Malviya, R. and Chaudhary, R., (2006). "Factors affecting hazardous waste solidification/stabilization: A review." *Journal of Hazardous Materials*, 137(1), 267-276.
- Neupane, K., (2016). "Fly ash and GGBFS based powder-activated geopolymer binders: A viable sustainable alternative of portland cement in concrete industry." *Mechanics of Materials*, 103, 110-122.
- Nikolić, V., Komljenović, M., Džunuzović, N., Ivanović, T. and Miladinović, Z., (2017). "Immobilization of hexavalent chromium by fly ash-based geopolymers." *Composites Part B*, 112(1), 213-223.
- Nikolić, I., Đurović, D., Tadić, M., Blečić, D. and Radmilović, V., (2013). "Immobilization of zinc from metallurgical waste and water solutions using geopolymerization technolog." *The 16th International Conference on Heavy Metals in the Environment*, 1, 4. (in Rome, Italy)
- Omotoso, O. E., Ivey, D. and Mikulab, R., (1996). "Quantitative X-ray diffraction analysis of chromium(III) doped tricalcium silicate pastes." *Cement and Concrete Research*, 26(9), 1369-1379.
- Palacios, M. and Palomo, A., (2004). "Alkali-activated fly ash matrices for lead immobilisation: a comparison of different leaching tests." *Advances in Cement Research*, 16(4), 137-144.
- Palomo, A., Krivenko, P., Garcia-Lodeiro, I., Kavalerova, E., Maltseva, O. and Fernández-Jiménez, A., (2014). "A review on alkaline activation: new analytical perspectives." *Materiales de Construcción*, 64(315), e022.
- Palomo, A. and López de la Fuente, J. I., (2003). "Alkali-activated cementitious materials: Alternative matrices for the immobilisation of hazardous wastes - Part I. Stabilisation of boron." *Cement and Concrete Research*, 33(2), 281-288.
- Palomo, A. and Palacios, M., (2003). "Alkali-activated cementitious materials: Alternative matrices for the immobilisation of hazardous wastes - Part II. Stabilisation of chromium and lead." *Cement and Concrete Research*, 33(2), 289-295.
- Pera, J., Boumaza, R. and Ambroise, J., (1997). "Development of a pozzolanic pigment from red mud." *Cement and Concrete Research*, 27(10), 1513-1522.
- Phair, J. W. and van Deventer, J. S. J., (2001). "Effect of silicate activator pH on the leaching and material characteristics of waste-based inorganic polymers." *Minerals Engineering*, 14(3), 289-304.
- Phair, J. W., van Deventer, J. S. J. and Smith, J. D., (2004). "Effect of Al source and alkali activation on Pb and Cu immobilisation in fly-ash based geopolymers." *Applied Geochemistry*, 19(3), 423-434.
- Portland Cement Associatio, (1991). "Solidification and Stabilization of Wastes Using Portland Cement." The United States of America: Report 7355.
- Power, G., Gräfe, M. and Klauber, C., (2011). "Bauxite residue issues: I. Current management, disposal and storage practices." *Hydrometallurgy*, 108(1-2), 33-45.
- Provis, J. L., (2014). "Geopolymers and other alkali activated materials: why, how, and what?." *Materials and Structures*, 47(1-2), 11-25.
- Provis, J. L. and Bernal, S. A., (2014a). "Binder Chemistry - Blended Systems and Intermediate Ca Content." In: J. L. Provis and J. S. J. van Deventer Eds. *Alkali Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM*. Dordrecht: Springer Netherlands, 125-144.
- Provis, J. L. and Bernal, S. A., (2014b). "Geopolymers and Related Alkali-Activated Materials." *Annual Review of Materials Research*, 44(3), 3-29.
- Provis, J. L., Fernández-Jiménez, A., Kamseu, E., Leonelli, C. and Palomo, A., (2014). "Binder chemistry-low-calcium alkali-activated materials." In: J. L. Provis and J. S. J. van Deventer Eds. *Alkali Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM*. Dordrecht: Springer Netherlands, 93-123.
- Rickard, W. D. A., Temuujin, J. and van Riessen, A., (2012). "Thermal analysis of geopolymer pastes synthesised from five fly ashes of variable composition." *Journal of Non-Crystalline Solids*, 358(15), 1830-1839.
- Rickard, W. D. A., Williams, R., Temuujin, J. and van Riessen, A., (2011). "Assessing the suitability of three Australian fly ashes as an aluminosilicate source for geopolymers in high temperature applications." *Materials Science and Engineering A*, 528, 3390-3397.
- Science Communication Unit of University of the West of England, (2013). "Soil contamination: impacts on human health." Bristol, England: European Commission DG Environment.
- Shi, C. and Spence, R., (2004). "Designing of cement-based formula for solidification/stabilization of hazardous, radioactive, and mixed wastes." *Critical Reviews in Environmental Science and Technology*, 34(4), 391-417.
- Singh, M., Upadhayay, S. N. and Prasad, P. M., (1996). "Preparation of special cements from red mud." *Waste Management*, 16(8), 665-670.
- Singh, M., Upadhayay, S. N. and Prasad, P. M., (1997). "Preparation of iron rich cements using red mud." *Cement and Concrete Research*, 27(7), 1037-1046.
- Steins, P., Poulesquen, A., Frizon, F., Diat, O., Jestin, J., Causse, J. and Rossignol, S., (2014). "Effect of aging and alkali activator on the porous structure of a geopolymer." *Journal of Applied Crystallography*, 47(1), 316-324.
- Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K. and Sutton, D. J., (2012). "Heavy metals toxicity and the environment." *EXS*, 101, 133-164.
- van Jaarsveld, J. G. S., van Deventer, J. S. J. and Lorenzen, L., (1998). "Factors affecting the immobilization of metals in geopolymerized flyash." *Metallurgical and Materials Transactions B*, 29(1),

- 283-291.
- van Jaarsveld, J. G. S., van Deventer, J. S. J. and Schwartzman, A., (1999). "The potential use of geopolymeric materials to immobilise toxic metals: Part II. Material and leaching characteristics." *Minerals Engineering*, 12(1), 75-91.
- Vespa, M., Dähn, R. and Wieland, E., (2014). "Competition behaviour of metal uptake in cementitious systems: An XRD and EXAFS investigation of Nd- and Zn-loaded 11A tobermorite." *Physics and Chemistry of the Earth*, 70-71, 32-38.
- Waijarean, N., Asavapisit, S. and Sombatsompop, K., (2014). "Strength and microstructure of water treatment residue-based geopolymers containing heavy metals." *Construction and Building Materials*, 50, 486-491.
- Xu, J. Z., Zhou, Y. L., Chang, Q. and Qu, H. Q., (2006). "Study on the factors of affecting the immobilization of heavy metals in fly ash-based geopolymers." *Materials Letters*, 60(6), 820-822.
- Ye, N., Yang, J., Ke, X., Zhu, J., Li, Y., Xiang, C. and Xiao, B., (2014). "Synthesis and characterization of geopolymer from bayer red mud with thermal pretreatment." *Journal of the American Ceramic Society*, 97(5), 1652-1660.
- Yunsheng, Z., Wei, S., Qianli, C. and Lin, C., (2007). "Synthesis and heavy metal immobilization behaviors of slag based geopolymer." *Journal of Hazardous Materials*, 143(1-2), 206-213.
- Zhang, J., Provis, J. L., Feng, D. and van Deventer, J. S. J., (2008). "Geopolymers for immobilization of Cr^{6+} , Cd^{2+} , and Pb^{2+} ." *Journal of Hazardous Materials*, 157, 587-598.
- Zhang, J., Provis, J. L., Feng, D. and van Deventer, J. S. J., (2008). "The role of sulfide in the immobilization of Cr(VI) in fly ash geopolymers." *Cement and Concrete Research*, 38, 681-688.
- Zhang, Z. H., Zhu, H. J., Zhou, C. H. and Wang, H., (2016). "Geopolymer from kaolin in China: An overview." *Applied Clay Science*, 119, 31-41.
- Zheng, L., Wang, W. and Shi, Y., (2010). "The effects of alkaline dosage and Si/Al ratio on the immobilization of heavy metals in municipal solid waste incineration fly ash-based geopolymer." *Chemosphere*, 79, 665-671.