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Solidification Versus Adsorption for Immobilization of Pollutants in Geopolymeric Materials: A Review

Bassam I. El-Eswed

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Abstract

Geopolymer (GP) is a class of three-dimensional aluminosilicate binder, which is superior to Portland cement materials in acid, heat and fire resistance. GP is produced by reacting an aluminosilicate source (metakaolin, fly ash or waste) with an alkali metal hydroxide or silicate. The aim of the present work is to review the latest developments in three lines of research that deal with application of GP in treatment of pollutants. The first “**intra-solidification**” that involves mixing real waste (containing heavy metal pollutants) with the GP precursors to obtain a high mechanical strength material. The second type of solidification is “**inter-solidification**” that involves incorporation of heavy metals solutions (as simulation of polluted water) during geopolymerization reaction. The third line of research “**adsorption**” involves agitating GP with heavy metals solutions and studying the ability of GP to remove heavy metals from water. These techniques will be investigated regarding efficiency and mechanism of immobilization, cost and environmental impact. GPs are strong low-cost adsorbents for heavy metals. In intra-solidification, despite the high mechanical strength of the produced GP-containing waste, geopolymerization reduces effectively the leaching of heavy metals. The reverse was observed in the case of inter-solidification which presents a greater challenge than intra-solidification.

Keywords: solidification, adsorption, geopolymer, heavy metals, fly ash

1. Introduction

Geopolymers (GPs), first named by Davidovits [1], are synthetic aluminosilicates prepared by reacting a reactive solid aluminosilicate (metakaolin, fly ash or blast furnace slag) with an aqueous alkaline activating solution that contains alkali (Na^+ or K^+) hydroxides and silicates [2, 3]. GPs are composed of tetrahedral silicate and aluminate units linked in a three-dimensional structure by covalent bonds. The negative charges associated with Al(III)

tetrahedra is usually balanced by alkali cations [4]. GPs possess many favorable properties such as high compressive strength, low shrinkage, acid resistance, fire resistance, low thermal conductivity, rapid hardening and durability [2, 4–6]. The main applications of GPs are low cost construction materials and protective coatings [6]. Furthermore, GPs have been used for solidification of toxic wastes especially those containing heavy metals. This is the first aspect that will be reviewed in the present work. Solidification is a pre-landfill waste treatment in which the waste is encapsulated in cementing material or any kind of organic or inorganic polymer to immobilize toxic contaminants and reducing their leachability [7]. The final aim of solidification is reduction of the overall environmental impact of waste disposal [8].

GPs are X-ray amorphous, however, the formation of some crystalline zeolitic phases was detected particularly. The transformation of typically X-ray amorphous GP synthesized in highly concentrated basic solution into zeolite structure provides a very powerful evidence for the similarity of the zeolitization and geopolymerization reaction mechanisms [9]. Zeolites are strong cation exchangers and were used extensively to remove heavy metal ions from polluted water. Thus, this similarity suggested using GP in water treatment for the removal of heavy metal ions. Adsorption of pollutants, especially heavy metals, on GP is the second aspect that will be discussed in the present work.

Any material that is rich in Si and Al in amorphous forms can be used as a source material for synthesis of GP. Natural resources like kaolin and metakaolin (MK, synthesized by dehydroxylation of phase pure kaolin at 750°C) can be used for GP preparation, as well as a considerable range of industrial waste, such as fly ash (FA) from coal, blast furnace slag (BFS) from metallurgical industries, and municipal and medical waste incineration ashes. Since GP production is mainly based on waste materials, their use could aid waste minimization and reduces the pressure on current and future limited resources used in ordinary Portland cement (OPC) and contribute significantly to the lowering of the CO₂ emission of the construction industry [2, 6]. Calcination of kaolin to produce MK is carried out at 750°C, which is lower than the temperature needed in OPC production (1400–1450°C), [4]. Coal fly ash (FA) is an industrial waste that is produced from coal electricity plants. The bulk of the FA is made up of silicon, aluminum and iron oxides, as well as small (type F) or significant amounts of CaO (type C) [9]. GPs are generally considered to be much more sustainable than OPC, in terms of reduced production energy requirement, lower CO₂ emissions and the inexhausting sources of wastes [4]. FA appears to be one of the most promising precursors for the production of GP due to its high workability, low water demand and high mechanical strength [2, 9].

Despite the typical attributes mentioned above, the properties of GP are highly dependent on Si/Al ratio, hydroxide concentration, alkali cation used and curing conditions [6]. For example, the compressive strength of MK-based GP was improved by using sodium or potassium silicate solution instead of hydroxide. This improvement is attributed to the presence of increased number of Si—O—Si bond, which possess higher bond energy compared to Si—O—Al bond [5]. It was observed that the microstructure changed from containing large to small pores as the Si/Al ratio was increased from 1.15 to 1.90 [9, 10]. The baseline stoichiometries for GP materials participating in the reaction are typically molar Na/Al = 1 and Si/Al = 2. The amount of water (H₂O/Na molar ratio ~7) is usually controlled to obtain a thick paste [11].

The mechanism of geopolymerization is out of the scope of the present article, but some points are discussed here. Dissolution of amorphous aluminosilicates (from MK, FA or BFS) is rapid at the high pH provided by the alkaline activator, and this quickly creates a supersaturated solution containing a complex mixture of silicate, aluminate and aluminosilicate species. Then the oligomers in the aqueous phase form large networks by condensation resulting in gel formation. After gelation, the system continues to rearrange and reorganize, as the connectivity of the gel network increases, resulting in the three-dimensional aluminosilicate network of GP. The Si(IV) and Al(III) in the framework of GP are tetrahedrally coordinated and linked by oxygen bridges with small amount of terminal hydroxyl groups at the surface of the gel [9]. Although these terminal hydroxyl groups were thought to be insignificant in determining the mechanical properties of GP, they were thought to be important in immobilization of heavy metals since they can be coordinated to the heavy metal cations through chemical bonds [12].

The aim of the present work is to review the latest developments in the techniques of immobilization of heavy metals and some organic pollutants in geopolymeric materials. Two techniques will be investigated and compared; the first is solidification and the second is adsorption. These will be reviewed regarding starting materials used for preparation of GP, efficiency, mechanism, cost and environmental impact.

2. Methodology and calculations

2.1. Solidification

The first part of the present study is devoted to reviewing published works on solidification of wastes containing heavy metals in GP matrix. This type of solidification, which will be called **intra-solidification (Figure 1)**, involves mixing the waste with aluminosilicate-rich precursor such as MK, FA and BFS. Then an activator composed from sodium or potassium hydroxide and silicate is added and the produced GP is cured at temperature usually ranges from 40 to 80°C. The prefix “intra” is used because it means “within” and thus intra-solidification means immobilization of the heavy metals within waste by reaction with GP precursor. The second type of solidification, which will be called **inter-solidification (Figure 1)**, involves mixing an aluminosilicate precursor with pure heavy metal salts or solutions added during preparation of GP. The prefix “inter” is used because it means “between” and thus inter-solidification means immobilization reaction between heavy metal added and the GP precursors.

Two criteria are usually used to test the efficiency of solidification, the first is mechanical strength of the GP and the second is the leaching of heavy metals from the GP. Toxicity characteristic leaching procedure (TCLP) formulated by the US Environmental Protection Agency (EPA) involves stirring granular solid GP material (containing heavy metal) < 9 mm with acetic acid solution at pH 3–5 (liquid:solid ratio 20 mL:1.0 g) followed by filtering and determining the amount of heavy metals [8, 13]. The European Norm EN-12457 test, which is less aggressive than TCLP test, involves immersing 4.0 g of GP in 40 mL deionized water [8, 13, 14]. Furthermore, other leaching solutions of different pH and ionic strength were applied by other authors: H₂SO₄ solutions (pH 1), 5% (w/w) MgSO₄, 5% Na₂CO₃ solutions [15], 0.1 M HCl, 0.1 M NaCl, 1.0 M NaCl and 0.1 M NaOH [12]. The time of leaching test is highly variable and



Figure 1. Intra-solidification, inter-solidification and adsorption processes for immobilization of heavy metals.

ranges from 1 to 90 days. The efficiency of solidification can be deduced from the concentration of metal in the leaching solution when compared with the allowed limit formulated by environmental organizations. If the concentration of heavy metal in the leaching solution is below the allowed limit, then it can be concluded that the solidification process is effective.

Another way for evaluating the efficiency of solidification depends on calculating the percentage of leaching of heavy metal from GP containing the heavy metal using Eq. (1) [12]:

$$\% \text{ leaching of heavy metal} = \frac{C_{GPM}}{C_t} \times 100 \quad (1)$$

where C_{GPM} is the concentration of heavy metal leached out of the GP-containing heavy metal (mg/L). C_t is the calculated concentration (mg/L) of heavy metal (Eqs. (2) or (3)) expected to leach out of specific mass (m , in mg) of GP into specific volume (V in liters) of leaching solution assuming 100% leaching:

$$\text{Intra - solidification: } C_t = \frac{\text{mass of heavy metal (g)}}{\text{mass of waste (kg)}} \times \frac{\text{mass of waste (g)}}{\text{mass of GP (g)}} \times \frac{m}{V} \quad (2)$$

$$\text{Inter – solidification: } C_t = \frac{\text{mass of metal salt used in mix design (g)}}{\text{mass of mix design of GP (g)}} \times \frac{m}{V} \times \frac{\text{atomic mass of heavy metal}}{\text{molar mass of heavy metal salt}} \quad (3)$$

It is worth to mention that the amount of heavy metal reported in the waste material used in Eq. (2) (in g/kg, **Table 1**) is problematic because semi-quantitative X-ray fluorescence (XRF) gives the amount of metal that exist in different forms. Some of these forms may be inert. For example, as shown in **Table 1**, the environmentally significant amount of Pb in lead smelting slag determined by digesting in 2 M HNO₃ (14.7 g/kg) was much lower than the amount indicated by X-ray fluorescence (319.3 g/kg) [14]. Furthermore, many authors reported the % metal in GP total mix design incorrectly and did not differentiate between % metal and % metal salt. For example, 0.50% Cu(NO₃)₂·3H₂O is equivalent to 0.13.% Cu.

2.2. Adsorption

GP was used as an adsorbent for the removal of heavy metals from polluted water (**Figure 1**). Adsorption involves agitating specific amount of GP (m , in g) with specific volume (V in L) of standard aqueous solution (C_i) of heavy metal (simulating polluted waste water) for different contact times. The concentration of heavy metal in solution decreases until it reaches steady value (C_e) at a time called equilibration time. The mount of heavy metal adsorbed at equilibrium (Q_e , mg/g) is determined from Eq. (4):

$$Q_e = \frac{C_i - C_e}{m} \times V \quad (4)$$

Langmuir model (Eq. (5)) is the most widely used in the studies reviewed in the present article. This model is used to fit the equilibrium adsorption data that results from determining C_e and Q_e at different C_i values at constant temperature (adsorption isotherm).

$$Q_e = \frac{Q_m \times K_L \times C_e}{1 + (K_L \times C_e)} \quad (5)$$

where Q_m is the maximum adsorption capacity (mg/g) and K_L is the Langmuir affinity constant related to the energy of binding sites on the surface of GP (L/mg) [16].

For analysis of kinetics adsorption data, pseudo-second order model (Eq. (6)) was the most frequently used in the works reviewed in the present article:

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (6)$$

where k_2 is the second-order reaction constant (g mg⁻¹ min⁻¹), Q_e and Q_t are the amount of metal ions adsorbed per unit mass of GP at equilibrium and time t , respectively. The model is usually used to determine the rate constant k_2 [17].

Waste [Ref.]	Zn	Cd	Cr	Pb	Cu	Ni	As	Mo	Co	Ba	Sn	Hg	Sb	Se	V	Sr
Carbon steel electric arc dust [8, 49]	342.9	0.29	2.108	2.29												
	260	0.8	9.5	13.0		2.0	2.9									
Lead smelting slag [14]	1.690*	<0.04	0.470	319.3	0.760	0.410	2.580	0.180	<0.037	1.970	4.25		11.0	0.420	0.070	<0.04
	0.770**	0.013	0.0035	14.7	0.437	0.034	0.362	0.005	0.059	0.039			0.171	0.008	0.010	0.012
Waste solution after plating of printed circuit board [27]	0.0061		0.0026	12.619	0.3475	0.0002					2.371					
Municipal solid waste incineration fly ash [28]		0.105	0.196	0.502	0.473	0.038										
Municipal solid waste incineration fly ash [29]	3.692	0.103	1.785	0.826	2.817	0.078										
Municipal solid waste incineration fly ash [13]	15.9	0.006	0.790	0.398	0.156	0.090	0.060	0.046	0.094	1.270	1.79	0.060	5.11	0.080	0.040	
Municipal solid waste incineration fly ash [30]	3.269	0.0367	0.157	1.515	0.563	0.071							0.0358			

*Semiquantitative XRF.
 **Environmentally significant available after 2 M HNO₃ digestion.

Table 1. Heavy metal content of different wastes (g/kg).

2.3. Cost calculations

The cost of GP used in solidification and adsorption of wastes was calculated depending on the cost values of the constituents of GP given by McLellan et al. [18]. The approximate cost of MK, FA, sodium hydroxide, sodium silicate solution, kaolin, zeolite and BFS used in calculation was 200, 50, 400, 200, 100, 100 and 50 US \$/t, respectively. Water and industrial waste solidified were assumed to have negligible cost if solidification is to be applied in the site of production of waste.

3. Immobilization of pollutants in geopolymeric materials

3.1. Intra-solidification of waste in geopolymer

Heavy metals exist in many types of wastes: coal fly ash, carbon steel electric arc furnace dust, lead smelting slag, chromite ore-processing residue, aluminum production waste, municipal solid waste incineration fly ash and medical waste incineration fly ash. The heavy metal content in some of these wastes was given in **Table 1**. Because of their toxic heavy metals content, regulations prohibit disposal of these wastes in landfill [19]. For solidification of these wastes in GP matrix, these wastes are usually mixed with MK, FA or BFS and then with alkali activator to get solid GP after curing.

3.1.1. Coal fly ash waste

Bankowski et al. investigated solidification of brown coal type C fly ash {30.6, 2.4, 1.2} in MK {0.1, 49.3, 35.0}-based GP using sodium hydroxide and sodium silicate as activators. The TCLP test (**Table 2**, I-1) indicated that geopolymerization reduces the leaching of some metals such as As, Ba, Se and Sr (0.002, 0.07, 0.130 and 5.500 mg/L) relative to the unreacted fly ash (0.012, 0.270, 0.740 and 31.200 mg/L). Other metals which exist in trace amounts (like Zn, Mn, Ni and Mo) in fly ash did not respond to solidification due to error in measurements of low concentrations of these metals. It is worth to mention that best immobilization efficiency was obtained when $\leq 40\%$ (w/w) of the fly ash was incorporated in the mix design of GP [19]. Similarly, Arioz et al. studied solidification of FA (F-type, low calcium) in GP without addition of any other source of aluminosilicate and using sodium hydroxide and silicate activators. TCLP leaching results indicated that heavy metals like As and Hg were immobilized effectively in GP while Zn, Pb and Cd were not (**Table 2**, I-2). The compressive strength of the produced GP ranged from 20 to 50 MPa [20]. The results in **Table 2** (I-1 and I-2) indicated that leaching of both unreacted FA and solidified FA-GP gives low concentrations of heavy metals.

3.1.2. Metal industry waste

Solidification of 20% (w/w) carbon steel arc furnace dust {8.60, 6.21, 2.0} in OPC and type-F FA {3.94, 63.91, 21.51}-based GP was studied using variable activators (sodium and potassium hydroxides and silicates). The compressive strength of the produced GP ranged from 10 to 40 MPa compared to 2.5 MPa in the case of OPC. TCLP leaching test (acetic acid buffer at pH 3) indicated that the leached amounts of Zn, Pb, Cr and Cd from OPC system were less than 1%

Waste [Ref.]	Host matrix	As	Ba	Cr	Cu	Mn	Mo	Ni	Se	Sr	V	Zn	Cd	Pb	Co	Sn	Hg	Sb
Brown coal fly ash (precipitator) [19] I-1	Unreacted*	0.012	0.270	0.004	0.018	0.010	0.011	0.026	0.740	31.20		0.038						
	Solidified in MK-GP*	0.001–0.002	0.07–0.12			0.140–0.28	0.012–0.017	0.09–0.16	0.06–0.13	1.1–11.5	0.010–0.130	0.030–0.070						
Fly ash (F-type) [20] I-2	Unreacted*	0.40		0.058								<0.002	<0.002	<0.01			0.394	
	Solidified in FA-GP*	<0.0004		0.0082–0.023								0.0015–0.035	0.002–0.009	0.008–0.011			<0.003	
Carbon steel arc furnace dust [8] I-3	Solidified in FA-GP*			0.005–0.09								508–1296	1.2–4.52	5.5–31.7				
	Solidified in OPC*			2.7								0.1	0.03	0.6				
Carbon steel arc furnace dust [21] I-4	FA-GP*			<0.05								500–1300	1–4.5	7–32				
	OPC*			2.7								0.1	0.03	0.6				
Lead smelting slag [14] I-5	Unreacted*	0.10–0.13	1.49–1.77	0.05–0.09								0.21–0.28	16.6–37.0					
	Solidified in FA/BFS-GP*	0.01–0.06	1.75–2.84	<0.0006								0.01–0.03	4.8–23.5					
Chromite processing residue [26] I-6	Unreacted*			67.89														
	Solidified in BFS-GP*			0.027–1.55														
Waste solution after plating of printed circuit boards [27] I-7	Solidified in MK/BA-GP*			0.046–0.083	0.08–1.0									0.045–0.160		0.05–0.20		
Municipal solid waste incineration fly ash [28] I-8	Unreacted**			2.31	2.63			0.00					3.22	3.94				
	Solidified in MK-GP**			0.64 (100)	0.07 (1.8)			0.00					0.00	0.03 (0.7)				

Waste [Ref.]	Host matrix	As	Ba	Cr	Cu	Mn	Mo	Ni	Se	Sr	V	Zn	Cd	Pb	Co	Sn	Hg	Sb
Municipal solid waste incineration fly ash [29] I-9	Solidified in FA-GP***			9.8–14.3 (11–16)	12.1–18.3 (9–13)							1.2–2.2 (0.7–1.2)						
Municipal solid waste incineration fly ash [13] I-10	Solidified in FA/MK-GP*	≤0.03	0.12–0.61 (0.2–1)	0.51–0.73 (1–2)	≤0.01		0.2–0.4 (10–17)	0.04–0.18	≤0.01		0.13–0.26 (7–13)	0.70–9.8 (0.9–1.2)	≤0.01	≤0.03	0.055–0.13	≤0.02	≤0.03	0.02–0.43
	Solidified in OPC*	≤0.03	0.24–0.58 (0.2–0.4)	0.21–0.52 (0.5–1.3)	≤0.01		0.18–0.43 (8–19)	≤0.01	≤0.01		0.02–0.1 (1–5)	≤0.01	≤0.01	≤0.03	≤0.01	≤0.02	≤0.03	0.18–1.4
Municipal solid waste incineration fly ash [30] I-11	Solidified in FA-GP*			0.16 (2.04)	0.04 (0.14)							0.02 (0.01)		<0.05	<0.06			
Medical waste incineration fly ash [7] I-12	BA unreacted*		2.5	0.34								0.15		0.01				
	FA unreacted*		1.8	0.19								11.8		6.0				
	Solidified in MK-GP*		0.25–0.99	0.025–0.73								0.012–2.15						
USEPA TCLP allowed limit (mg/L)		5	100	5					1			300	1	5			0.2	

*Leaching tests were according to USEPA TCLP procedure.

**Leaching test was according to European EN 12457 procedure.

***Leaching test was done using HNO₃ solution, pH 4, liquid to solid ratio 20 mL/g.

MK: metakaolin, FA: fly ash, BA: bottom ash, BFS: blast furnace slag.

Table 2. Leaching of heavy metals (mg/L) from geopolymer matrix containing solidified waste—intra solidification (values in brackets give calculated % leaching).

of the amount leached from GP. Furthermore, the amounts of metals leached from GP were higher than USEPA limit (**Table 2**, I-3, I-4). This was explained by the high alkalinity of OPC leachate (pH 11.2–11.8) compared to neutral pH of GP leachate (pH 5.2–6.7). However, less aggressive EN leaching test (deionized water) showed much lower leaching concentration for GP samples and much higher leaching concentrations for OPC [8, 21]. This reflects the effect of leaching solution on efficiency of immobilization.

Ogundiran et al. studied solidification of lead smelting slag in (2, 1 w,w) FA {6.03, 48.9, 27.8}- and BFS {42.0, 37.2, 11.8}-based GP using potassium silicate as activator. The compressive strength was remarkably high 80–100 MPa. TCLP leaching test indicated that Pb, Zn, Cr and Ba leaching concentrations were below the recommended limit (**Table 2**, I-5). Many mechanisms were suggested for solidification of Pb in GP. The first, Pb is a network forming element replacing Si, the second, Pb(II) ions balance the negatively charge Al tetrahedra and the third, insoluble Pb(OH)₂ be encapsulated in the GP structure [14].

Perna and Hazliceck solidified semi-liquid red waste {24.76, 13.45, 13.88} and gray slag {1.17, 0.01, 54.55} from aluminum production in GP matrix. The geopolymerization of the low silicate waste was carried out with addition of silicon-rich fired clay dust {0.14, 50.28, 4.99} and potassium silicate activator to obtain SiO₂/Al₂O₃ and K₂O/Al₂O₃ molar ratio of 2.96 and 0.73, respectively. The mechanical strength of the produced GP was 30–40 MPa. Foamed GP products with thermal conductivity 0.169 Wm⁻¹ K⁻¹ were prepared. The high porosity of the foamed GP could be used in insulation and passive house construction and it has fire and elevated temperature resistance advantage over polystyrene [22].

Salihoglu et al. investigated solidification of 25% (w/w) antimony waste slag in FA {4.65, 51.84, 24.68}-based GP with OPC, clay, BFS and gypsum additives and using sodium hydroxide and silicate activators. The EN leaching concentration ranged from 0.83 to 3.29 mg/L in the case of Arsenic (As) and from 3.91 to 8.10 mg/L in the case of antimony (Sb). These concentrations were higher than the regulatory limit 2.5 and 0.5 mg/L in the case of As and Sb, respectively [23].

Rao and Liu reviewed literature (dated to 2015) on the potential of using geopolymerization reactions in solidification of mine and oil sands tailings which contain aluminosilicate materials. The review showed conflicting conclusions in the geopolymerization processes regarding for instance the suitable Na/Al and Si/Al ratios, the function of metal cations such as sodium and potassium, and the effect of calcination (for removal of organic content) [24].

Chromite ore-processing residue (COPR) was a target for solidification in several studies. Sun et al. solidified 12% (w/w) COPR {34.27, 6.46, 8.15} in MK {0.05, 46.58, 37.02}-based GP in the presence of Na₂S (reducing agent) and using sodium hydroxide and silicate activators. The mechanical strength of the produced GP was 40–60 MPa. The TCLP leaching test indicated that the concentration of leached Cr from GP was below the allowed limit (5 mg/L) when the S²⁻/Cr molar ratio > 6 compared to 45 mg/L when Na₂S was not used. The effect of geopolymerization on the efficiency of solidification was remarkable because the leaching of total Cr from of unreacted COPR was 279.84 mg/L. The suggested mechanism of solidification was that S²⁻ anion reduces anionic Cr(VI) in COPR to cationic Cr(III) which balances the negatively charged Al tetrahedra in the GP [25]. Huang et al. studied solidification of COPR {0.69, 6.19,

11.4} in BFS {40.43, 10.77, 30.18}-based GP using sodium hydroxide and silicate activators. The mechanical strength was found to decrease from 50.4 to 13.4 MPa and the TLCP leaching concentration increases only from 0.027 to 1.553 mg/L (**Table 2**, I-6) when the % (w/w) COPR in GP increased from 10 to 60%. This indicated that 60% (w/w) COPR could be effectively solidified with leaching concentration of Cr below the recommended limit (5 mg/L) [26].

Antunes Boca Santa et al. solidified the waste solution of plating printed circuit boards in MK {0.06, 47.4, 37.9} and bottom ash {1.71, 57.3, 23.7} GP, and using sodium hydroxide and silicate activators. The mechanical strength of the produced GP ranged from 5 to 25 MPa. The concentrations of metals in the TCLP leachate were below the recommended limit for Pb, Cu, Cr, Sn, Fe, Ni and Zn (**Table 2**, I-7). The results indicated that increasing the concentration of NaOH activator from 8 to 12 M causes increase in the concentration of heavy metals in the leachate and thus reduces the efficiency of solidification [27].

3.1.3. Municipal solid waste incineration fly ash

Lancellotti et al. studied solidification of 20% (w/w) of municipal solid waste incineration fly ash {10.46, 5.63, 2.10} in MK-based GP using sodium hydroxide and sodium silicate activators (Si/Al and Na/Al molar ratios of 2 and 1, respectively). EN leaching test revealed that the release of heavy metals from GP is low compared to unreacted waste, consequently, indicating efficient solidification (**Table 2**, I-8). The % leaching for Cu, Pb and Cd was 1.8, 0.7 and 0%, respectively. The effective immobilization of these heavy metals was ascribed to formation of metal hydroxides in the high alkalinity medium of GP preparation. On the other hand, the failure in Cr immobilization was ascribed to the effect of high Cl content of fly ash (26.40%) which promotes dissolution of Cr [28].

Zheng et al. investigated the effect alkaline dose of sodium hydroxide and silicate (Na/fly ash and Si/Al molar ratios) on geopolymerization of municipal solid waste incineration fly ash {28.8, 15.4, 7.2} without addition of extra aluminosilicate source. Using HNO₃ leaching solution (pH 4 with liquid/solid ratio 20), the % leaching of Cr, Zn, Cu was low: 11–16, 0.7–1.2 and 9–13, respectively (**Table 2**, I-9). However, the concentrations of metals in the leaching solution were higher than the TCLP allowed limits. The high Si/Al molar ratio (2.5) was found to reduce leaching of Cr and Cu because this ratio decreases depolymerization during leaching since Si-O-Si bond has higher strength than Si-O-Al bond. An intermediate alkaline dosage (2.4 mol Na/kg FA) favored immobilization of Cr, Cu and Zn [29].

Luna Galiano et al. studied solidification of municipal solid waste incineration fly ash {44.7, 26.8, 12.0} in GP prepared using FA (type F) mixed with kaolin or MK, BFS and different sodium and potassium hydroxides and silicates activators. The leachate pH (TCLP test) was inferred to be the most important variable on immobilization of metals. The results indicated that Zn, Co, Ni, Cu and Sn were the best immobilized, while elements forming oxyanions like Sb, Mo, V and Cr were the least immobilized in GP (**Table 2**, I-10) [13].

Guo et al. solidified 10% (w/w) municipal solid waste incineration fly ash {30.7, 17.7, 4.59} in type C fly ash {13.6, 40.2, 17.0}-based GP using sodium hydroxide and silicate as activators to obtain Na₂O/SiO₂ molar ratio of 0.7. The compressive strength of the produced GP was 50 MPa

and the leaching concentrations of Zn, Pb, Cu and Cr were much less than the recommended limits (**Table 2**, I-11) [30].

Tzanakos et al. investigated solidification of bottom ash {27.77, 39.74, 5.16} and fly ash {89.20, 6.00, 0.00} generated from incinerated medical waste in MK-based GP using sodium hydroxide and silicate activators. The TCLP leaching test indicated that the concentrations of Cr, Ni, Zn, Cd, Ba and Pb in the leachate were lower than the permitted limits and lower than the amounts leached out of unreacted bottom and fly ash (**Table 2**, I-12). The mixing of bottom, fly ash and MK with CaCO_3 was shown to improve the mechanical strength of the produced GP without affecting the leachability of heavy metals [7]. Thus, both the works of Guo et al. [30] and Tzanakos [7] reflects the positive effect Ca on immobilization of heavy metals in GP matrix.

3.1.4. Exhausted adsorbents

Xu et al. reported an interesting study on solidification of zeolite A {0.54, 54.6, 27.8} loaded with ^{90}Sr radionuclide in MK {0.13, 45.25, 43.92}-based GP using sodium silicate as activator. The performance of solidification in GP was compared with that in OPC. The mechanical strength of the produced GP was about 40 MPa compared with 11 MPa in the case of OPC. Furthermore, the GP was found to have better leaching resistance than OPC in different leaching solutions: deionized water, H_2SO_4 solution at pH 1, 4% (w/w) MgSO_4 solution and acetic acid solution at pH 3.6. This study proved that solidification in GP is complementary to adsorption process where the exhausted adsorbents containing pollutants could be solidified in a form with high mechanical strength and low leachability for construction purpose or landfill [31].

3.1.5. Nuclear waste

The solidification of nuclear waste by GP was reviewed by Vance and Perera and will not be discussed here. It was concluded that GP can have significant advantage over other cements: fire resistance, good immobilization and lack of freeze-thaw problem. There has been actual disposal of low level nuclear waste in GP on an industrial scale in the Slovak Republic [11].

3.2. Inter-solidification of pollutants in geopolymers

The present section reviews literature on immobilization of highly soluble metal salts ($\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, etc.) in aluminosilicate-rich sources like FA (type F), MK and BFS, etc. The heavy metal nitrates are usually introduced during the synthesis of GP and can be added either to the aqueous activator (sodium hydroxide and sodium silicate solution) or added to solid aluminosilicate precursor (**Figure 1**). This technique can be applied for solidification of waste water contaminated with heavy metals. As will be discussed in the forthcoming paragraphs, the effect of incorporation of heavy metal nitrates on the mechanical strength of the produced GP and the % leaching of heavy metals from the GP matrix are the two major criteria for evaluating the efficiency of solidification. Other microstructural properties of GP (revealed by XRD, SEM and FTIR) are not usually affected by incorporation of heavy metals.

3.2.1. Alkali and alkaline earth metals

Lee et al. investigated the effect of incorporation of inorganic salts (0.18 mol/kg FA) KCl, CaCl₂, MgCl₂, K₂CO₃, CaCO₃, MgCO₃, Ca(OH)₂ and Mg(OH)₂ on the mechanical strength of GP prepared from type F FA {3.5, 50.0, 28.0} and kaolin {0.2, 54.5, 29.4}. Two systems of alkali activators were employed: the first contained 15 M NaOH and the second contained 20 M NaOH in addition to sodium silicate. The first system was found to have higher mechanical strength. Ca(OH)₂ and Mg(OH)₂ did not exert any negative effect on the mechanical strength, KCl, CaCl₂, MgCl₂ decreased the mechanical strength and K₂CO₃, CaCO₃, MgCO₃ increased the mechanical strength of GP. The conclusion was that chloride contamination and excessive alkalinity in the activating solution should be avoided in GP synthesis [32].

Li et al. demonstrated that FA {63.86, 21.87, 4.33}-based GP are more effective hosts for ¹³³Cs(I) than ordinary Portland cement (OPC). ¹³³Cs(I) was incorporated (2% w/w) into GP and OPC, separately. The concentration of Cs(I) leached out of the GP was found to be 5.4 and 9% of the leaching concentration of OPC when deionized water and MgSO₄ solutions were used as leaching reagents, respectively. This was ascribed to the fact that GP has much lower porosity than OPC. On the other hand, when H₂SO₄ was used as leaching reagent, Cs(I) leaching from GP was comparable to leaching from OPC. The high extent of leaching in H₂SO₄ leaching reagent (30 times that of deionized water) was ascribed to dissolution of Ca(OH)₂ from GP and OPC. The GP-containing Cs(I) was superior to OPC in many properties like higher mechanical strength, thermal stability and acid resistance. The mechanical strength of GP was 57.15 MPa compared with 33.73 in the case of OPC. The GP block can retain a compressive strength of 30 MPa after 2 h calcination at 1000°C. The mass loss of GP after 60 days in acetic acid/acetate buffer (pH 3.6) was 7.1% that of OPC [33].

3.2.2. Pb(II), Cu(II), Cd(II), Cr(III)

Van Jaarsveld et al. studied solidification of Cu(II) and Pb(II) nitrates (0.1% w/w) in GP prepared from FA {8.2, 50.1, 28.3} and either MK or kaolin additives and using sodium hydroxide activator. The concentrations of Cu and Pb in the TCLP leaching solutions were higher than the allowed limit (**Table 3**, I-1). Furthermore, the % leaching was relatively high (23–65%) [34]. The compressive strength of Pb-containing GP samples (33.7 MPa) was found to be slightly higher than Cu-containing GP samples (28.1 MPa). Two basic mechanisms for immobilization of heavy metals in GP matrix were proposed. The first is physical: positively charged metal Pb(II) or Cu(II) ions balance the negatively charged Al tetrahedra of GP. The second is chemical: metal ions are bonded to the silicate chain through oxide and/or hydroxide links [35].

Phair et al. incorporated 0.5% w/w Pb(II) and Cu(II) nitrates in FA-based GP. The FA {6.1, 48.5, 29.6} was either used alone or mixed with kaolin {0.1, 52.4, 28.6}, MK or K-feldspar {0.21, 67.1, 17.6} additives using sodium hydroxide and/or silicate activators. The efficiency of immobilization of Pb(II) followed the order: FA-GP > FA/kaolin-GP > FA/feldspar-GP > FA/MK-GP as indicated by TCLP leaching tests (**Table 3**, I-2). The concentrations of heavy metals were higher than the TCPL limit and the % leaching were relatively high. There was no correlation between

GP matrix	Code	Leaching test	Mass % of metal solidified	Cu(II)	Pb(II)	Cr(VI)	Cd(II)	Cr (III)	Ni (II)	Ref.
FA/MK	I-1	TCLP, pH 3, 24 h	0.1	22 (55)	23 (58)					[34]
FA/kaolin				26.1 (65)	9.1 (23)					
FA/kaolin	I-2	TCLP, 28 days	0.5	85.7 (43)	8.5 (43)					[36]
FA/MK				101 (51)	17.5 (9)					
FA/feldspar				116 (58)	11 (6)					
FA				113 (57)	7.5 (4)					
MK/FA	I-3	TCLP, pH 3, 24 h	0.1	17 (125)	17 (68)					[37]
		HCl solution, pH 3		8 (59)	3 (12)					
Kaolin/FA		TCLP, pH 3, 24 h		9 (67)	7 (28)					
		HCl solution, pH 3		17 (125)	10 (40)					
FA/MK	I-4	TCLP	0.1	0.0075	0.0025		0.020	0.001		[38]
BFS/MK(1:1)	I-7	TCLP, 24 h	0.1	0.176 (0.44)	0.292 (0.73)					[42]
			0.2	0.384 (0.48)	0.864 (0.72)					
			0.3	0.396 (0.33)	0.192 (0.16)					
FA	I-5	H ₂ SO ₄ , pH 1, 90 days	0.5		(0.4)	(88)	(37)			[15]
		5% MgSO ₄ , 90 days			(0.0)	(75)	(0.02)			
		5% Na ₂ CO ₃ , 90 days			(0.1)	(78)				
		Water, 90 days			(0.004)	(80)	(0.04)			
MK, sodium silicate activator	I-8	Deionized water, L/S ratio 6	0.1	22.1 (28.4)	10.3 (4.10)		20.5 (14.82)			[12]
		0.1 M HCl		15.0 (21.04)	7.5 (2.71)		10.7 (7.28)			
		0.1 M NaCl		11.3 (15.51)	4.7 (1.81)		7.7 (4.89)			
		1.0 M NaCl		7.4 (0.82)	18.1 (7.71)		10.0 (6.16)			
		0.1 M NaOH		14.3 (21.22)	7.1 (2.52)		7.7 (5.01)			
Ferronickel slag	I-9	TCLP, pH 3 24 h	0.5 nitrates	25.5 (4)	7.9 (0.5)			0.3	34.7	[44]
			0.5 sulfate	46.6 (7)	9.0 (0.5)			0.1	47.3	
FA	I-6	EN-12457-2 deionized water, 28 days	0		1.0					[40]
			0.5		4.0 (0.8)					
			1.0		7.0 (1.4)					

GP matrix	Code	Leaching test	Mass % of metal solidified	Cu(II)	Pb(II)	Cr(VI)	Cd(II)	Cr (III)	Ni (II)	Ref.
Mechanically activated FA			0		0.5					
			0.5		0.9 (0.2)					
			1.0		1.0 (0.2)					
FA	I-10		0.5			126 (25)				[46]
			1.0			338 (34)				
			2.0			735 (37)				
Mechanically activated FA			0.5			44 (9)				
			1.0			219 (22)				
			2.0			530 (27)				
USEPA TCLP allowed limit (mg/L)					5	5	1	5		

MK: metakaolin; FA: fly ash; BFS: blast furnace slag. L/S ratio: liquid leaching solution (mL) to solid geopolymer (g).

Table 3. Leaching of heavy metals (mg/L) from geopolymer matrix containing solidified heavy metal nitrates—intersolidification (values in brackets give calculated % leaching).

the efficiency of immobilization and the compressive strength where the order of mechanical strength was FA/kaolin-GP > FA/MK-GP > FA/feldspar-GP > FA-GP

	FA-GP	FA/kaolin-GP	FA/feldspar-GP	FA/MK-GP
% leaching of Pb	7.5	8.5	11	17.5
Mechanical strength (MPa)	7.7	32.7	13.9	26.8

The efficiency of immobilization of Cu was lower than that of Pb. An interesting conclusion withdrawn from this study was that Cu and Pb are less labile to leaching from bulky poly-silicates of GP than from their mono-silicates and hydroxides [36]. In a similar study, van Jaarsveld et al. compared the effect of addition of 15% (w/w) kaolin or MK to FA-based GP on solidification of 0.1% (w/w) Pb(NO₃)₂ and Cu(NO₃)₂. The FA used was of type F {8.2, 50.1, 28.3}, sodium hydroxide was used as activator and the Si/Al molar ratio was 1.5. The results are given in **Table 3**, I-3. MK was shown to be preferred over kaolin as additive to FA when high resistance to HCl leaching solution (pH 3.3) is required [37].

Xu et al. solidified Pb(II), Cd(II), Cu(II), and Cr(III) nitrates in GP prepared from FA {1.88, 47.42, 30.90} and MK {0.13, 53.3, 41.8} additive using potassium hydroxide and silicate activators. TCLP leaching tests (**Table 3**, I-4) indicated negligible leaching concentrations of heavy metals ≤0.02 mg/L (% leaching <1%) which are much lower than the TCLP limits. Except for Cr

(III), It has been found that heavy metals improve the compressive strength of GP. Furthermore, immobilization of Pb(II) and Cr(III) were better than Cu(II) and Cd(II). Increasing the % sodium hydroxide from 2 to 6% in GP mix design was found to result in decreasing of the concentration of Cu(II) and Cd(II) in the leaching solution [38]. The high efficiency of immobilization of heavy metals compared the work of Van Jaarsveld [34, 35, 37] may be due to the use of two sodium silicate in addition to sodium hydroxide.

Zhang et al. investigated solidification of 0.5% (w/w) Pb(II) and Cd(II) nitrates in FA {5.1, 46.4, 28.3}-based GP prepared using sodium hydroxide and silicate activators. H_2SO_4 (pH 1), 5% (w/w) MgSO_4 and 5% Na_2CO_3 leaching solutions were used. H_2SO_4 leaching solution showed the highest % leaching. Pb(II) resist leaching using all these leaching solution and Cd(II) also showed similar behavior except in the case of H_2SO_4 leaching solution (**Table 3**, I-5). The mechanism of immobilization suggested was that heavy metal ions undergo chemical bonding either with the GP gel or with the low solubility silicate or aluminate phases. Another possible mechanism was that the soluble salts of heavy metals may undergo some chemical conversion in the highly alkaline conditions of GP synthesis and then trapped in the GP matrix [15].

Guo et al. studied solidification of 0.025% (w/w) $\text{Pb}(\text{NO}_3)_2$ in FA {20.0, 38.0, 19.0}-based GP using sodium hydroxide and silicate activators (mass ratio, 5 NaOH:35 sodium silicate:60 FA). Incorporation of Pb induced slight reduction in compressive strength. The leaching concentration of Pb was 0.003 mg/L and the % leaching was 0.024%. The shift of FTIR OH stretching to lower frequency in the case of GP-containing heavy metal compared with GP-blank [39] suggests binding of nonbridging Si—OH and Al—OH to heavy metal.

Nikolic et al. studied the effect of mechanical activation of FA {5.67, 62.13, 17.20} on the efficiency of immobilization of Pb(II) nitrate in FA-based GP. Mechanical activation involves milling FA before reacting with sodium hydroxide and silicate activators. EN leaching test indicated that Pb (II) was more effectively immobilized in mechanically activated FA-based GP (the leaching concentration is less than the allowed limit) than untreated FA-based GP (**Table 3**, I-6). This was ascribed to the fact that mechanical activation of FA reduces the porosity, increase the compactness (as reflected by SEM) and increase the mechanical strength of the GP [40].

Guo et al. investigated solidification of up to 8% (w/w) of three Pb compounds (PbO , PbSO_4 and PbS) in FA {7.6, 52.1, 23.5}-based GP using sodium hydroxide and silicate activators (Si/Al molar ratio 2.3). The three compounds have variable solubility: PbO is soluble in acetic acid and NaOH, PbSO_4 is insoluble in acetic acid and soluble in NaOH, and PbS is insoluble in both solutions. Incorporation of PbO was found to increase the mechanical strength of GP while PbSO_4 and PbS have the reverse effect. The % leaching was very low (<1%), but the leached Pb concentration (6–27 mg/L) was higher than the TCLP limit [41].

MK and BFS-based GP received less attention than FA-based GP as hosts for highly soluble heavy metal salts. However, some studies will be discussed here. Yunsheng et al. investigated solidification of Pb(II) and Cu(II) in GP prepared from (1:1, w:w) MK {0.6, 62.97, 26.91} and BFS {41.7, 34.20, 14.20} using sodium hydroxide and silicate activators. TCLP tests (**Table 3**, I-7) indicated that MK/BFS-based GP can very effectively immobilize Cu (II) and Pb(II) with % leaching less than 1% and concentrations of heavy metals in leaching solution less than the

TCLP limit. Kinetics of leaching revealed that the heavy metals rapidly leached out the GP and reach steady concentration after 4 h. The mechanical strength of the produced GP was high and slight reduction in mechanical strength (from 72.68 to 70.28 MPa) was observed when the heavy metal dosage increases from 0.1 to 0.3% [42]. Perera et al. showed that heating of MK-based GP containing 1% (w/w) $\text{Pb}(\text{NO}_3)_2$ from 200 to 800°C, resulted in an increase of the leached Pb concentration from 2.8 to 14.8 mg/L [43]. El-Eswed et al. studied immobilization of Pb(II), Cd(II) and Cu(II) in MK {0.4, 50.62, 46.21}-based GP using sodium silicate activator either alone (Na/Al molar ratio 1) or mixed with sodium hydroxide (Na/Al molar ratio 2). The Si/Al molar ratio used was 2 for both cases. In most cases, one and two activators have similar immobilization performance which suggests that the high alkalinity is not the limiting factor for immobilization of heavy metals. The % leaching and the concentrations in the leaching solutions are given in **Table 3**, I-8. The concentrations of Pb and Cd were higher than the allowed limit. When water was used as leaching solution, the efficiency of immobilization was $\text{Pb(II)} > \text{Cd(II)} > \text{Cu(II)}$ which is consistent with the order of decreasing ionic radius. An interesting observation was that the efficiency of immobilization of total ions (revealed by conductivity measurements) increases with increase in efficiency of immobilization of heavy metals, which excluded the mechanism those heavy metals cations were exchanged with the alkali metals in the Al tetrahedra. Evidences for the presence of nonbridging Si—OH and Al—OH in the GP were obtained from infrared study which may be the active sites for complexation with heavy metal ions [12].

Komnitsas et al. investigated solidification of (0.5% w/w) Pb(II), Cu(II) Cr(III) and Ni(II) nitrates and sulfates in ferronickel slag {3.73, 32.74, 8.32} using potassium hydroxide and sodium silicate activators (mass ratio, 82 slag:6H₂O:3KOH:9 sodium silicate). The results (**Table 3**, I-9) reflected that the efficiency of immobilization was very high >90%. The GP undergo 70% reduction in mechanical strength when 3% PbSO₄ was incorporated. Except in the case of Cr(III), the metal concentration leached in the case heavy metal sulfates were more than nitrates [44]. El-Eswed et al. studied solidification of 200–1000 ppm solutions of Pb(II), Cu (II), Cd(II) and Cr(III) nitrates solutions by mixing with zeolite, kaolin and NaOH (1:7:7:1 mass ratio) followed by pressing under 15 MPa. The mechanical strength of the obtained GP was about 18 MPa. The % leaching of Pb ranged from 25 to 50 depending on the leaching solutions used; deionized water, 0.1 M NaCl, 1.0 M NaCl, 0.1 M HCl and 0.1 M NaOH leaching solutions. The worst immobilized heavy metals were Pb(II) and Cu(II) and the most effectively immobilized were Cd(II) and Cr(III) [45].

3.2.3. Cr(VI) anions

Zhang et al. investigated solidification of 0.5% Cr(VI) (Na_2CrO_4) in FA {5.1, 46.4, 28.3}-based GP prepared using sodium hydroxide and silicate activators. Cr(VI) was not effectively immobilized where the % leaching ranged from 75 to 88% [15]. Guo et al. studied solidification of 0.025% (w/w) Cr(VI) (CrO_3) in FA {20.0, 38.0, 19.0}-based GP using sodium hydroxide and silicate activators (5 NaOH:35 sodium silicate:60 FA). The leaching concentration of Cr was 0.015 mg/L and the % leaching was 12% [39]. To improve efficiency of immobilization, solidification of Cr(VI) (K_2CrO_4) in mechanically activated FA was investigated. Although

mechanical activation of fly ash improved immobilization of Cr, the leaching concentration was much more than the allowed limit (**Table 3**, I-10). Thus Cr(VI) is not easy to be immobilized effectively in FA-based GP. GP has a limited capacity for heavy metals and the % leaching of Cr increases from 8.84 to 26.5% by increasing dosage of Cr from 0.5 to 2.0% (w/w) [46]. The addition of Cr to the GP matrix did not affect the mechanical strength of GP [46].

Chen et al. [47, 48] effectively solidified highly soluble $K_2Cr_2O_7$ in MK-based GP using sodium hydroxide and silicate activators by addition of Fe^{2+} reducing agent. The mass ratio of MK, sodium silicate solution and NaOH were set to be 6:5:1. The compressive strength of GP containing 0.1% (w/w) Cr(VI) was 60 MPa which decreased to 31 MPa when the amount of Cr(VI) increased to 0.8% (w/w) (keeping the Fe^{2+} /Cr(VI) molar ratio 4). The concentration of Cr leached using TCLP test decreased from 20.05 to 0.42 mg/L when the amount of $FeCl_2 \cdot 4H_2O$ increased from 0.5 to 3% (w/w) keeping the 0.1% Cr (w/w) constant. On the other hand, the concentration of Cr leached increased only from 0.0135 to 0.42 mg/L when the % Cr (VI) increased from 0.1 to 0.8% (w/w) keeping Fe^{2+} /Cr(VI) molar ratio = 4. The mechanism of immobilization suggested was that Fe^{2+} reduced Cr(VI) to Cr(III) which could attached to the negatively charged Al tetrahedra of the GP framework [47]. Chen et al. showed that the concentration of Cr leached out of GP containing 0.1% (w/w) Cr(VI) dropped from 47 to 0.69 mg/L when Fe^{2+} was added to GP during reaction of the MK with the alkali activator. However, the drop was more (0.0942 mg/L) if Fe^{2+} was added to Cr(VI) in water first [48].

3.2.4. As(IV) anions

Fernandez et al. studied solidification of 1% (w/w) $NaAsO_2$ in MK {0.0, 49.85, 36.34} and FA {4.39, 51.51, 27.47}-based GP, separately, using sodium hydroxide and silicate activators in the former and sodium hydroxide activator in the latter. The mechanical strength of MK-GP (4 MPa) was less than that of FA-GP (7.6 MPa). The % leaching of As from MK-GP and FA-GP was high (67.6 and 49.2%, respectively) and the concentrations of As leached were higher than the TCLP limit. Interestingly, the low level of Si and Al leached (about 1%) showed that the GP matrix is stable in the aggressive leaching solution of acetic acid buffer at pH 3 (TCLP test) [49].

3.2.5. Solidification of organic pollutants

Few works were reported on solidification of organic pollutants in GP. Gokhale reported a technique for removal of phenols from aqueous solution using natural zeolite (clinoptilolite) followed by encapsulation in FA {1.7, 55.0, 28.4}-based GP. The mass ratio of precursors was 10 FA:1 kaolin:1.2 potassium hydroxide:2.2 sodium silicate:1.6 water. The mechanical strength of GP containing 1% (w/w) phenol and chlorophenol was 35 and 40 MPa, respectively. The TCLP leaching concentration of phenols was less than 2 mg/L and the corresponding % leaching about 40% [50]. Shvarzman studied solidification of 0.3% (w/w) phenol in FA {0.0, 47.04, 29.37} and MK {0.0, 52.18, 43.36}-based GPs, separately, with Si/Al molar ratio of about 3 and using sodium hydroxide and silicates activators. The compressive strength of FA-GP and MK-GP was 90 and 50 MPa, respectively, which was not influenced by addition of phenols. The concentration of phenol leached out of the FA-GP and MK-GP (using distilled water as

leaching reagent, liquid/solid ratio 40 mL/g) was 12 and 2.9 mg/L, respectively. The corresponding % leaching was 16 and 4%, respectively [51].

Cantarel et al. solidified liquid oil (simulating radioactive oil waste from nuclear industry) in MK {0.3, 54.4, 38.4}-based GP using sodium hydroxide and silicate activators with Si/Al and Na/Al molar ratios 3.8 and 1.0, respectively. The compressive strength of GP containing oil ranged from 22 to 31 MPa depending on the oil fraction (from 7 to 20% (v/v)). The % leaching was less than 0.19% using water leaching solution (the increased alkalinity during leaching was neutralized with HNO₃). The mechanism suggested for immobilization of oil was that the alkali from the aqueous activator reacts with alkanolic acids in the oil producing surfactants which reduces the interfacial tension between the oil and the aqueous phase [52].

3.3. Adsorption of pollutants onto geopolymer

The chemical structure of GP is composed of a negatively charged aluminosilicate framework balanced by alkali metals (such as Na⁺ and K⁺). The latter can be exchanged with heavy metals cations in aqueous solution and thus GP could be used for the removal of heavy metal cations from water. It is worth to mention that in all the reviewed studies below, the prepared GP adsorbent was extensively washed with distilled water (until neutral pH 7 is achieved) to remove excess alkali used in preparation of GP. This was an essential step to avoid precipitation of heavy metal hydroxides which result in overestimation of the calculated adsorption capacity of GP.

3.3.1. Fly ash-based geopolymeric adsorbents

Many studies indicated that FA-based GP is a potential adsorbent for heavy metals ions. Some results of these studies are summarized in **Table 4**. Some of the values of adsorption capacity (Q_m , mg/g) were 99 (Cu(II)) [53], 134.95 Pb(II) [54] and 98.84 Cu(II) [55], 69.85 (Cu(II)) [56] and 50.03 (Co(II)) [57]. The affinity constants (K_L , L/mg) were 0.0607 (Pb(II)) [54] and 0.061 (Cu(II)) [55]. Interestingly, the adsorption capacity of Cu(II) on the different FA-based GPs reviewed in this section (**Table 4**) is 98 ± 12 and the affinity constant K_L is 0.08 ± 0.03 which reveals that the values of adsorption parameters is somewhat independent on the FA source, GP preparation conditions and adsorption conditions. The adsorption rate constants (k_2 , mg/g min) were of the same order; 1.8×10^{-2} (Cu(II)) [55], 2.8×10^{-2} – 1.5×10^{-2} (Cu(II)) [56], 5.4×10^{-2} – 4.2×10^{-2} (Co(II)) [57]. However, the adsorption process was reported sometimes to be slow (30 h equilibration time) [53] and sometimes fast (30 min [54] and 15 min) [55]. The adsorption capacity Q_m obtained for GP was much higher than the fly ash itself (0.1 mg/g), which revealed the efficiency of geopolymerization in creating new sites for adsorption. Furthermore, geopolymerization increases the surface area from 8.4 m²/g in FA to 56.0 m²/g in GP [53].

The work of Muzek was distinguished from others in studying the amounts of Na, K, Ca, Mg, Al and Si leached out of the GP as a result of adsorption of Cu(II) and Co(II). The total amount of ingoing heavy metals was found to be higher than the amount of Na⁺ outgoing, indicating that the adsorption of Cu(II) and Co(II) is not only ion exchange with Na⁺ (balancing the negatively charged Al tetrahedra). The amounts of Si and Al leached (<3%) were small because of the stability of GP [58].

Adsorbent	Precursors { %CaO, %SiO ₂ , % Al ₂ O ₃ }	Alkali activator	Adsorption conditions	Parameter	Cu(II)	Pb(II)	Cs(I)	Ref.
FA-GP	FA {1.6, 55.0, 29.0}	Sodium hydroxide	C _i : 100–250 mg/ L, pH 7, solid/ liquid = 0.15 g/L	Q_m K_L k_2	99 0.13 2.8×10^{-5}			[53]
FA-GP	FA {1.75, 50.73, 28.87}	Sodium hydroxide	C _i : 10–140 mg/L, pH 5–6, solid/ liquid = 1.4–2.0/ L	Q_m K_L k_2	96.84 0.061 1.8×10^{-2}	134.95 0.0607		[54]
FA	FA {5.14, 29.12, 51.39}	Sodium hydroxide and sodium silicate	C _i : 100– 1000 mg/L, pH 3, solid/ liquid = 4.0 g/L	Q_m K_L k_2		53.47 0.1769 3.4×10^{-4}		[59]
FA-GP				Q_m K_L k_2		111.1 0.6429 2.7×10^{-3}		
Faujasite from FA-GP				Q_m K_L k_2		142.86 0.2966 1.3×10^{-3}		
Mesoporous FA/BFS-GP	FA {4.79, 57.0, 21.0} BFS {47.7, 32.4, 11.5}	Sodium hydroxide and sodium silicate	C _i : 10–150 mg/L, pH 6, solid/ liquid = 4.4 g/L	Q_m K_L k_2			15.244 0.1816 3.03×10^{-4}	[61]
Porous FA/ iron ore tailing- GP	FA {5.21, 29.47, 51.72} Iron ore tailing {7.63, 34.72, 16.22}	Sodium silicate	C _i : 100–200 mg/ L, pH 6, solid/ liquid = 3.0/L	Q_m K_L	113.41 0.073			[62]
			C _i : 100–200 mg/ L, pH 5, solid/ liquid = 3.0/L	Q_m K_L	100.81 0.069			
			C _i : 100–200 mg/ L, pH 4, solid/ liquid = 3.0/L	Q_m K_L	79.31 0.064			

MK: metakaolin; FA: fly ash; BA: bottom ash; BFS: blast furnace slag.

Table 4. Langmuir adsorption capacity (Q_m , mg/g) and affinity constant (K_L , L/mg) and pseudo second order rate constant (k_2 , g/mg min) parameters for adsorption of heavy metal on FA-based GP.

Muzek et al. found that the adsorption behavior of FA-based GP was similar to zeolite NaX [57]. Furthermore, Liu et al. showed that FA-based GP is similar in adsorption properties to faujasite zeolite. The GP was prepared first and then turned into faujasite via in situ

	Faujasite	GP	FA
Specific surface area (m ² /g)	174.35	20.48	16.45
Q_m (mg Pb(II)/g)	142.86	111.11	53.47
K_L (L/mg)	0.2966	0.6429	0.1769
k_2	13.5×10^{-4}	26.73×10^{-4}	3.418×10^{-4}

hydrothermal method (by soaking in 1.0 M NaOH solution at 70°C). Interesting trends about specific surface area and adsorption capacity were obtained (**Table 4**).

The authors concluded that both GP and faujasite have the same adsorption mechanism because they have similar adsorption behavior. However, GP was distinguished in that it has the highest K_L (affinity constant) and k_2 (rate constant) [59].

In order to improve the adsorption behavior further, Novais et al. prepared a porous GP using FA {36.72, 25.34, 6.05} and MK {0.10, 54.4, 39.40} as precursors (1:2, w:w), sodium hydroxide as activator and different amounts of H₂O₂ foaming agent. In this basic medium, H₂O₂ is decomposed to water and oxygen gas. As the amount of H₂O₂ increases from 0.30 to 1.2% (w/w), the total porosity increases from 52.0 to 78.4% and the apparent density decreases from 0.98 to 0.44 g/cm³. However, the maximum adsorption capacity of Pb(II) was low (6.34 mg/g) and the adsorption capacity of Pb(II) was not directly related to the porosity of GP [60]. A similar study was conducted by Lee et al. for the adsorption of Cs(I) on mesoporous GP. The GP was prepared from (4:1) FA {4.79, 57.0, 21.0} and BFS {47.7, 32.4, 11.5} as precursors and sodium hydroxide and silicate as activators. The XRD of the prepared GP was found to have zeolites peaks and the cation exchange capacity was 202.04 cmol_c/kg which close to those of zeolites. One disadvantage was that the mesoporous GP was unstable in acidic environment at pH 2. However, the adsorption capacity of Cs(I) was low 15.244 mg/g at pH 6. The adsorption process was slow where 24 h is required to reach equilibration time, however, for pulverized samples, the equilibration time was 30 min. This was an indication that considerable time is required for diffusion of Cs(I) through the bulk of mesoporous GP. The adsorption mechanism was assumed to be ion exchange and electrostatic adsorption of Cs(I) cations on the negatively charged Al tetrahedra in the GP matrix [61].

Duan et al. studied adsorption of Cu(II) on porous GP prepared from FA {5.21, 29.47, 51.72} and iron ore tailing {7.63, 34.72, 16.22} precursors, sodium silicate activator and H₂O₂ foaming agent. The total porosity of the prepared GP ranges from 56.9 to 74.6%. The adsorption capacity of the porous GP was high (**Table 4**) and about three times that of reference (nonporous) GP [62]. As in the nonporous GP [54, 55, 59], the adsorption process was found to be endothermic and the positive value of entropy indicated that entropy is increasing by desolvation of Cu(II) ion as a result of adsorption on GP. The results for the effect of pH on the adsorption capacity Q_m are shown in **Table 4**. When the pH increases from 4 to 6, the adsorption capacity of Cu(II) Q_m increases from 79.31 to 113.41 mg/g [62]. This strong pH dependence, which was observed by other researchers [54, 59], may reveal that pH sensitive sites like Si—OH and Al—OH similar to those found in kaolin may contribute to adsorption by complexation mechanism (chemisorption) [63].

3.3.2. Metakaolin-based geopolymeric adsorbents

Cheng et al. studied adsorption of Pb(II), Cu(II), Cr(III) and Cd(II) on MK {0.2, 41.5, 19.6}-based GP synthesized using sodium hydroxide and silicate as activators. Some of the results are given in **Table 5**. The adsorption selectivity order deduced by the authors, depending on the calculated Q_m values in mg metal/g adsorbents, was

	Pb(II)>	Cd(II)>	Cu(II)>	Cr(III)
Q_m (mg metal/g adsorbent)	147.06	67.57	48.78	19.94
Hydrated ionic radius (Å)	4.01	4.26	4.19	4.61

Depending on this trend, the authors deduced that metals with large hydrated ionic radii have greater affinity for water and so they tend to remain in the aqueous phase and consequently will be weakly adsorbed on the GP. However, the correct order of selectivity should depend on Q_m values in mmol metal/g adsorbent

	Cu(II)>	Pb(II)>	Cd(II)>	Cr(III)
Q_m (mmol metal/g adsorbent)	0.768	0.710	0.6011	0.383

This order does not support the same conclusion. The mechanism for adsorption onto GP was assumed to be ion exchange rather than specific chemical adsorption because the adsorption process was found to be endothermic. However, the desorption of Cr(III), Pb(II), Cu(II) and Cd(II) from GP loaded with maximum capacity was almost negligible (after 48 h) 14.7, 5.9, 1.9 and 2.1%, respectively, which suggests specific rather than electrostatic interaction [64].

A similar study was conducted by Lopez et al. for adsorption of Cs(I), Pb(II), Cu(II), Zn(II), Ni(II) and Cd(II) (**Table 5**) on MK {0.2, 52.0, 42.8}-based GP with variable Si/Al molar ratio. As the Si/Al ratio ranged from 1 to 5, the surface area decreased from 27.5 to 2.1 m²/g and the bulk density increased from 0.8 to 1.23 g/cm³. The GP with Si/Al ratio of 2 was found to have the highest adsorptivity toward Pb(II). The high selectivity for adsorption of large size atoms like Cs(I) and Pb(II) as well as the fact that adsorption process was independent on ionic strength which indicates that the adsorption process has non-electrostatic mechanism [65].

Luukkonen et al. investigated adsorption of As(III) and Sb(III) onto MK {0.06, 53.1, 40.3}-based GP and compared the results with adsorption of the same heavy metals onto BFS {38.5, 27.2, 8.4}-based GP. The specific surface area increases significantly upon geopolymerization of MK and BFS from 11.5 to 22.4 m²/g and from 2.79 to 64.5 m²/g, respectively. The adsorption properties are shown in **Table 5**. The adsorption capacity of the GP samples was, in general, higher than the corresponding precursors (MK and BFS), which revealed the importance of geopolymerization in generation of new active sites for metal ions. However, the adsorption capacities were low, may be because As(III) occurs primarily as arsenite and arsenate and Sb

Adsorbent	Adsorption conditions	Parameter	Pb(II)	Cu(II)	Cr(III)	Cd(II)	Ni(II)	As(III)	Sb(III)	Zn(II)	Cs(I)	Ref.
MK-GP	C_i : 50–300 mg/L, pH 4, solid/liquid = 1.5 g/L	Q_m	147.1	48.78	19.94	67.57						[64]
		K_L	0.1135	0.025	0.158	0.449						
		k_2	1.8×10^{-5}	2.3×10^{-5}	1.8×10^{-3}	8.3×10^{-5}						
MK-GP	C_i : 50–500 mg/L, pH 5, solid/liquid = 1.25 g/L	Q_m	63.40	59.22							57.81	[65]
		K_L	0.0181	0.0117							0.0211	
Porous MK-GP	C_i : 100 mg/L, pH 5, solid/liquid = 1.5 g/L	Q_m	45.1	34.5								[68]
		K_L										
		k_2		3.8×10^{-5}								
Porous MK-GP	C_i : 50 mg/L, pH 5, solid/liquid = 1.5 g/L	Q_m		52.63								[69]
		K_L		0.1359								
		k_2		2.9×10^{-3}								
MK	C_i : 3.74 mg Ni/L, 0.52 mg As/L, 0.34 mg Sb/L, pH 7–8, solid/liquid = 5.0 g/L	Q_m					0.449	0.0416	0.0102			[66]
		k_2					0.025	3.137	1.996			
MK-GP		Q_m					0.748	0.078	0.0578			[67]
		k_2					0.119		10.944			
BFS		Q_m					0.374	0.0208	0.0034			[67]
		k_2					0.168	0.080	3.866			
BFS-GP		Q_m					0.673	0.0104	0.0034			[67]
		k_2					1.124	0.233	1.702			
MK-GP		Q_m					42.61			74.54		[67]
		K_L					19.6			346		
		k_2					8.4×10^{-3}			3.8×10^{-3}		

MK: metakaolin; FA: fly ash; BFS: blast furnace slag.

Table 5. Langmuir adsorption capacity (Q_m , mg/g) and affinity constant (K_L , L/mg) and pseudo second order rate constant (k_2 , g/mg min) parameters for adsorption of heavy metal on MK-based GP.

(III) occurs as antimonite and antimonate (oxyanions) in aqueous solutions. The equilibration time for adsorption of heavy metals on MK and BFS GP was 24 and 6 h, respectively [66].

Kara et al. studied adsorption of Zn(II) and Ni(II) on MK {0.0, 52.9, 41.9}-based GP. The GP was prepared with $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratios of 3.2 and 0.7, respectively. The adsorption capacity Q_m (mg/g) of Zn(II) and Ni(II) was found to follow the order

	MK-GP>	Zeolite>	Kaolinite
Zn(II)	74.53	18.66	7.20
Ni(II)	42.61	1.98	1.69

Thus, GPs were thought to be more effective than traditional adsorbents like zeolite and kaolinite [67]. An interesting observation on this study was the high values of K_L (Table 5) which reflects high affinity of GP sites to interact with heavy metals.

In order to increase the surface area of MK-based GP adsorbents, Tang et al. prepared porous MK {0.0, 56.91, 42.35}-based GP in the presence of sodium dodecyl sulfate foaming agent with Si/Al and Na/Al molar ratios 1.6 and 1, respectively. The prepared GP was found to have surface area $53.95 \text{ m}^2/\text{g}$ (which is much higher than that of ordinary MK-GP ($20\text{--}30 \text{ m}^2/\text{g}$ [65, 66]) and bulk density $0.79 \text{ g}/\text{cm}^3$. The adsorption data (Table 5) showed that the adsorption capacity of porous GP toward Cu(II) is less than that of ordinary MK-based GP, which indicated that the employment of foaming agent may decrease surface active sites on the GP. Furthermore, the adsorption process was slow where 36–50 h is required to reach equilibration time which reflects diffusion limitations [68]. Similarly, porous MK-based GP was prepared by Yuanyuan, using H_2O_2 and sodium dodecyl sulfate as foaming agents. The adsorption properties are shown in Table 5, where the adsorption capacity of Cu(II) on the porous GP was $52.63 \text{ mg}/\text{g}$, which is comparable to ordinary MK-based GP (Table 5). However, the adsorption process was slow and needed 36 h to reach equilibration time. Furthermore, the adsorption capacity increased significantly from 1.02 to $38.55 \text{ mg}/\text{g}$ as the pH increased from 2 to 5 [69], which indicated that the pH dependent sites are responsible for adsorption of Cu(II).

Medpeli et al. studied adsorption of As(V) as HAsO_4^{2-} oxyanions onto MK-based GP. The prepared GP was found to have surface area $75 \text{ m}^2/\text{g}$ which increases to $298 \text{ m}^2/\text{g}$ after impregnation with iron (hydr)oxide nanoparticles. The highest adsorption capacity obtained was $0.950 \text{ mg}/\text{g}$ which is very low compared to the values in Table 5. Thus, the authors concluded that fabricating media of high specific surface area and high iron hydroxide content does not necessarily give highest adsorption capacity because much of the iron hydroxide may not be accessible for sorption due to pore clogging during impregnation [70]. However, like the work of Luukkenon et al. [66], it seems that adsorption of metals that form oxyanions like arsenic onto GP is difficult.

3.3.3. Zeolite-based geopolymeric adsorbents

Adsorption of Cu(II), Pb(II), Ni(II), Zn(II) and Cd(II) onto kaolin-/zeolite-based GP was investigated. The GP was made from low cost natural kaolin and zeolite (phillipsite) using sodium

hydroxide as activator. The adsorption capacity of GP (61.31 mg/g for Pb(II)) was higher than that of natural kaolin (9.61 mg/g) and zeolite (40.19 mg/g) [71–73]. The rate constant of adsorption (k_2) of GP samples was found to be less than that of natural kaolin due to the kinetic limitations imposed by formation GP network [73]. Furthermore, Andrejkovicova et al. investigated adsorption of Pb(II), Zn(II), Cu(II), Cd(II) and Cr(III) onto GP made from MK {0.10, 54.39, 39.36}, zeolite-clinoptilolite {3.38, 70.61, 12.06} and sodium hydroxide and silicate as activators. The adsorption data revealed the following order of adsorption capacity Q_m [74]

	Pb(II)>	Cd(II)>	Cu(II)>	Zn(II)>	Cr(III)
Q_m (mg/g)	202.72	53.99	35.71	30.79	18.02

3.3.4. Adsorption of organic pollutants on geopolymeric adsorbents

Few works were reported for adsorption of organic pollutants on GP. Li et al. studied adsorption of methylene blue and crystal violet on FA {1.6, 55.0, 29.3}-based GP using sodium hydroxide as activator. The adsorption capacity (Q_m) was 32.0 and 40.8 mg/g, respectively, the affinity constant (K_L) was 105 and 4.53 L/mg, respectively, and the rate constant (k_2) was 3.76×10^{-3} and 2.29×10^{-5} g/mg min, respectively. The adsorption capacities on GP were much higher than that on unreacted FA, while the rate constants of GP were much lower than those of unreacted GP [75]. Less adsorption capacity was obtained in the case of zeolite-/kaolin-based GP which was 26 mg/g [72]. However, the effect of alkali activator on methylene blue and crystal violet should be investigated since it has been reported that these dyes are hydrolyzed in the highly basic medium [76].

3.4. Cost

Solidification technologies are attracting great interest from mining and energy industries to solve waste disposal problems. According to many authors, green chemistry geopolymerization can be applied to a variety of waste sources at low cost and low energy demand and environmental impact yielding added value products [36, 77]. However, this claim must not be taken for granted and should be analyzed in this section.

The annual production of coal FA waste was estimated to be about 500 million t from which 16% is used. The disposal of the unused FA has become a series of environmental problem [78]. Although considerable research has been published on FA-based GP technology, application of this technology is not yet widespread [4]. China and Australia have less restricted regulation about the use of alternative concrete than Europe in this regard [79]. Currently, there is a commercial GP concrete producer in Australia, namely The Zeobond Group, founded by Prof. van Deventer. One of their products is E-Crete™ made from FA (the by-product of burning coal at power stations) and BFS (the by-product of steel manufacturing). E-Crete™ is now used in footpaths, driveways, house-slabs, in-situ pours, etc. Its performance is superior to OPC in chemical, salt and fire resistance [80]. Furthermore, the CO₂ emission due to production of GPs is generally reported to be 60–90% less than OPC [4, 79].

The most critical reagent in the cost of GP preparation is the alkali activator. However, the amount of activator is usually kept minimal in the FA-GP preparation (less than 10% of the total mix design). For the above reviewed works, the cost of GP adsorbent was calculated from their mix design used in synthesis of GP adsorbent (Section 3.3). The calculated costs of MK-based GP adsorbents prepared in Refs. [64, 66, 67] are US \$218/t, 205/t and 190/t, respectively. The cost reduced to US \$141/t in the case FA-based GP adsorbents [59]. Thus, GP adsorbents have much lower cost than granular activated carbon and peanut hulls used in water purification which is about US \$2000/t, but comparable to natural zeolite (US \$120/t) and coconut shell charcoal (US \$250/t) [81]. The unreacted NaOH remained after geopolymerization reaction (or Na_2CO_3 due to absorption of CO_2 from atmosphere) may be useful because it can be utilized in precipitation of high concentrations of heavy metals in water treatment.

The cost of GP prepared from industrial waste for the purpose of solidification of heavy metal pollutants already present in the waste can also be calculated from the total mix design compositions reported in the above reviewed works (intra-solidification, Section 3.1). The obtained values obtained assuming negligible cost for waste transportation are US \$122/t GP in the case of coal FA [19], US \$91/t GP in the case of carbon steel arc furnace dust [8], US \$79–194/t in the case of municipal solid waste incineration fly ash [13, 28–30], US \$176–192/t GP in the case of chromite ore processing residue [25, 26] and US \$200/t GP in the case medical waste incineration fly ash [7]. However, the cost ranges from US \$400 to 4000/t waste, because the % waste in the GP is low (6–30%). Thus, it may not be wise to use the prepared GP in landfill and so it will worthy to use the prepared GP for construction and insulation purposes [82].

4. Conclusions

1. The present review differentiates between three lines of research that deals with application of GP in treatment of pollutants: intra-solidification, inter-solidification and adsorption.
2. Adsorption line of research has the most consistent results. Fly ash and metakaolin-based GP adsorbents, which have much lower cost than activated carbon, seems to be very effective adsorbents for heavy metal ions like Pb(II), Cd(II), Cu(II) and Zn(II). However, they are poor adsorbents for heavy metals forming oxyanions like As(III) and Sb(III). There are strong evidences that geopolymerization reaction generates new adsorption sites for heavy metals. The adsorption performance of geopolymers is similar or better than zeolites and to some extent independent on the nature of raw material and preparation conditions of GP. Note that GP has more acid resistance than zeolites. The observations that adsorption is pH dependent and ionic strength independent and the irreversibility of adsorption process all support specific rather than electrostatic interaction between heavy metal and GP sites. Strangely, increasing the porosity of GP does not lead to improvement of its adsorption capacity.
3. Intra-solidification of waste: Despite the high mechanical strength of the produced GP-containing waste, geopolymerization reduces the leaching of heavy metals from GP matrix. The concentrations of heavy metals leached are lower than the allowed limit and the % leaching is low. A number of studies reflect the positive effect Ca on immobilization

of heavy metals present in waste in GP matrix. Pb, Cu Zn are the best immobilized, while elements forming oxyanions like Sb, Mo, V and Cr are the least immobilized in GP. There were no conclusive results on the effect of Si/Al ratio, alkali activator dose and the nature of leaching solution on the efficiency of immobilization.

4. Inter-solidification presents a greater challenge because highly soluble heavy metals salts are usually incorporated in the GP preparation. On the other hand, in intra-solidification, heavy metals may exist in less soluble oxide form. In many works reviewed, the concentrations of heavy metals in the leaching solution are higher than the allowed limit and the % leaching is high. The counter ions associated with the heavy metal in inter-solidification such as sulfate and chlorides present greater difficulties in immobilization than nitrates. Fly ash-based GP is an efficient host for heavy metals nitrates if sodium silicates are used in addition to sodium hydroxide activator. Pb(II), Cu(II), Cd(II) and Cr(III) salts are much more effectively immobilized than heavy metals salts forming oxyanions like As(IV) and Cr(VI). However, addition of reducing agents makes immobilization of Cr (VI) very effective because of reduction of oxyanion Cr(VI) to cationic Cr(III). GP has a limited capacity up to 0.5% (w/w) in the GP mix design. The leaching of heavy metals is fast and reaches steady state after 4 h.
5. Two criteria must be applied to evaluate the efficiency of immobilization. The first is the concentration of heavy metal in the leaching solution, which should be less than the allowed limit. The second is that the % leaching should be small. These two criteria may give contradicted conclusions in some cases about the efficiency of immobilization.
6. The target of adsorption should be water contaminated with relatively low heavy metals concentrations (up to 100 mg/L). On the other hand, the target of solidification is water contaminated with high heavy metals concentrations up to 10,000 mg/L (assuming 0.5% w/w heavy metal in mix design of GP and 50% water content). Adsorption techniques have some advantages over solidification, for example, the purified water is useful. However, adsorption has disadvantages such as the adsorbent loaded with heavy metals could not be safely disposed by landfill. On the other hand solidification has many advantages such as utilization of water polluted with heavy metals in making construction materials.
7. Both solidification and adsorption processes can be used in an integrative manner. After removal of pollutants by adsorption on zeolite, kaolin or any aluminosilicate material, the adsorbent material can then be introduced into solidification (geopolymerization) process for final disposal in the environment or for construction purposes.
8. The relatively high cost and the high mechanical strength of the solidified GP products containing waste necessitates that the product should be used in outdoor applications like insulation, roads, tsunami walls, etc.

Abbreviations

GP geopolymer

MK metakaolin

FA fly ash from coal (type F, low calcium)

BFS blast furnace slag from iron manufacturing

OPC ordinary Portland cement

Values between brackets after MK, FA and BFS: {% CaO, % SiO₂, % Al₂O₃}

Author details

Bassam I. El-Eswed

Address all correspondence to: bassameswed@bau.edu.jo

Zarqa College, Al-Balqa Applied University, Zarqa, Jordan

References

- [1] Davidovits J. Geopolymers: Inorganic polymeric new materials. *Journal of Thermal Analysis*. 1991;**37**:1633-1656
- [2] Ducman V, Korat L. Characterization of geopolymer fly-ash based foams obtained with the. *Materials Characterization*. 2016;**113**:207-213. DOI: 10.1016/j.matchar.2016.01.019
- [3] Melar J, Renaudin G, Leroux F, Hardy-Dessources A, Nedelec J, Taviot-Gueho C, Petit E, Steins P, Poulesquen A, Frizon F. The porous network and its Interface inside Geopolymers as a function of alkali cation and aging. *Journal of Physical Chemistry C*. 2015;**119**(31):17619-17632. DOI: 10.1021/acs.jpcc.5b02340
- [4] Zhang Z, Provis JL, Reid A, Wang H. Geopolymer foam concrete: An emerging material for sustainable construction. *Construction and Building Materials*. 2014;**56**:113-127. DOI: 10.1016/j.conbuildmat.2014.01.081
- [5] Zhang F, Zhang L, Liu M, Mu C, Liang YN, Hu X. Role of alkali cation in compressive strength of metakaolin based geopolymers. *Ceramics International*. 2017;**43**(4):3811-3817. DOI: 10.1016/j.ceramint.2016.12.034
- [6] Zhang L, Zhang F, Liu M, Hu X. Novel sustainable geopolymer based syntactic foams: An eco-friendly alternative to polymer based syntactic foams. *Chemical Engineering Journal*. 2017;**313**:74-82. DOI: 10.1016/j.cej.2016.12.046
- [7] Tzanakos K, Mimilidou A, Anastasiadou K, Stratakis A, Gidarakos E. Solidification/stabilization of ash from medical waste incineration into geopolymers. *Waste Management*. 2014;**34**(10):1823-1828. DOI: 10.1016/j.wasman.2014.03.021
- [8] Fernández Pereira C, Luna Y, Querol X, Antenucci D, Vale J. Waste stabilization/solidification of an electric arc furnace dust using fly ash-based geopolymers. *Fuel*. 2009;**88**(7): 1185-1193. DOI: 10.1016/j.fuel.2008.01.021

- [9] Duxson P, Fernandez-Jimenez A, Provis JL, Lukey GC, Palomo A, Van Deventer JSJ. Geopolymer technology: The current state of the art. *Journal of Materials Science*. 2007;**42**:2917-2933
- [10] Duxson P, Mallicoate SW, Lukey GC, Kriven WM, Van Deventer JSJ. The effect of alkali and Si/al ratio on the development of mechanical properties of metakaolin-based geopolymers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2007;**292**:8-20. DOI: 10.1016/j.colsurfa.2006.05.044
- [11] Vance ER, Perera DS. Geopolymers for nuclear waste immobilization. In: Provis JL, Van Deventer JSJ, editors. *Geopolymers: Structure, Processing, Properties and Industrial Applications*. Oxford: CRC Press and Woodhead Publishing Limited; 2009. pp. 401-420
- [12] El-Eswed BI, Aldagag OM, Khalili FI. Efficiency and mechanism of stabilization/solidification of Pb(II), Cd(II), Cu(II), Th(IV) and U(VI) in metakaolin based geopolymers. *Applied Clay Science*. 2017;**140**:148-156. DOI: 10.1016/j.clay.2017.02.003
- [13] Luna Galiano Y, Fernández Pereira C, Vale J. Stabilization/solidification of a municipal solid waste incineration residue using fly ash-based geopolymers. *Journal of Hazardous Materials*. 2011;**185**(1):373-381. DOI: 10.1016/j.jhazmat.2010.08.127
- [14] Ogundiran MB, Nugteren HW, Witkamp GJ. Immobilisation of lead smelting slag within spent aluminate—Fly ash based geopolymers. *Journal of Hazardous Materials*. 2013;**248–249**(15):29-36. DOI: 10.1016/j.jhazmat.2012.12.040
- [15] Zhang J, Provis JL, Feng D, Van Deventer JSJ. Geopolymers for immobilization of Cr^{6+} , Cd^{2+} , and Pb^{2+} . *Journal of Hazardous Materials*. 2008;**157**:587-598. DOI: <https://doi.org/10.1016/j.jhazmat.2008.01.053>
- [16] Foo KY, Hameed BH. Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*. 2010;**156**(1):2-10. DOI: <https://doi.org/10.1016/j.cej.2009.09.013>
- [17] Tan KL, Hameed BH. Insight into the adsorption kinetics models for the removal of contaminants from aqueous solutions. *Journal of the Taiwan Institute of Chemical Engineers*. 2017;**74**:25-48. DOI: <https://doi.org/10.1016/j.jtice.2017.01.024>
- [18] McLellan BC, Williams RP, Lay J, van Riessen A, Corder GD. Costs and carbon emissions for geopolymer pastes in comparison to ordinary portland cement. *Journal of Cleaner Production*. 2011;**19**:1080-1090. DOI: <https://doi.org/10.1016/j.jclepro.2011.02.010>
- [19] Bankowski P, Zou L, Hodges R. Reduction of metal leaching in brown coal fly ash using geopolymers. *Journal of Hazardous Materials*. 2004;**114**:59-67. DOI: <https://doi.org/10.1016/j.jhazmat.2004.06.034>
- [20] Arioz E, Arioz O, Kockar M, Leaching O. Of F-type fly ash based geopolymers. *Procedia Engineering*. 2012;**42**:1114-1120. DOI: <https://doi.org/10.1016/j.proeng.2012.07.503>
- [21] Luna Y, Querol X, Antenucci D, Jdid E, Pereira F, Vale J. Immobilization of a metallurgical waste using fly ash-based geopolymers. In: *World of Coal Ash (WOCA)*; May 7–10; Kentucky, USA. 2007

- [22] Perná I, Hanzlíček T. The solidification of aluminum production waste in geopolymer matrix. *Journal of Cleaner Production*. 2014;**84**:657-662. DOI: <https://doi.org/10.1016/j.jclepro.2014.04.043>
- [23] Salihoglu G. Immobilization of antimony waste slag by applying geopolymerization and stabilization/solidification technologies. *Journal of the Air & Waste Management Association* 2014;**64**(11):1288-1298. DOI: <http://dx.doi.org/10.1080/10962247.2014.943352>
- [24] Rao F, Liu Q. Geopolymerization and its potential application in mine. *Mineral Processing and Extractive Metallurgy Review*. 2015;**36**:399-409. DOI: 10.1080/08827508.2015.1055625
- [25] Sun T, Chen J, Lei X, Zhou C. Detoxification and immobilization of chromite ore processing residue with metakaolin-based geopolymer. *Journal of Environmental Chemical Engineering*. 2014;**2**(1):304-309. DOI: <https://doi.org/10.1016/j.jece.2013.12.022>
- [26] Huang X, Huang T, Li S, Muhammad F, Xu G, Zhao Z, Yu L, Yan Y, Li D, Jiao B. Immobilization of chromite ore processing residue with alkali-activated blast furnace slag-based geopolymer. *Ceramics International*. 2016;**42**(8):9538-9549. DOI: <https://doi.org/10.1016/j.ceramint.2016.03.033>
- [27] Antunes Boca Santa RA, Soares C, Gracher Riella H. Geopolymers with a high percentage of bottom ash for solidification/immobilization of different toxic metals. *Journal of Hazardous Materials*. 2016;**218**(15):145-153. DOI: <https://doi.org/10.1016/j.jhazmat.2016.06.059>
- [28] Lancellotti I, Kamseu E, Michelazzi M, Barbieri L, Corradi A, Leonelli C. Chemical stability of geopolymers containing municipal solid waste incinerator fly ash. *Waste Management*. 2010;**30**(4):673-679. DOI: <https://doi.org/10.1016/j.wasman.2009.09.032>
- [29] Zheng L, Wang W, Shi Y. 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*. 2010;**79**(6):665-671. DOI: <https://doi.org/10.1016/j.chemosphere.2010.02.018>
- [30] Guo X, Hu W, Shi H. Microstructure and self-solidification/stabilization (S/S) of heavy metals of nano-modified CFA-MSWIFA composite geopolymers. *Construction and Building Materials*. 2014;**56**(15):81-86. DOI: <https://doi.org/10.1016/j.conbuildmat.2014.01.062>
- [31] Xu Z, Jiang Z, Wu D, Peng X, Xu Y, Li N, Qi Y, Li P. Immobilization of strontium-loaded zeolite A by metakaolin based-geopolymer. *Ceramics International*. 2017;**43**(5):4434-4439. DOI: <https://doi.org/10.1016/j.ceramint.2016.12.092>
- [32] Lee WKW, van Deventer JSJ. The effects of inorganic salt contamination on the strength and durability of geopolymers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2002;**211**:115-126. DOI: [https://doi.org/10.1016/S0927-7757\(02\)00239-X](https://doi.org/10.1016/S0927-7757(02)00239-X)
- [33] Li Q, Sun Z, Tao D, Xu Y, Li P, Cui H, Zhai J. Immobilization of simulated radionuclide ¹³³Cs+ by fly ash-based geopolymer. *Journal of Hazardous Materials*. 2013;**262**:325-331. DOI: <https://doi.org/10.1016/j.jhazmat.2013.08.049>

- [34] Van Jaarsveld JGS, Van Deventer JSJ, Schwartzman A. The potential use of geopolymeric materials to immobilise toxic metals: Part II. Material and leaching characteristics. *Minerals Engineering*. 1999;**12**(1):75-91. DOI: [https://doi.org/10.1016/S0892-6875\(98\)00121-6](https://doi.org/10.1016/S0892-6875(98)00121-6)
- [35] Van Jaarsveld JGS, Van Deventer JSJ. The effect of metal contaminants on the formation and properties of waste-based geopolymers. *Cement and Concrete Research*. 1999;**29**: 1189-1200. DOI: [https://doi.org/10.1016/S0008-8846\(99\)00032-0](https://doi.org/10.1016/S0008-8846(99)00032-0)
- [36] Phair JW, Van Deventer JSJ, Smith JD. Effect of Al source and alkali activation on Pb and Cu immobilisation in fly-ash based "geopolymers". *Applied Geochemistry*. 2004;**19**(3): 423-434. DOI: [https://doi.org/10.1016/S0883-2927\(03\)00151-3](https://doi.org/10.1016/S0883-2927(03)00151-3)
- [37] Van Jaarsveld JGS, Van Deventer JSJ. A comparative study of kaolinite versus metakaolinite in fly ash based geopolymers containing immobilized metals. *Chemical Engineering Communications*. 2004;**191**:531-549. DOI: <http://dx.doi.org/10.1080/00986440490277974>
- [38] Xu JZ, Zhou YL, Chang Q, Qu HQ. Study on the factors of affecting the immobilization of heavy metals in fly ash-based geopolymers. *Materials Letters*. 2006;**60**(6):820-822. DOI: <https://doi.org/10.1016/j.matlet.2005.10.019>
- [39] Guo X, Shi H. Self-solidification/stabilization of heavy metal wastes of class C fly ash-based geopolymers. *Journal of Materials in Civil Engineering*. 2013;**25**(4):491-496. DOI: [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000595](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000595)
- [40] Nikolić V, Komljenović M, Marjanović N, Baščarević Z, Petrović R. Lead immobilization by geopolymers based on mechanically activated fly ash. *Ceramics International*. 2014;**40** (6):8479-8488. DOI: <https://doi.org/10.1016/j.ceramint.2014.01.059>
- [41] Guo B, Pan D, Liu B, Volinsky AA, Fincan M, Du J, Zhang S. Immobilization mechanism of Pb in fly ash-based geopolymer. *Construction and Building Materials*. 2017;**134**:123-130. DOI: <https://doi.org/10.1016/j.conbuildmat.2016.12.139>
- [42] Yunsheng Z, Wei S, Qianli C, Lin C. Synthesis and heavy metal immobilization behaviors of slag based geopolymer. *Journal of Hazardous Materials*. 2007;**143**:206-213. DOI: <https://doi.org/10.1016/j.jhazmat.2006.09.033>
- [43] Perera DS, Aly Z, Vance ER, Mizumo M. Immobilization of Pb in a geopolymer matrix. *Journal of the American Ceramic Society*. 2005;**88**(9):2586-2588. DOI: 10.1111/j.1551-2916.2005.00438.x
- [44] Komnitsas K, Zaharaki D, Bartzas G. Effect of sulphate and nitrate anions on heavy metal immobilisation in ferronickel slag geopolymers. *Applied Clay Science*. 2013;**73**:103-109. DOI: <https://doi.org/10.1016/j.clay.2012.09.018>
- [45] El-Eswed BI, Yousef RI, Alshaaer M, Hamadneh I, Al-Gharabli SI, Khalili F. Stabilization/solidification of heavy metals in kaolin/zeolite based geopolymers. *International Journal of Mineral Processing*. 2015;**137**:34-42. DOI: <https://doi.org/10.1016/j.minpro.2015.03.002>

- [46] Nikolić V, Komljenović M, Džunuzović N, Ivanović T, Miladinović Z. Immobilization of hexavalent chromium by fly ash-based geopolymers. *Composites Part B: Engineering*. 2017;**112**:213-223. DOI: <https://doi.org/10.1016/j.compositesb.2016.12.024>
- [47] Chen J, Wang Y, Zhou S, Lei X. Reduction/immobilization processes of hexavalent chromium using metakaolin-based geopolymer. *Journal of Environmental Chemical Engineering*. 2017;**5**(1):373-380. DOI: <https://doi.org/10.1016/j.jece.2016.11.028>
- [48] Chena J, Wang Y, Wang H, Zhou S, Wu H. Detoxification/immobilization of hexavalent chromium using metakaolin-based geopolymer coupled with ferrous chloride. *Journal of Environmental Chemical Engineering*. 2016;**4**(2):2084-2089. DOI: <https://doi.org/10.1016/j.jece.2016.03.038>
- [49] Fernandez-Jimenez A, Palomo A. Fixing arsenic in alkali-activated cementitious matrices. *Journal of the American Ceramic Society*. 2005;**88**(5):1122-1126. DOI: 10.1111/j.1551-2916.2005.00224.x
- [50] Gokhale C. The immobilization of organic waste by geopolymerization [Thesis]. Stellenbosch: University of Stellenbosch; 2001. 189 p. Available from: <http://hdl.handle.net/10019.1/52533>
- [51] Tavor D, Wolfson A, Shamaev A, Shvarzman A. Recycling of industrial wastewater by its immobilization in geopolymer cement. *Industrial and Engineering Chemistry Research*. 2007;**46**:6801-6805. DOI: 10.1021/ie0616996
- [52] Cantarel V, Nouaille F, Rooses A, Lambertin D, Poulesquen A, Frizon F. Solidification/stabilisation of liquid oil waste in metakaolin-based geopolymer. *Journal of Nuclear Materials*. 2015;**464**:16-19. DOI: <https://doi.org/10.1016/j.jnucmat.2015.04.036>
- [53] Wang S, Li L, Zhu ZH. Solid-state conversion of fly ash to effective adsorbents for Cu removal from wastewater. *Journal of Hazardous Materials*. 2007;**139**(2):254-259. DOI: <https://doi.org/10.1016/j.jhazmat.2006.06.018>
- [54] Al-Zboon K, Al-Harashsheh MS, Bani Hani F. Fly ash-based geopolymer for Pb removal from aqueous solution. *Journal of Hazardous Materials*. 2011;**188**:414-421. DOI: <https://doi.org/10.1016/j.jhazmat.2011.01.133>
- [55] Al-Harashsheh MS, Al Zboon K, Al-Makhadmeh L, Hararah M, Mahasneh M. Fly ash based geopolymer for heavy metal removal: A case study on copper removal. *Journal of Environmental Chemical Engineering*. 2015;**3**(3):1669-1677. DOI: <https://doi.org/10.1016/j.jece.2015.06.005>
- [56] Mužek MN, Svilović S, Zelić J. Fly ash-based geopolymeric adsorbent for copper ion. *Desalination and Water Treatment*. 2013;**52**:2519-2526. DOI: 10.1080/19443994.2013.792015
- [57] Mužek MN, Svilović S, Zelić J. Kinetic studies of cobalt ion removal from aqueous solutions using fly ash-based geopolymer and zeolite NaX as sorbents. *Separation Science and Technology*. 2016;**51**(18):2868-2875. DOI: <http://dx.doi.org/10.1080/01496395.2016.1228675>

- [58] Muzek MN, Svilovic S, Ugrina M, Zelic J. Removal of copper and cobalt ions by fly ash-based geopolymer from. *Desalination and Water Treatment*. 2016;**57**:10689-10699. DOI: 10.1080/19443994.2015.1040077
- [59] Liu Y, Yan C, Zhang Z, Wang H, Zhou S, Zhou W. A comparative study on fly ash, geopolymer and faujasite block for Pb removal from aqueous solution. *Fuel*. 2016;**185**: 181-189. DOI: <https://doi.org/10.1016/j.fuel.2016.07.116>
- [60] Novais RM, Buruberry LH, Seabra MP, Labrincha JA. Novel porous fly-ash containing geopolymer monoliths for lead adsorption from wastewaters. *Journal of Hazardous Materials*. 2016;**318**:631-640. DOI: <https://doi.org/10.1016/j.jhazmat.2016.07.059>
- [61] Lee NK, Khalid HR, Lee HK. Adsorption characteristics of cesium onto mesoporous geopolymers containing nano-crystalline zeolites. *Microporous and Mesoporous Materials*. 2017;**242**:238-244. DOI: <https://doi.org/10.1016/j.micromeso.2017.01.030>
- [62] Duan P, Yan C, Zhou W, Ren D. Development of fly ash and iron ore tailing based porous geopolymer for removal of Cu(II) from wastewater. *Ceramics International*. 2016;**42**(12): 13507-13518. DOI: <https://doi.org/10.1016/j.ceramint.2016.05.143>
- [63] Gräfe M, Singh B, Balasubramanian M. Surface speciation of Cd(II) and Pb(II) on kaolin-ite by XAFS spectroscopy. *Journal of Colloid and Interface Science*. 2007;**315**(1):21-32. DOI: <https://doi.org/10.1016/j.jcis.2007.05.022>
- [64] Cheng TW, Lee ML, Ko MS, Ueng TH, Yang SF. The heavy metal adsorption characteristics on metakaolin-based geopolymer. *Applied Clay Science*. 2012;**56**:90-96. DOI: <https://doi.org/10.1016/j.clay.2011.11.027>
- [65] López FJ, Sugita S, Tagaya M, Kobayashi T. Metakaolin-based geopolymers for targeted adsorbents to heavy metal ion separation. *Journal of Materials Science and Chemical Engineering*. 2014;**2**:16-27. DOI: <http://dx.doi.org/10.4236/msce.2014.27002>
- [66] Luukkonen T, Runtti H, Niskanen M, Tolonen E, Sarkkinen M, Kemppainen K, Ramo J, Lassi U. Simultaneous removal of Ni(II), As(III), and Sb(III) from spiked mine effluent with metakaolin and blast-furnace-slag geopolymers. *Journal of Environmental Management*. 2016;**166**:579-588. DOI: <https://doi.org/10.1016/j.jenvman.2015.11.007>
- [67] Kara İ, Yilmazer D, Akar STI. Metakaolin based geopolymer as an effective adsorbent for adsorption of zinc(II) and nickel(II) ions from aqueous solutions. *Applied Clay Science*. 2017;**139**:54-63. DOI: <https://doi.org/10.1016/j.clay.2017.01.008>
- [68] Tang Q, Ge Y, Wang K, He Y, Cui X. Preparation and characterization of porous metakaolin-based inorganic polymer spheres as an adsorbent. *Materials and Design*. 2015;**88**:1244-1249. DOI: <https://doi.org/10.1016/j.matdes.2015.09.126>
- [69] Ge Y, Cui X, Kong Y, Li Z, He Y, Zhou Q. Porous geopolymeric spheres for removal of Cu (II) from aqueous solution: Synthesis and evaluation. *Journal of Hazardous Materials*. 2015;**283**:244-251. DOI: <https://doi.org/10.1016/j.jhazmat.2014.09.038>

- [70] Medpelli D, Sandoval R, Sherrill L, Hristovski K, Seo D. Iron oxide-modified nanoporous geopolymers for arsenic removal from ground water. *Resource-Efficient Technologies*. 2015;1(1):19-27. DOI: <https://doi.org/10.1016/j.reffit.2015.06.007>
- [71] Yousef RI, El-Eswed B, Alshaaer M, Khalili F, Khoury H. The influence of using Jordanian natural zeolite on the adsorption, physical, and mechanical properties of geopolymers products. *Journal of Hazardous Materials*. 2009;165:379-387. DOI: <https://doi.org/10.1016/j.jhazmat.2008.10.004>
- [72] El-Eswed B, Yousef RI, Alshaaer M, Khalili F, Khoury H. Alkali solid-state conversion of kaolin and zeolite to effective adsorbents for removal of lead from aqueous solution. *Desalination and Water Treatment*. 2009;8:124-130. DOI: <http://dx.doi.org/10.5004/dwt.2009.672>
- [73] El-Eswed B, Alshaaer M, Yousef RI, Hamadneh I, Khalili F. Adsorption of Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) onto kaolin/zeolite based-geopolymers. *Advances in Materials Physics and Chemistry*. 2012;2:119-125. DOI: 10.4236/ampc.2012.24B032
- [74] Andrejkovič S, Sudagar A, Rocha J, Patinha C, Hajjaji W, Ferreira da Silva E, Velosa A, Rocha F. The effect of natural zeolite on microstructure, mechanical and heavy metals adsorption properties of metakaolin based geopolymers. *Applied Clay Science*. 2016;126:141-152. DOI: <https://doi.org/10.1016/j.clay.2016.03.009>
- [75] Li L, Wang S, Zhu Z. Geopolymeric adsorbents from fly ash for dye removal from aqueous solution. *Journal of Colloid and Interface Science*. 2006;30(1):52-59. DOI: <https://doi.org/10.1016/j.jcis.2006.03.062>
- [76] Mills A, Hazafy D, Parkinson J, Tuttle T, Hutchings MG. Effect of alkali on methylene blue (C.I. basic blue 9) and other thiazine dyes. *Dyes and Pigments*. 2011;88(2):149-155. DOI: <https://doi.org/10.1016/j.dyepig.2010.05.015>
- [77] Benito P, Leonelli C, Medri V, Vaccari A. Geopolymers: A new and smart way for a sustainable development. *Applied Clay Science*. 2013;73:1. DOI: <https://doi.org/10.1016/j.clay.2013.03.008>
- [78] De Weerd K. Geopolymers—State of the Art. Oslo: SINTEF Building and Infrastructure, Consortium Concrete Innovation Centre; 2011. 39 pp
- [79] Griffin PW, Hammond GP, Norman JB. Industrial energy use and carbon emissions reduction: A UK perspective. *WIREs Energy Environment*. 2016;5:684-714. DOI: 10.1002/wene.212
- [80] The Zeobond Group. E-Crete [Internet]. 2012. Available from: <http://www.zeobond.com/products-e-crete.html>
- [81] Kurniawan TA, Chan GYS, Lo W, Babel S. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *The Science of the Total Environment*. 2006;366:409-426. DOI: <https://doi.org/10.1016/j.scitotenv.2005.10.001>
- [82] U.S. Environmental Protection Agency's Technology Innovation Office. Solidification/Stabilization Use at Superfund Sites [Internet]. 2000. Available from: <https://www.epa.gov/remedytech>