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# Effect of sulphate and nitrate anions on heavy metal immobilisation in ferronickel slag geopolymers

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#### ABSTRACT

Industrial wastes need to be valorised and new techniques need to be developed for the production of secondary materials or immobilisation of hazardous elements in order to improve sustainability of the respective industrial sector. In the present experimental study the effect of monovalent and divalent anions, such as sulphate and nitrate, on heavy metal immobilisation in ferronickel slag geopolymers was investigated. Low calcium electric arc ferronickel slag was geopolymerised using KOH and Na<sub>2</sub>SiO<sub>3</sub> as activators, in the presence of limited quantities of sulphate and nitrate salts of Pb, Cu, Cr or Ni. Gel properties, final strength of the specimens produced and immobilisation of heavy metals were determined, in order to explore the potential of geopolymerisation in developing a hazardous waste encapsulation matrix. In addition, the Toxicity Characteristics Leaching Procedure was used to assess the potential toxicity of the produced geopolymers. The experimental results indicate that even limited quantities of sulphates and nitrates in the starting mixture affect adversely geopolymerisation of ferronickel slag. XRD (X-ray diffraction), SEM (scanning electron microscopy) and FTIR (Fourier transform infrared spectroscopy) studies were carried out to identify new phases, reactions taking place and thus elucidate the main mechanisms involved.

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#### 1. Introduction

It is known that geopolymers are amorphous to semi-crystalline materials that are formed by transformation of alumino-silicates at low temperature in a very short time. Their production involves reactions between aluminosilicate powder and concentrated caustic alkali metal silicate solution while the geopolymeric network consists of alternately linked SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra (Davidovits, 1998; Duxson et al., 2007).

During the last 20 years, the potential of various industrial wastes such as fly ash and slag has been investigated for the production of geopolymers. Due to the complex nature of these wastes, the exact mechanisms involving mainly dissolution, transportation and polycondensation, need to be further elucidated (Komnitsas and Zaharaki, 2007; Lancellotti et al., 2010; Oh et al., 2010; Sakulich et al., 2009; Temuujin et al., 2009). Several analytical techniques such as SEM, FTIR, XRD and TG have been used to shed light in geopolymerisation mechanisms (Komnitsas et al., 2009; Simonsen et al., 2009).

Geopolymers may exhibit very good physical and chemical properties such as high compressive strength, low shrinkage, low permeability  $(10^{-9} \text{ cm/s})$ , acid resistance and thermal stability up to 1000 °C (Bakharev et al., 2003; Kamseu et al., 2012). Potential products and applications include among others concrete, building components and temperature stable resins, encapsulation of toxic wastes, surface capping and stabilisation of tailing dams (Habert et al., 2011; Kamseu et al., 2010; Lampris et al., 2009; McLellan et al., 2011). The efficiency of the geopolymer matrix for the immobilisation of hazardous heavy metal depends primarily on the initial concentration of the alkali activator and the microstructure of the hardened paste (Fernández-Pereira et al., 2009; Hanzlicek et al., 2006).

Fly ash was the first raw material studied for the production of geopolymers and simultaneous immobilisation of hazardous elements. Results have shown that metals such as Co, Cd, Ni, Zn, Pd, As, Ra and U can be efficiently stabilised in the three-dimensional geopolymeric matrix. In most cases though heavy metals are not incorporated in the crystalline matrix but are encapsulated in the amorphous phase formed, the volume of which depends mainly on the properties of the raw materials and the operating conditions (Phair et al., 2004; Provis et al., 2008; Van Jaarsveld et al., 1998, 1999; Xu et al., 2006; Zhang et al., 2008; Zheng et al., 2011).

So far limited studies have attempted to elucidate the effect of anions on geopolymer properties (Criado et al., 2010; Desbats-Le Chequer and Frizon, 2011; Lee and Van Deventer, 2002a, 2002b). These very interesting studies have focused on the effect of anions either on fly ash or metakaolin based geopolymers. The present study is the first one that attempts to investigate the effect of monovalent and divalent anions, such as sulphate and nitrate, on the

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production of ferronickel slag geopolymers and the subsequent heavy metal immobilisation.

### Table 2 Experimental configuration.

#### 2. Materials and methodology

The raw material used in the present experimental study is electric arc slag produced at the LARCO S.A. ferronickel plant in Greece. Olivines (fayalite and forsterite), anorthite, quartz, tridymite, cristobalite, magnetite and chromite are the main mineralogical phases present, while its amorphous content exceeds 50%. Table 1 presents the chemical composition of slag in the form of oxides and trace elements, using an X-ray fluorescence energy dispersive spectrometer (XRF–EDS) Bruker-AXS S2Range type.

The particle size of the as received brittle slag, which is cooled at the plant with the use of seawater, varies between 0.075 mm and 4 mm. Slag was dried and crushed ( $-120 \mu$ m and  $d_{50}$ :  $-12 \mu$ m) using a FRITSCH pulveriser (Germany) to increase surface area and accelerate geopolymeric reactions.

For the production of geopolymers an activating solution was prepared and then slag was added slowly under continuous mechanical mixing, so that a reactive and homogeneous paste was obtained. The activating solution consists of potassium hydroxide anhydrous pellets (ACS-ISO for analysis) dissolved in deionised water and mixed with sodium silicate solution (Merck). An indicative composition of the starting mixture is (% w/w): slag 82%, H<sub>2</sub>O 6%, KOH 3% (6.7 M) and Na<sub>2</sub>SiO<sub>3</sub> 9%. A higher KOH molarity (11.2 M) was also used in additional experiments.

Monovalent and divalent anions, namely nitrate or sulphate, were added in the initial mixture as metal (Pb, Cu, Cr and Ni) salts (Alfa Aesar GmbH, Germany). The experimental configuration is shown in Table 2. The code numbers indicate the addition percentage; when for example Pb was added as  $PbSO_4$  the code numbers used are PBS05, PBS1, PBS2, PBS25 and PBS3, for each addition percentage (0.5, 1, 2, 2,5 and 3% w/w of slag respectively).

The resulting paste was cast in plastic cubic moulds (edge 5 cm) which were vibrated for 5 min to remove trapped air and eliminate the development of voids. Specimens were pre-cured at room temperature for 2 days to initiate geopolymeric reactions and then heated in a laboratory oven (MMM GmbH, Germany) at 80 °C for 48 h. After de-moulding aging took place for 7 days at room temperature to enhance the development of structural bonds. The compressive strength of each specimen was measured using an MTS 1600 load frame (USA). Control specimens, with the use of only ferronickel slag and alkali activators, were also prepared. All tests were carried out in duplicate; if the difference in the final compressive strength exceeded 10% a third test was carried out.

TCLP tests were performed, using pulverised specimens, to determine the concentration of heavy metals in the extract and subsequently to assess the potential toxicity of the produced geopolymers (USEPA, 1990).

Table 1			
Chemical analysis	(% w/w	) of ferronickel	slag.

	% w/w
Fe <sub>2</sub> O <sub>3(tot)</sub>	43.83
SiO <sub>2</sub>	32.74
Al <sub>2</sub> O <sub>3</sub>	8.32
CaO	3.73
Cr <sub>2</sub> O <sub>3</sub>	3.07
MgO	2.76
$Mn_3O_4$	0.44
S	0.18
С	0.11
Ni	0.1
Со	0.02
Total	95.27

Code no	Metal salt added (% w/w slag)
PBS05-PBS3	0.5–3% w/w Pb as PbSO <sub>4</sub>
PBN05-PBN3	0.5–3% w/w Pb as Pb(NO <sub>3</sub> ) <sub>2</sub>
CUS05-CUS3	0.5–3% w/w Cu as CuSO <sub>4</sub> ·5H <sub>2</sub> O
CUN05-CUN3	0.5–3% w/w Cu as Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O
CRS05-CRS3	$0.5-3\%$ w/w Cr as $Cr_2(SO_4)_3 \cdot xH_2O$
CRN05-CRN3	$0.5-3\%$ w/w Cr as $Cr(NO_3)_3 \cdot 9H_2O$
NIS05-NIS3	0.5-3% w/w Ni as NiSO <sub>4</sub> · 6H <sub>2</sub> O
NIN05-NIN3	0.5-3% w/w Ni as Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O
Control	Only ferronickel slag is used/no metal salt has been added

X-ray diffraction (XRD) analysis of the geopolymers was performed using a Siemens D500 (Germany) diffractometer with a Co tube and a scanning range from 3° to 70° 20 with a step 0.03° and 4° s/step measuring time. Qualitative analysis was carried out using the Diffrac<sub>plus</sub> Software (Bruker AXS) and the PDF database.

A JEOL 6380LV (USA) scanning electron microscope equipped with an Oxford INCA energy dispersive X-ray spectrometer (EDS) was used for the SEM studies.

FTIR analysis on KBr pellets was carried out using a Perkin-Elmer 1000 Spectrometer (USA); for the production of the pellets each sample was mixed with KBr at a ratio 1:100 w/w.

#### 3. Results and discussion

#### 3.1. Effect of anions and heavy metals on compressive strength

Fig. 1 shows the evolution of geopolymer compressive strength in the presence of sulphate and nitrate anions, expressed as % w/w addition of the respective heavy metal in the initial mixture. It is mentioned that the average compressive strength of the control specimens was 52 MPa.

It is seen from this figure that the addition of sulphate ions as PbSO<sub>4</sub> (PBS, 0.5% w/w Pb) barely affects compressive strength. When the metal addition percentage increases to 3% w/w of slag the compressive strength decreases respectively by almost 70% (15 MPa). On the other hand, addition of nitrate ions as Pb(NO<sub>3</sub>)<sub>2</sub> (PBN) results in higher decrease of strength.

Addition of sulphate or nitrate ions as Cu, Ni or Cr salts results in sharp decrease of the compressive strength even when the metal addition percentage is just 1% w/w of slag. Practically no geopolymer structure is formed when higher addition percentages are used.

The first conclusions drawn from these results are the following: a) nitrate ions have a more distinct negative impact compared to sulphates on the compressive strength of the produced geopolymers and b) the type of heavy metal added may also have an impact on the resulting compressive strength. Previous studies (Lee and Van



**Fig. 1.** Evolution of geopolymer compressive strength in the presence of sulphate and nitrate anions (expressed as % w/w addition of the respective heavy metal).

Deventer, 2002b; Provis et al., 2008; Van Jaarsveld and Van Deventer, 1999) also show that the presence of  $NO_3^-$  or/and  $SO_4^{-2}$  anions, even in low quantities, prevents hardening of the gel, development of sufficient compressive strength and effective encapsulation of hazardous heavy metals in fly ash/kaolin/metakaolinite based geopolymers.

Fig. 2 shows the evolution of the compressive strength of geopolymers in relation to the percentage of consumed KOH moles by sulphate or nitrate anions. Since it is known that the reaction between KOH and sulphates or nitrates is very fast it is assumed that  $NO_3^-$  or  $SO_4^{-2}$  ions present in the initial pulp react first with KOH. This reaction, even if in practice is not completed, reduces substantially the number of KOH moles that are available to react with ferronickel slag and produce geopolymeric gel, resulting thus in substantial decrease of the compressive strength. The assumption that almost all sulphates or nitrates react first with KOH is confirmed by the shape of the curves in Fig. 2 which are quite similar to those in Fig. 1. It is important to note that the quantity of  $NO_3^-$  or  $SO_4^{-2}$  ions present in the initial mixture depends on the type of the metal salt added. For example, when Pb, Cu, Ni or Cr are added in the starting mixture as 0.5% w/w of slag, the quantity of sulphate or nitrate ions present in the pulp is 0.8 or 1, 2.5 or 3.2, 2.7 or 3.7 and 4.5 or 7.8 g, respectively.

In order to further elucidate this issue additional experiments were carried out using KOH with higher molarity, so that the anticipated losses from its reaction with sulphate or nitrate anions were partially offset. Fig. 3 shows the evolution of the compressive strength of PBS3, PBN3, CUS1 and CUN1 geopolymers in relation to the molarity of the KOH solution used.

It is deduced from this data that the molarity of KOH solution plays a very important role in geopolymerisation. When the molarity increases from 6.7 to 11.4 M a noticeable increase in the strength of all geopolymers produced is observed, varying between 65% for CUN1 and 115% for PBS3.

#### 3.2. Mineralogical studies

In XRD, SEM and FTIR studies, specimens with the highest addition percentage (3% w/w) of Pb and Cu as nitrate (PBN3/CUN3) or sulphate salt (PBS3/CUS3) were investigated, to identify new phases and elucidate the main mechanisms involved. Geopolymers in which Cu or Ni salts were added, were not studied due to the presence of these metals in slag.

#### 3.2.1. XRD studies

Despite the substantial amorphous nature of ideal geopolymers, XRD is often used to identify new phases, define the extent to which starting materials have reacted and assess the degree of amorphicity of the final products. Figs. 4 and 5 show the XRD patterns



Fig. 2. Compressive strength of geopolymers in relation to the percentage of KOH moles consumed by  $NO_3^-$  or  $SO_4^{-2}$  ions.



**Fig. 3.** Effect of KOH molarity on the compressive strength of geopolymers containing Pb (3% w/w of slag, PBS3, PBN3) or Cu (1% w/w of slag, CUS1, CUN1).

of geopolymers containing the highest Pb or Cu percentage as sulphate/ nitrate salt; Pb or Cu addition equals to 3% w/w of slag. The XRD pattern of the control geopolymer is shown in Fig. 6. The curve between 28° and 42° 20, which is more clearly shown in the control specimen, indicates that geopolymers are characterised by a certain degree of amorphicity; the amorphicity of the specimens is also indicated by the shape of the XRD patterns. The main phases already present in slag such as quartz, tridymite, cristobalite, magnetite, albite and orthoclase, are also shown. The only new phases detected as a result of atmospheric carbonation is trona, Na<sub>3</sub>(CO<sub>3</sub>)(HCO<sub>3</sub>) $\cdot$ 2(H<sub>2</sub>O), in control, PBS3 and PBN3 specimens, and K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub> in PBS3 specimen.

Phases such as  $(Na,K)_2SO_4$  and  $Cu_4(OH)_6SO_4$  (reaction (1)) are detected in specimen CUS3, while  $Cu_2(OH)_3NO_3$  is detected in CUN3 (reaction (2)). It is assumed that these hydrated phases adversely affect geopolymerisation by causing pressure development in the matrix and thus weakening of bonds (Zaharaki et al., 2010).

$$4\text{KOH} + 4[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}] + \text{Na}_2\text{SiO}_3 \rightarrow \text{Cu}_4(\text{OH})_6\text{SO}_4 + 2\text{K}_2\text{SO}_4 \qquad (1)$$
$$+ \text{Na}_2\text{SO}_4 + \text{SiO}_2 + 19\text{H}_2\text{O}$$

 $\begin{aligned} \text{KOH} + 2[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}] + \text{Na}_2\text{SiO}_3 \rightarrow \text{Cu}_2(\text{OH})_3\text{NO}_3 + \text{KNO}_3 \\ + 2\text{NaNO}_3 + \text{SiO}_2 + 5\text{H}_2\text{O} \end{aligned} \tag{2}$ 

It is important to mention that potassium is also detected, in efflorescences formed at the surface of the specimens after drying, as soluble sulphate or nitrate phases that coexists with hydrated carbonates (CUS1, Fig. 7). This is another indication that  $NO_3^-$  and  $SO_4^{-2}$  ions present in the initial pulp react and consume KOH reducing thus its availability to attack ferronickel slag.

#### 3.2.2. SEM studies

Fig. 8 shows selected backscattered electron images (BSI) that display the morphology of the slag-based geopolymers CUS3 and PBS3 which have acquired compressive strength of 0.8 and 16 MPa, respectively.

It is seen from these images that the matrix of both geopolymers is quite heterogeneous; slag grains, denoted by "S", with sharp angular shape and various dimensions are clearly shown. The geopolymeric gel, points "G1" to "G10", is formed between slag grains and acts as binder. It consists of various elements solubilised from slag (mainly Fe, Al, Ca and some Cr) as well as silicon which is also provided from sodium silicate solution used as activator.

The geopolymeric gel in specimen PBS3, points "G1", "G2" and "G4", contains Ca, Al, Fe, Mg and Na, K, Si solubilised from slag or provided from the activating solution. The gel contains also encapsulated Pb in various percentages (52.1, 7.1 and 36.1% w/w, respectively). The absence of sulphur indicates that almost all available sulphate anions react with KOH or Na<sub>2</sub>SiO<sub>3</sub> to form efflorescence, as discussed in

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Fig. 4. XRD patterns of geopolymers PBN3 and PBS3; 1: quartz, SiO<sub>2</sub>, 2: magnetite, Fe<sub>3</sub>O<sub>4</sub>, 3: albite, NaAlSi<sub>3</sub>O<sub>8</sub>, 4: trona, Na<sub>3</sub>(CO<sub>3</sub>)(HCO<sub>3</sub>)·2(H<sub>2</sub>O), 5: tridymite, 6: K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>.



Fig. 5. XRD patterns of geopolymers CUN3 and CUS3; 1: quartz, SiO<sub>2</sub>, 2: magnetite, Fe<sub>3</sub>O<sub>4</sub>, 3: albite, NaAlSi<sub>3</sub>O<sub>8</sub>, 4: orthoclase, KAlSi<sub>3</sub>O<sub>8</sub>, 5: Cu<sub>2</sub>(OH)<sub>3</sub>NO<sub>3</sub>, 6: Cu<sub>4</sub>(OH)<sub>6</sub>SO<sub>4</sub>, 7: (Na,K)<sub>2</sub>SO<sub>4</sub>,

Section 3.2.1. The remaining quantity of KOH attacks slag and participates in gel formation. Fe observed in "G3" is released from slag after the attack of KOH.

"G5" and "G9" show that the geopolymeric gel of specimen CUS3 contains Fe, Al and Si solubilised from slag or provided from the sodium silicate solution; some Cu encapsulated in gel is also observed. The presence of sulphur indicates the formation of hydrated sulphate compounds which results in poor final compressive strength.

Fe, Ni, Ca, Al, Si and Mg are the main elements in gel "G6", "G7" and "G8". The outer white layer in "G8" indicates the presence of small quantities of Cu (5.7% w/w) and S (1% w/w). The vain in "G10" consists mainly of Cu (55.2% w/w) provided from the copper

salt added in the starting mixture and some Al (9.5% w/w) released from the ferronickel slag.

Fig. 9 shows the element spectrum of a) geopolymer gel "G2" as shown in Fig. 8a and b) geopolymer gel "G7" as shown in Fig. 8c. The high concentration of Pb and Cu indicates that the added metal salts are most probably not well homogenised in the geopolymeric mixture or some Pb or Cu is encapsulated in gel. All other elements present are released from slag, except for sulphur which comes from copper sulphate that was added in the geopolymeric mixture.

SEM studies indicate in general that the composition of the geopolymer gel phase varies greatly between samples. This variability shows that the degree of in-homogeneity in gel is in most cases quite



Fig. 6. XRD pattern of control geopolymer; 1: quartz, SiO<sub>2</sub>, 2: magnetite, Fe<sub>3</sub>O<sub>4</sub>, 3: albite, NaAlSi<sub>3</sub>O<sub>8</sub>, 4: trona, Na<sub>3</sub>(CO<sub>3</sub>)(HCO<sub>3</sub>)·2(H<sub>2</sub>O), 5: cristobalite, SiO<sub>2</sub>.

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Fig. 7. XRD pattern of efflorescences formed at the surface of geopolymer CUS1; 1: K<sub>3</sub>Na(SO<sub>4</sub>)<sub>2</sub>, 2: KAl(SO<sub>4</sub>)<sub>2</sub>, 3: Na<sub>2</sub>CO<sub>3</sub>(H<sub>2</sub>O)<sub>7</sub>.

high. This may suggest that there is limited movement of aluminosilicates after dissolution, even in cases where the activating solution is sufficient, and thus the composition of the gel may be quite similar to the composition of the neighbouring slag particles. It is therefore believed that the dissolution of aluminosilicates takes place in a highly viscous rather than in a liquid state.



Fig. 8. SEM-BSI of geopolymers PBS3 (images a and b) and CUS3 (images c and d) (S: slag grains, G1-G10: geopolymeric gel).

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Fig. 9. Element spectrum of a) geopolymer gel "G2" as shown in Fig. 8a and b) geopolymer gel "G7" as shown in Fig. 8c.

#### 3.2.3. FTIR studies

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Fig. 10 shows the FTIR spectra of specimens PBS3, CUS3, PBN3, CUN3 and control.

The bands around 465 cm<sup>-1</sup> detected in all specimens and mainly in the control are due to in plane Si–O bending and Al–O linkages (Yip et al., 2008). The very small peak at 852 cm<sup>-1</sup> in the control geopolymer is assigned to T–OH (T:Si or Al) stretching modes and corresponds to dissolved silicate and/or aluminosilicate species (Bakharev, 2005; Rees et al., 2007).

The peaks between 950 and  $1200 \text{ cm}^{-1}$  are due to T–O–Si asymmetric stretching vibrations as a result of TO<sub>4</sub> reorganisation that takes place during geopolymer production (Davidovits, 1994). All these bands are major fingerprints of the geopolymeric matrix and define the extent of polysialation or aluminium incorporation. This peak is quite sharp for the control specimen due to



Fig. 10. FTIR spectra of slag-based geopolymer (control) and specimens PBS3, CUS3, PBN3 and CUN3.

Table 3	
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CLP results and EPA TCLP regulatory limits.	
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Geopolymer	Metal of concern	Metal concentration in extract (mg/L)	EPA TCLP regulatory limits (mg/L) <sup>a</sup>
CRN05	Cr	$0.3\pm0.02$	5
CRS05	Cr	$0.1 \pm 0.02$	5
PBN05	Pb	$7.9 \pm 0.9$	5
PBS05	Pb	$9.0 \pm 0.9$	5
CUN05	Cu	$25.5 \pm 2.1$	-
CUS05	Cu	$46.6 \pm 3.2$	-
NIN05	Ni	$34.7 \pm 2.9$	-
NIS05	Ni	$47.3 \pm 3.3$	-

<sup>a</sup> No regulatory limits are available for Cu and Ni.

the production of more homogenous gel; when sulphate or nitrate ions are present in the initial pulp (e.g. specimens PBS3, CUS3, PBN3 and CUN3) the quality of the gel deteriorates and thus the peaks become less sharp or even shift to higher band positions. It has been reported that the location of the bands depends on the length and the angle of the bonds in the silicate network (Van Jaarsveld et al., 1999).

The characteristic bands at 1386 cm<sup>-1</sup>, only in PBN3 and CUN3 specimens are due to the very strong absorption of nitrate ions which is usually identified between 1340 and 1410 cm<sup>-1</sup>. The small bands at around 618 cm<sup>-1</sup> in PBS3 and CUS3 specimens are due to the presence of sulphate ions (Socrates, 2001).

Atmospheric carbonation is evident at around 1490 cm<sup>-1</sup> and it is more clearly observed in the control specimen (Panias et al., 2007). The band, broader for the control specimen, at around 1640 cm<sup>-1</sup> in all geopolymers, is attributed to bending vibrations (H–O–H) and is typical for polymeric structures with aluminosilicate networks.

#### 3.3. Geopolymer toxicity

Table 3 shows the TCLP results for the geopolymers produced using the lowest addition percentage of sulphate/nitrate anions and heavy metals (0.5% w/w of slag) as well as the available EPA regulatory limits.

It is evident from this data that with the exception of Cr, which has quite low concentration in the extract, high concentrations of Pb, Cu and Ni are detected in the extract when these metals are added as sulphate ions in the starting mixture. Geopolymers exhibit increased toxicity in terms of Pb whereas no TCLP limits are available for Ni and Cu. The concentration though of these two elements in the extract is considered high and thus increased risk for contamination of soils and groundwater is anticipated if wastes containing Ni and Cu in the form of sulphate or nitrate salts are geopolymerised and disposed of without proper care in the environment.

It is noted that the concentration of Ni in the extract is net. The as received slag was also subjected to the TCLP test and the concentration of Ni in the extract (13.4 mg/L) was subtracted from the respective value determined for the geopolymeric specimens. Finally, it has to be noted that no Cr is detected in the extract of the as received slag.

#### 4. Conclusions

The present experimental study investigates the effect of sulphate and nitrate ions on heavy metal immobilisation during the production of geopolymers from low calcium ferronickel slag. The major findings of this study are the following.

The compressive strength of geopolymers is negatively affected by the presence of  $NO_3^-$  or  $SO_4^{-2}$  ions in the starting mixture. Both anions consume most of the available alkali activator moles, hinder geopolymerisation reactions and thus the quantity of the gel produced is limited.

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Heavy metals seem to be encapsulated in the geopolymer matrix, while the degree of encapsulation depends on the properties of the produced gel. The presence of Pb, even in limited quantities in the starting mixture as sulphate or nitrate salt, seems to affect less the structural integrity of the produced geopolymers. On the other hand, the presence of Cu, Cr and Ni, in percentages varying between 0.5 and 3% w/w of slag, has a clear detrimental effect on the final compressive strength. Another important finding of this study is that if the molarity of KOH is increased, some of the previously mentioned disadvantages are offset, since the number of the available KOH moles that participate in geopolymeric reactions increases.

XRD, SEM and FTIR studies identified new phases and elucidated to a certain degree reactions taking place and involving raw materials, anions and heavy metals. These techniques though have certain limitations in cases when Ni and Cr salts are present in the starting mixture, since these two elements are also present in ferronickel slag.

Additional research efforts are required though to further elucidate the effect of anions on the immobilisation of heavy metals in geopolymers produced from mining and metallurgical wastes. These studies may include geopolymerisation of pure oxides in the presence of sulphates, nitrates and heavy metals in order to overcome interactions involved in cases when materials with complex mineralogy, such as metallurgical slags, are subjected to geopolymerisation.

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