Role of alkali metals on the synthesis of low Ca ferronickel slag-based inorganic polymers

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ABSTRACT

In the present experimental study, inorganic polymers were synthesised using low Ca electric arc ferronickel slag and alkali activating solution. Specimens were pre-cured at room temperature for 2 days and then heated at 80 ^oC for 48 hours; aging took place under room temperature for 7 or 28 days. The effect of alkali metals of the activating solutions, on the compressive strength of the final products is assessed. The experimental results show that the presence of alkalis contributes to strong structure formation. Inorganic polymers acquire the highest compressive strength of almost 60 MPa when 8 M KOH and 8 % w/w Na_2SiO_3 are used. Dissolution of Si and Al from slag was estimated through batch leaching tests. XRD analysis was carried out to identify new formed phases and predict the degree of amorphicity of the final products.

1. INTRODUCTION

Inorganic polymers (geopolymers) are amorphous tridimensional alumino-silicates, synthesised at ambient temperature and short time. The sialate network consists of SiO_4 and AlO_4 tetrahedra linked alternately by sharing all oxygen atoms. Positive ions must be present in the framework cavities to balance the negative charge of Al^{3+} in 4-fold coordination (Davidovits, 1988).

The formation of these cementitious materials ($M_2O–Al_2O_3–SiO_2–H_2O$) is in general complex and involves dissolution of solid alumino-silicate oxides in MOH solution (M: alkali metal), diffusion or transportation of dissolved Al and Si complexes from particle surface to the inter-particle space and hardening of the gel phase formed during polymerisation between added silicate solution and Al - Si complexes (Krivenko and Kovalchuk, 2007).

De Silva and Sagoe-Crenstil (2008) state that the initial molar content of Na_2O, Al_2O_3 and SiO_2 plays a key role in controlling transformations from amorphous to crystalline phase; a tentative link exists between phase transformation/stability and strength characteristics, since systems that favor the formation of zeolitic products usually possess lower strength.

Inorganic polymers, exhibiting excellent physical and chemical properties may be also obtained under specific conditions from utilization of mining and metallurgical wastes such as fly ash, red mud and various types of slags (Komnitsas and Zaharaki, 2007; Chindaprasirt et al., 2009; Provis et al., 2009).

Slags are commonly used in Portland cement production while the remaining substantial quantities, are currently disposed of either on surface heaps or under the sea. The need for the development of new low cost technologies that utilise various by-products such as slags, for the development of high added value materials is expected soon to increase.

The final structure and physical properties of these novel materials depend on several parameters such as particle size, alkali metal and water content as well as the degree of crystallinity (or amorphicity) (Van Jaarsveld et al., 2003). Inorganic polymers are characterised by less porous microstructure, advanced mechanical and thermal properties and good resistance to attack by aggressive solutions (Yunsheng et al., 2007; Hu et al., 2008). Their rapid hardening at room temperature may yield high compressive strength values up to 100 MPa. The behavior of the produced binders is similar to that of zeolites and feldspathoids; they may immobilize hazardous elements within the geopolymeric matrix and convert semi-solid wastes into adhesive solids (Hermann et al., 1999).

Some inorganic polymers such as new special and blended cements, building products and temperature stable resins are already used in industrial applications (Davidovits, 1988). Other environmentally oriented applications may include immobilization of hazardous wastes, surface capping of waste dumps and stabilization of tailing dams (Van Jaarsveld et al., 1999).

Additional research efforts are required though for the increase of the degree of utilization of various wastes and the production of inorganic polymers with advanced properties. When this technology becomes fully established it will definitely contribute to the sustainable development of the minerals sector (Komnitsas and Zaharaki, 2007).

In the present study, inorganic polymers are produced by mixing low Ca ferronickel slag and alkali activating solution. The main operating parameters include pre-curing (2 days), temperature (80 °C), heating period (48 hours) and aging period (7 or 28 days). The effect of alkali metals used on the compressive strength of the final products is assessed. Batch leaching tests were carried out to estimate the extent of dissolution of Si and Al from slag. XRD analysis was used to identify new formed phases and predict the degree of amorphicity of the final products.

2. MATERIALS AND METHODOLOGY

The raw material used is electric arc slag produced at the LARCO ferronickel plant in Greece. The annual slag production is about 1,700,000 t of which approximately 450,000 t is used in the cement industry. Disposal cost of the remaining quantities reaches 650,000 €/year.

Slag is a brittle material and its particle size varies between 0.075 and 4 mm (most of it is seen in the 0.1-1.5 mm fraction). Table 1 shows its chemical composition in the form of oxides and trace elements, while the main mineralogical phases detected by XRD are quartz-tridymite-cristobalite (SiO_2), magnetite (Fe_3O_4), olivine $(Fe,Mg)_2SiO_4$), anorthite ($CaAl_2Si_2O_8$) and chromite ($FeCr_2O_4$). The estimated amorphous content exceeds 50%.

Table 1: Chemical composition of ferronickel slag

	%		%		%
Fe_2O_3	43.83	Cr_2O_3	3.07	C	0.11
SiO_2	32.74	MgO	2.76	Ni	0.1
Al_2O_3	8.32	Mn_3O_4	0.44	Co	0.02
CaO	3.73	S	0.18		

Slag was dried and crushed (−120 μm, d_{50}: −12 μm) using a FRITSCH BICO pulveriser in order to increase surface area and improve the compressive strength of the produced inorganic polymers (Zaharaki et al., 2006).

Pulverized slag was added slowly into the activating solution prepared by dissolving sodium or potassium hydroxide anhydrous pellets (ACS-ISO for analysis) in distilled water and mixing with sodium silicate solution (Merck, $Na_2O:SiO_2 = 0.3$). Under continuous mechanical mixing a reactive and homogeneous paste was obtained. The wt% addition of slag and activating solution varies so that a workable paste is produced.

The paste was cast in plastic cubic moulds (5 cm each side) which were vibrated for five minutes to remove trapped air bubbles. Specimens were pre-cured at room temperature for 2 days and then heated in a laboratory oven (MMM GmbH) at 80 °C for 48 hours. After demoulding, aging took place at room temperature for either 7 or 28 days in order to enhance the development of structural bonds. The compressive strength of the produced inorganic polymers was measured using the MTS 1600 load frame. Only in a few cases, when deviation in the experimental results was higher than 10 %, additional specimens were prepared.

Identification of new formed phases in order to elucidate geopolymerisation mechanisms, was carried out by XRD. The analysis was performed by a Siemens D500 diffractometer using a Fe tube and a scanning range from 3° to 70° 2θ, with a step 0.03° and 4 sec/step measuring time. Qualitative analysis was carried out by the Diffrac*plus* Software (Bruker AXS) and the PDF database.

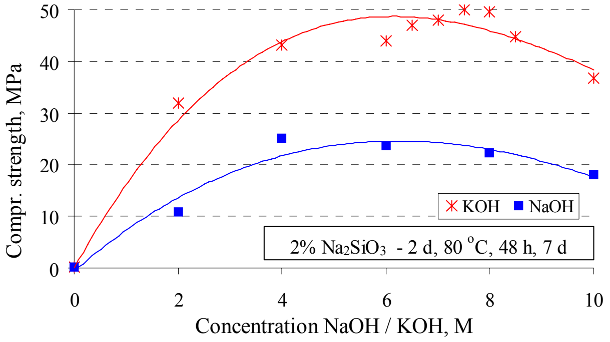

Figure 1: Effect of alkali hydroxide concentration on the compressive strength of inorganic polymers.

3. RESULTS AND DISCUSSION

3.1 Effect of alkali activating solution

Figure 1 shows the effect of alkali hydroxide concentration on the compressive strength of inorganic polymers. It is seen that the use of KOH solution is more beneficial and the maximum compressive strength reaches 50 MPa. The optimum strength is acquired for KOH concentration close to 8 M; it is underlined though that when the concentration of KOH varies between 4 M and 8 M the strength of the specimens exceeds 40 MPa whereas when higher than 8 M concentration is used the strength decreases. Excess KOH does not accelerate geopolymerisation reactions while it assists the formation of carbonates reducing thus strength.

From the same figure it is seen that the optimum range of NaOH concentration is similar to that of KOH. However when NaOH is used the compressive strength acquired is much lower and does not exceed 25 MPa. It has to be mentioned though that when no alkali hydroxide solution is used the paste becomes too viscous, cannot solidify and the specimens acquire practically no strength (0.22 MPa).

It is believed that KOH provides more inorganic polymer precursors since the larger size of K^+ (atomic radius of 1.3 Å) compared to Na^+ (atomic radius of 0.98 Å) favors the formation of larger silicate oligomers with which $Al(OH)_4^-$ prefer to bind; thus better setting and higher compressive strength is obtained. It is seen therefore that the presence of alkalis plays a catalytic role and enables an appropriate structure formation of inorganic polymer gel (Phair and Van Deventer, 2002; Komnitsas et al., 2009).

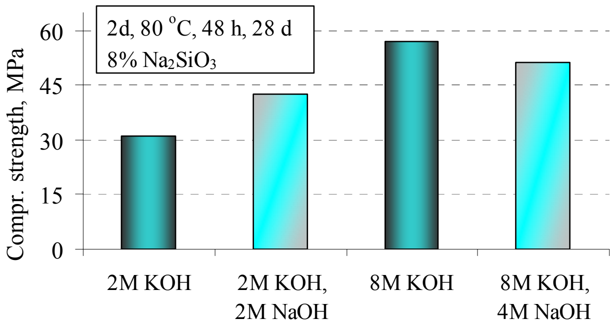

Figure 2: Effect of simultaneous NaOH and KOH addition on the compressive strength of inorganic polymers.

Figure 2 shows the effect of simultaneous NaOH and KOH addition on the compressive strength of slag-based inorganic polymers which were synthesized using the concentrations seen in Figure 1. The concentrations of the alkaline solutions were 2 M KOH and 2 M NaOH for which inorganic polymers acquired the lowest strength as well as 8 M KOH and 4 M NaOH which resulted in the highest strength. Control specimens with 2 M and 8 M KOH reaching the lowest and highest compressive strength, respectively, are also seen in Figure 2.

It is deduced from this figure that simultaneous NaOH and KOH addition increases the compressive strength by 37% compared to the control specimen with 2 M KOH. On the other hand, when the solution concentration is 8 M KOH and 4 M NaOH, strength decreases by 10 % compared to the control specimen with 8 M KOH. Therefore when alkali hydroxide concentration exceeds 8 M (optimum concentration) the compressive strength is negatively affected. Similar results are obtained for slag-kaolinite inorganic polymers; strength reaches only 17 MPa when the solution concentration is 2 M KOH and 3 M NaOH (Komnitsas et al., 2009).

Figure 3 shows the effect of KOH concentration, when Na_2SiO_3 addition is 0, 2 and 8 % w/w, on the compressive strength of slag-based inorganic polymers. It is seen from these data that when no sodium silicate solution is added during synthesis, the paste requires longer time to solidify and the final strength does not exceed 30 MPa. Addition of 2 % w/w Na_2SiO_3 improves paste properties and the maximum compressive strength acquired is 50 MPa when the concentration of KOH is 8 M. Slightly higher strength values are acquired for 8 % w/w addi-

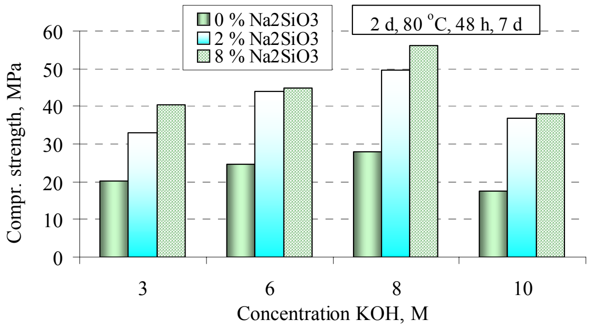

Figure 3: Effect of KOH concentration, when Na_2SiO_3 addition varies between 0, 2 and 8 % w/w, on the compressive strength of inorganic polymers.

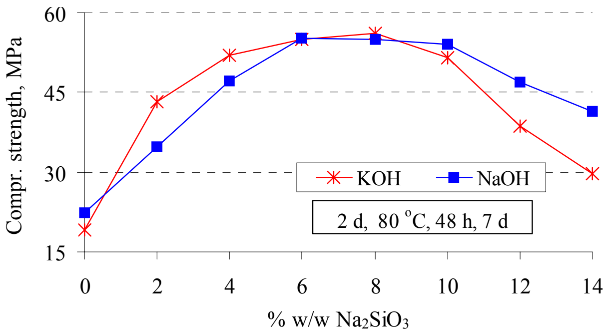

Figure 4: Effect of % w/w addition of Na_2SiO_3 on the compressive strength of inorganic polymers, when either KOH or NaOH is used.

tion of Na_2SiO_3, reaching 56 MPa at the optimum KOH concentration of 8 M.

It is concluded therefore that sodium silicate solution provides extra soluble silicates and acts as binder or plasticizer resulting thus in denser structures that enhance the development of Si-O-Al bonds and improve the workability of the paste (Van Jaarsveld et al., 1997; Andini et al., 2008).

Figure 4 shows the evolution of the compressive strength of slag-based inorganic polymers vs. the % w/w addition of Na_2SiO_3, varying between 0 and 14%. In each case, water percentage was adjusted accordingly, affecting thus also alkali hydroxide concentration, so that a workable paste was obtained. It is seen from this figure that the optimum percentage addition of sodium silicate is close to 8 % w/w when either KOH (8.7 M) or NaOH (12.2 M) is used. The maximum compressive strength acquired is 56 MPa which decreases when higher percentages of alkali silicates are used.

3.2 Dissolution of Si and Al

Alkali hydroxide solution causes partial solubilisation of Si and Al from slag enhancing thus the development of inorganic polymeric bonds. In order to investigate the extent of dissolution of Si and Al from slag, batch leaching tests were carried out. Slag was mixed with 1 N KOH at a solid to liquid ratio of 1:20 and the solution was stirred continuously (400 rpm, 40 °C) for 24 hours.

The experimental results (Fig. 5) show a similar dissolution trend for Si and Al from the slag, which gradually increases with leaching time and after 6 hours reaches 95 and 33 mg/L, respectively. After 24 hours Al dissolution increases gradually to 70 mg/L, while Si dissolution increases sharply to 309 mg/L. This is due to the high solubility of silica and alumina (Mason, 1966) under the specific conditions used in this study and the fast dissolution of olivine and anorthite present in slag. In this case, the number of OH^- ions that can be adsorbed onto the surface lead to the formation of labile Si-O and Al-O bonds; detachment of metal cations from the surface is the rate-limiting step (Carroll-Webb and Walther, 1988).

The Si/Al ratio (Fig. 5) is in line with Si and Al dissolution. The initial available ratio Si/Al of 3.5 (not shown) increases to 7 after 2 hours of leaching, indicating the higher dissolution of Si; after 24 hours Si/Al ratio almost reaches its initial value.

Therefore higher concentrations of alkaline solutions are required during inorganic polymer synthesis, so that substantial amounts of Si and Al (solubilised from slag) are crucial for the formation of Si-O-Al bonds and the development of a gel with the desired properties.

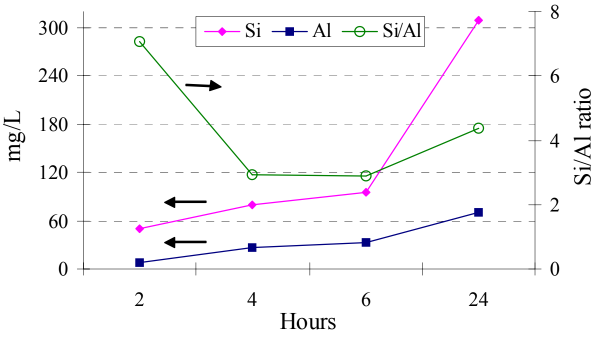

Figure 5: Dissolution of Si and Al (mg/L) from slag over time.

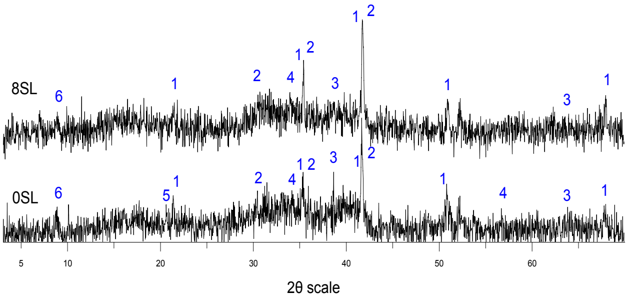

Figure 6: X-ray patterns of inorganic polymers synthesised using 0% (0SL) and 8% w/w Na_2SiO_3 (8SL) (1: magnetite, 2: maghemite, 3: hematite, 4: mangano-calcite, 5: cristo-balite and 6: calcium silicate hydroxide).

3.3 Mineralogy

XRD is often used to identify new formed phases, define the degree to which starting materials have reacted and assess the level of amorphicity of the final products. XRD patterns of inorganic polymers synthesised using 0% (0SL) and 8% w/w Na_2SiO_3 (8SL) are presented in Figure 6. XRD analysis of inorganic polymer 0SL reveals the presence of magnetite and cristobalite which are phases present in slag and the formation of new phases such as maghemite, hematite, manganocalcite and calcium silicate hydroxide.

Maghemite, γ-Fe_2O_3, is formed by low-temperature oxidation of ferrous iron phases present in the raw slag. These ferrous iron phases result also in the formation of hematite, Fe_2O_3, due to the reductive environment prevailing during inorganic polymer synthesis.

Manganocalcite, $(Ca,Mn)CO_3$, is formed when calcium or manganese hydroxide reacts with atmospheric carbon dioxide. The same phases are seen in inorganic polymers synthesized using 8% w/w Na_2SiO_3.

Figure 7 shows the XRD patterns of inorganic polymers synthesised using 8 M KOH (NOK) or 11 M NaOH (NON). No new phases are formed in detectable quantities. However, the broad peak seen between 28° and 42° 2θ indicates that all specimens are characterized by a certain degree of amorphicity.

4. CONCLUSIONS

The concentration of alkali hydroxide and activator is a crucial factor that affects synthesis of ferronickel slag-based inorganic polymers. Metal cations play a catalytic role and control the formation of inorganic polymer gel.

When NaOH is used the compressive strength does not exceed 25 MPa. Better setting and higher compressive strength (almost 60 MPa) is acquired when 8 M KOH and 8% Na_2SiO_3 are used for the synthesis of inorganic polymers. It is believed that due to the larger size of K^+, KOH provides more inorganic polymer precursors compared to NaOH.

Dissolution of Al and Si shows a similar trend in the first 6 hours, while after 24 hours more Si is dissolved and the final concentration is 70 and 309 mg/L, respectively.

Maghemite, hematite, manganocalcite and calcium silicate hydroxide are the main new formed phases. XRD analysis shows also a certain degree of amorphicity in all specimens.

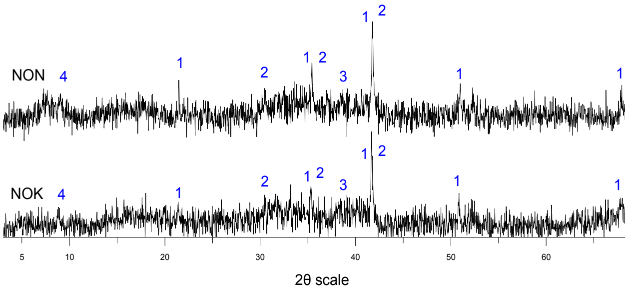

Figure 7: X-ray patterns of inorganic polymers synthesised using 8 M KOH (NOK) or 8 M NaOH (NON) (1: magnetite, 2: maghemite, 3: hematite, 4: calcium silicate hydroxide).

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