

EFFECT OF ADDITIVES ON THE COMPRESSIVE STRENGTH OF SLAG-BASED INORGANIC POLYMERS

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Received: 01/09/08
Accepted: 04/11/08

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ABSTRACT

The present paper aims to assess the effect of various additives on the compressive strength of inorganic polymers (geopolymers) synthesised using low Ca electric arc ferronickel slag and alkali activating solutions. The main operating parameters include pre-curing (48 hours), temperature (40 to 80 °C), heating time (24 or 48 h) and aging period (7 days). Addition of kaolinite, pozzolan, fly ash, red mud or CaO in the initial mixture has a detrimental effect on the final compressive strength. Addition of pulverised silica sand improves strength slightly, whereas addition of commercial glass results in strength values exceeding 60 MPa. XRD analysis was carried out to identify new formed phases and the degree of amorphicity, while SEM and element mapping analysis were used to identify the morphology of the final products as well as to elucidate to a certain degree the mechanisms involved in inorganic polymer synthesis.

KEYWORDS: inorganic polymer, compressive strength, slag, glass.

1. INTRODUCTION

Alkali activated systems formed under low temperature and pressure and containing calcium silicate hydrated (CSH) and aluminosilicate phases, were first introduced by Glukhovsky (1965). Later, these products were called soil silicates while nowadays the most commonly used terms are inorganic polymers or geopolymers (Davidovits, 2005).

Inorganic polymers are similar to zeolites in chemical composition but they are characterised by an amorphous to semi-crystalline three-dimensional alumino-silicate microstructure (Davidovits, 1991; 1994). The exothermic process of inorganic polymer synthesis starts with the dissolution of Si and Al in alkaline solutions forming thus a $M_x(\text{AlO}_2)_y(\text{SiO}_2)_z \cdot n\text{MOH} \cdot m\text{H}_2\text{O}$ gel (M: K^+ or Na^+) that quickly hardens (Xu and Van Deventer, 2000; Xu, 2001). Due to the complex nature of most raw materials present in the initial mixture, the exact mechanisms involved in synthesis of inorganic polymers need to be further elucidated; it is believed though that the main mechanisms are dissolution, transportation or orientation and polycondensation.

The structure and physical properties of inorganic polymers depend on several parameters such as particle size, thermal history, alkali metal and water content as well as degree of crystallinity (or amorphicity) (Van Jaarsveld *et al.*, 2003). Depending on synthesis conditions, structural integrity and strength may be acquired in a relatively short time, even within 60 min. The products are often characterised by excellent durability and chemical resistance as well as by a much smaller CO_2 footprint compared to Portland cement (Duxson *et al.*, 2007). Some inorganic polymers such as new special and blended cements, building materials and temperature stable resins are already used in industrial applications (Davidovits, 1988). Other environmentally oriented applications may include immobilisation of hazardous elements present in wastes, surface capping of waste dumps and stabilisation of tailing dams (Van Jaarsveld *et al.*, 1999).

Natural minerals (e.g. kaolinite, albite) as well as a number of mining and metallurgical wastes may be used during inorganic polymer synthesis. Various types of fly ashes have been extensively investigated for immobilisation of toxic metals (Krivenko and Skurchinskaya, 1991; Palomo *et al.*, 1999; Van Jaarsveld *et al.*, 1999; Bakharev, 2005). Alkali-activation of high calcium blast furnace slags has been also studied over the past years with promising results (Glukhovskiy, 1994; Roy, 1999; Astutiningsih and Liu, 2005; Komnitsas *et al.*, 2007; Van Deventer *et al.*, 2007; Zhang *et al.*, 2007). Additional research efforts are required though for the increase of the degree of utilisation of mining and metallurgical wastes and the production of inorganic polymers with advanced properties (Provis *et al.*, 2005). When this technology overcomes several industrial barriers and becomes fully established it will definitely contribute to the sustainable development of the broader minerals sector (Komnitsas and Zaharaki, 2007).

The present experimental study aims to assess the effect of various additives, namely kaolinite, pozzolan, fly ash, red mud, CaO, pulverised silica sand or commercial glass on the compressive strength of inorganic polymers synthesised using low Ca electric arc ferronickel slag and alkali activating solutions. XRD, SEM and element mapping analysis were used to identify new formed phases, the degree of amorphicity, the morphology of the final products and elucidate to a certain degree the mechanisms involved during inorganic polymer synthesis.

2. MATERIALS AND METHODS

The raw material used is electric arc furnace ferronickel slag obtained from LARCO S.A (Larymna plant) in Greece. The annual slag production is about 1,700,000 t of which approximately 450,000 t are used in the cement industry. The disposal cost of the remaining quantities is estimated at 650,000 €/year. Slag is a brittle material and its grain size varies between 0.075 mm and 4 mm. Slag was dried and crushed (-120 µm, d_{50} : -12 µm) using a FRITSCH pulveriser in order to increase surface area and improve the compressive strength of the produced inorganic polymers (Zaharaki, 2005; Zaharaki *et al.*, 2006). Additives used include kaolinite (Fluka), CaO (Alfa Aesar), silica sand as well as pozzolan, fly ash, red mud and commercial glass. Particle size analysis of all raw materials used was determined using a laser analyser (Mastersizer S, Malvern Instruments).

Table 1 shows the chemical analysis of the slag and the additives used in the form of oxides and trace elements. Olivines (fayalite and forsterite), anorthite, quartz, tridymite, cristobalite, magnetite and chromite are the main mineralogical phases present in slag. It is estimated that the amorphous content exceeds 50%.

Table 1. Chemical analysis and size distribution of ferronickel slag and additives

%	Ferronickel slag	Pozzolan	Fly ash	Red mud	Commercial glass
Fe ₂ O ₃	43.83	1.09	5.60	45.48	-
SiO ₂	32.74	72.22	33.40	6.96	74.00
Al ₂ O ₃	8.32	17.73	13.10	15.65	1.30
CaO	3.73	0.95	35.31	14.84	10.50
Cr ₂ O ₃	3.07	-	-	-	-
MgO	2.76	1.10	3.67	-	-
Mn ₃ O ₄	0.44	0.19	0.19	-	-
Na ₂ O	-	3.30	0.46	3.26	13.00
K ₂ O	-	3.05	0.76	-	-
P ₂ O ₅	-	0.56	-	-	-
TiO ₂	-	0.14	0.71	4.80	-
SO ₃	-	-	6.58	-	-
S	0.18	-	-	-	-
C	0.11	-	-	-	-
Ni	0.10	-	-	-	-
Co	0.02	-	-	-	-

Silica sand, purchased in a granular form (-1+0.5 mm), consists of quartz; it was pulverised prior to use (-300 µm, d_{50} : -13 µm). Pozzolan (-350 µm, d_{50} : -25 µm), was obtained from Milos

island, Greece, is a very cheap material and when used in Portland cement concrete increases its long-term compressive strength. Fly ash (-400 μm , d_{50} : -32 μm) was obtained from Ptolemais, N.W. Greece, thermal power station and is classified according to ASTM as type C; its main mineralogical phases are quartz SiO_2 , calcite CaCO_3 , anhydrite CaSO_4 , gehlenite $\text{Ca}_2(\text{Al}(\text{AlSi})\text{O}_7)$, albite $\text{NaAlSi}_3\text{O}_8$, lime CaO and portlandite $\text{Ca}(\text{OH})_2$. Red mud (-76 μm , d_{50} : -4 μm) was obtained from "Aluminum of Greece" S.A. and consists of quartz SiO_2 , hematite Fe_2O_3 , gibbsite $\text{Al}(\text{OH})_3$, diaspore $\text{AlO}(\text{OH})$, calcite CaCO_3 , cancrinite $\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_2$ and katoite $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$. Commercial glass is an amorphous material consisting mainly of silicon, calcium and sodium oxides; it was pulverised prior to use (-350 μm , d_{50} : -23 μm).

The activating solution was prepared by dissolving potassium hydroxide anhydrous pellets (ACS-ISO for analysis) in deionised water and mixing with sodium silicate solution (Merck, $\text{Na}_2\text{O} = 7.5\text{-}8.5\%$, $\text{SiO}_2 = 25.5\text{-}28.5\%$). Slag and additives were then slowly added into the solution and the resulting paste was well mixed. The wt% addition of slag and additives varies and depends on the reagents used in each case to produce a workable paste. Control specimens were prepared in each experimental series using only slag and activating solution; a typical composition is (% w/w): slag 82%, water 7%, KOH 3%, Na_2SiO_3 8%.

The cement like pulp was cast in high resistant plastic cubic moulds (5 cm each side), which were then vibrated for 5 min so that practically all air trapped within the reactive mass was removed. Pre-curing of the sealed moulds took place for 2 days at room temperature ($\sim 22^\circ\text{C}$) in order to utilise the existing moisture of the paste and initiate inorganic polymer reactions enhancing thus strength development. If the paste is not pre-cured but heated immediately most of the water evaporates fast, cannot participate in reactions involved in strength development and the final strength acquired is in general low (Komnitsas *et al.*, 2007; 2009).

The moulds were then placed into a laboratory oven (MMM GmbH) and heated at the required temperature for a specific period. Aging took place under room temperature for 7 days in order to enhance the development of structural bonds. Compressive strength measurements of the produced inorganic polymers were carried out using an MTS 1600 load frame.

XRD 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. The qualitative analysis was carried out using the *Diffra_{plus}* Software (Bruker AXS) and the PDF database. Imaging of the inorganic polymer microstructure was carried out using a JEOL JSM-5400 scanning electron microscope equipped with an Oxford energy dispersive X-ray spectrometer (EDS). Specimens were coated with carbon prior to analysis to increase conductivity of the surface.

3. RESULTS AND DISCUSSION

3.1 Effect of additives

In order to study the effect of kaolinite and pozzolan addition on the compressive strength of inorganic polymers, 5% w/w of each material was added in the initial mixture and the resulting products were heated at 40, 60 and 80°C for 24 or 48 hours. Figure 1 shows the evolution of the compressive strength vs. temperature and heating time. It is seen that addition of kaolinite or pozzolan does not practically improve compressive strength. Addition of pozzolan results in a decrease of compressive strength by more than 50% compared to the control specimen over the temperature range studied; obtained strength varies between 12 and 20 MPa. On the other hand, addition of kaolinite results in higher compressive strength almost reaching at 80°C the values obtained for the control specimen. Limited improvement is seen when duration of heating increases from 24 to 48 hours over the entire temperature range; this means that most inorganic polymer bonds are developed in a very short time.

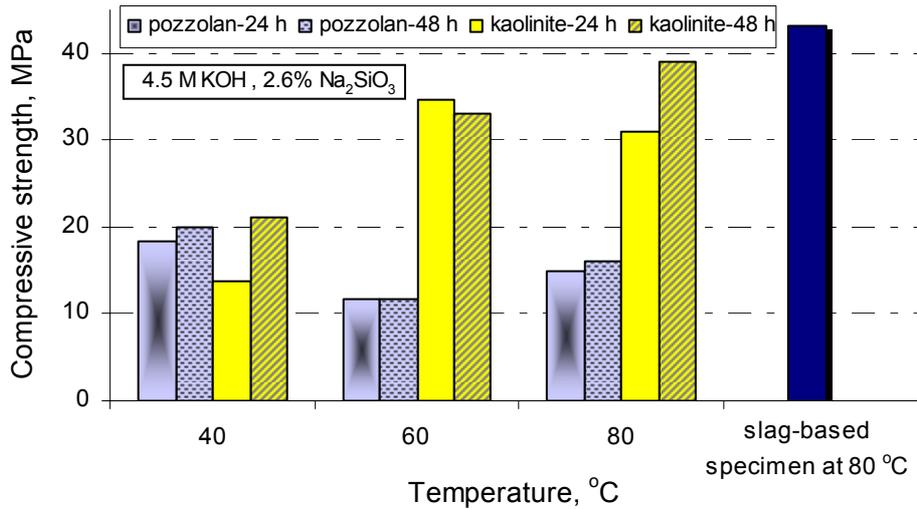


Figure 1. Evolution of the compressive strength vs. temperature and heating time in the presence of 5% w/w of pozzolan or kaolinite in the starting mixture

The effect of fly ash and red mud addition on the compressive strength is shown in Figure 2; these tests were carried out to explore the possibility of co-utilisation of mining and metallurgical wastes. It is seen from this figure that very low strength values are obtained in both cases when addition percentages vary between 20 and 50 % w/w. Slag as well as both additives used consist of various oxides exhibiting different degree of solubilisation when they react with the activating solution; as a result the number of Si and Al ions provided in the system cannot be easily assessed. The experimental results indicate that a part of these ions do not participate in reactions involved in inorganic polymer bond development and therefore limited strength is acquired.

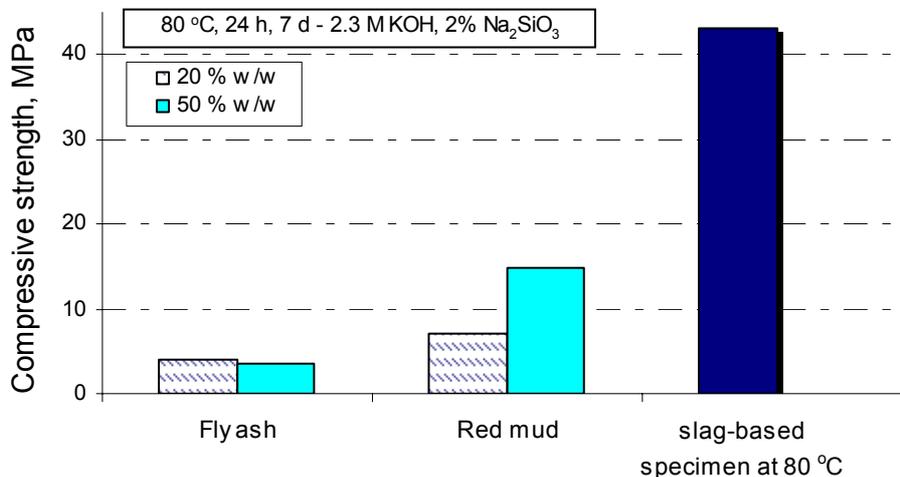


Figure 2. Effect of fly ash / red mud addition on the compressive strength

Figure 3 shows the effect of silica sand and CaO addition, varying between 5% and 20% w/w, on the compressive strength. Silica sand addition improves in all cases the compressive strength that reaches almost 60 MPa when the addition percentage is 5% w/w. The compressive strength drops slightly when the percentage addition increases to 20% w/w; this is probably due to the fact that the activating solution used is not sufficient to react with the increased quantity added and form strong bonds. The particle size of silica sand barely affects compressive strength; almost identical values were obtained when either coarse or pulverised silica sand was used (data not shown). On the other hand CaO addition results in low strength not exceeding 25 MPa; strength decreases in a linear manner when higher % CaO is used. Similar results were reported in previous studies (Zaharaki *et al.*, 2007, Yip *et*

al., 2008; Komnitsas *et al.*, 2009). An overdose of CaO binds almost all the available silica to form weak linear chains, therefore insufficient silica is left to nucleate the gel. In addition, part of the excess calcium may remain un-reacted; as a result the quantity of C-S-H gel produced is not sufficient and the inorganic polymer network is disrupted (Zaharaki *et al.*, 2007; Yip *et al.*, 2008). It is also probable that at high alkalinity, calcium forms precipitates rather than hydrated gels.

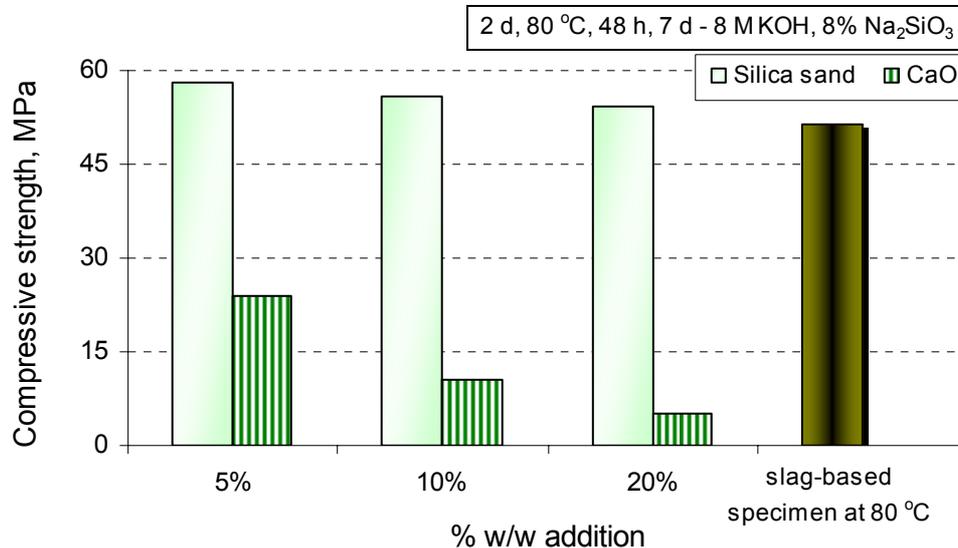


Figure 3. Effect of silica sand / CaO addition percentage (% w/w) on the compressive strength

The high Fe_2O_3 content present in slag may also play an important role during synthesis, since it may react with the activating solution to form phases contributing to strength development (Zaharaki *et al.*, 2007); this issue requires further investigation by using pure iron oxides. It should be underlined though that iron does not take part in the formation of inorganic polymer gel tetrahedral networks but may reduce the release of silica and alumina into the gel.

Figure 4 shows the evolution of the compressive strength of inorganic polymers vs. the % w/w glass addition; the compressive strength of pure slag and pure glass specimens (used as controls) is also seen. Addition of glass up to 50 % w/w in the starting mixture does not practically improve strength which remains close to 52 MPa. When the percentage of glass increases to 90% w/w the acquired strength reaches 64 MPa. When only glass is used as raw material the compressive strength of the inorganic polymers produced is extremely high and reaches almost 125 MPa. It is believed that this is due to the homogeneity and the high amorphicity of the raw material used resulting thus in the development of extremely strong bonds, typical of three dimensional alumino-silicates.

The effect of 20% w/w kaolinite addition on the compressive strength of glass-based inorganic polymers synthesised at 40, 60 and 80°C is seen in Figure 5; the strength of pure glass specimens, used as controls, is also presented. The experimental results show that addition of kaolinite results in much lower strength which barely exceeds 35 MPa at 80°C; at 40 °C the obtained strength value is just 10 MPa. Kaolinite reacts only partially in the system under the conditions used, the available Si:Al ratio in the initial paste is affected and as a result the compressive strength acquired is relatively low; similar behavior is seen for slag-kaolinite inorganic polymers (Figure 1). On the other hand the effect of temperature is highly beneficial for pure glass inorganic polymers (Zaharaki, 2004; 2005); almost 30% increase in the compressive strength is seen when temperature increases from 40 to 60 °C, while an additional 50% increase is recorded when temperature increases further to 80 °C.

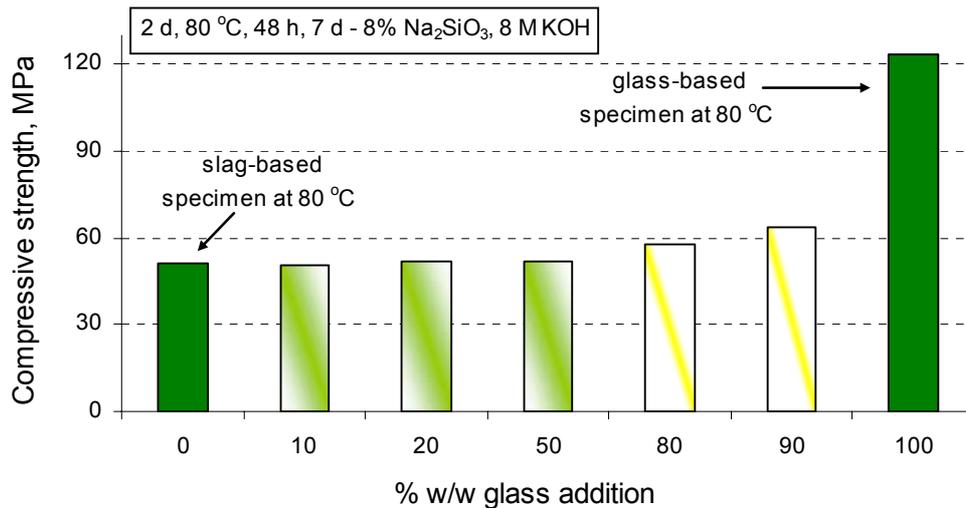


Figure 4. Evolution of compressive strength vs. the % w/w glass addition

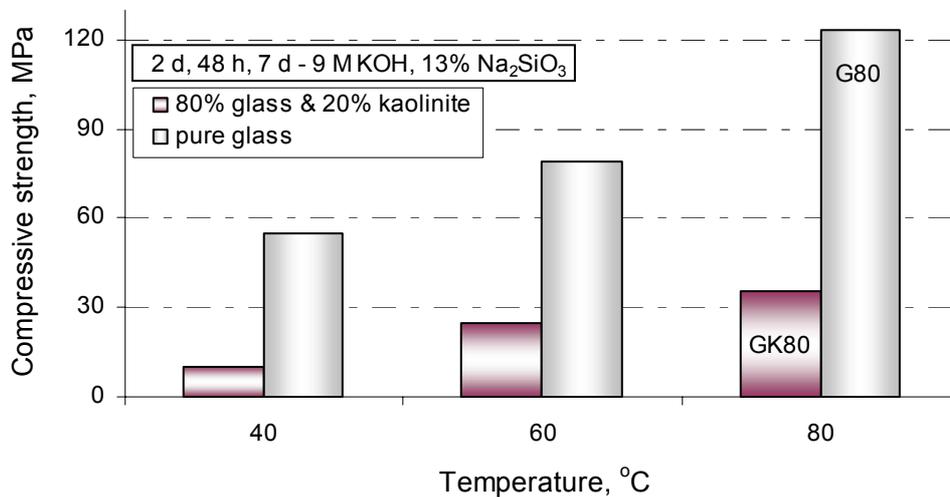


Figure 5. Effect of 20% w/w kaolinite addition on the compressive strength of glass-based inorganic polymers vs temperature

3.2 XRD analysis

Despite the substantial amorphous nature of ideal inorganic polymers, XRD is often used to identify new formed phases, define the extent to which starting materials have reacted and assess the degree of amorphicity of the final products. The XRD patterns (not shown) of inorganic polymers synthesised using slag-silica sand-kaolinite, slag-kaolinite and slag-pozzolan, heated at 80 °C for 48 hours and aged under room temperature for 7 days, reveal the presence of quartz, magnetite and maghemite which were initially present in the slag. The presence of remaining kaolinite indicates that the initially used quantity has not fully reacted during inorganic polymer synthesis. Orthoclase, $K_{0.58}Na_{0.42}AlSi_3O_8$, is formed when raw materials react with sodium silicate and KOH activating solution. Calcite, $CaCO_3$, is formed when calcium hydroxide reacts with atmospheric carbon dioxide.

X-ray patterns of raw glass (G) as well as pure glass (G80) and glass-kaolinite (GK80) inorganic polymers synthesised at 80 °C are seen in Figure 6. The broad peaks seen between 17° and 34° 2θ in all patterns indicate a high degree of amorphicity. Pirssonite, $CaNa_2(CO_3)_2(H_2O)_2$, which is detected in G80 specimen, is an evaporite formed through atmospheric carbonation of glass which is characterised by high calcium content (10.5 % w/w). Phases such as kaolinite and quartz present in the raw materials can be detected also in GK80 inorganic polymer. New phases such as illite, $K(Al_4Si_2O_9(OH)_3)$, orthoclase,

$K_{0.58}Na_{0.42}AlSi_3O_8$ and natrolite, $Na_2Al_2Si_3O_{10}$, are formed when kaolinite reacts with KOH and Na_2SiO_3 .

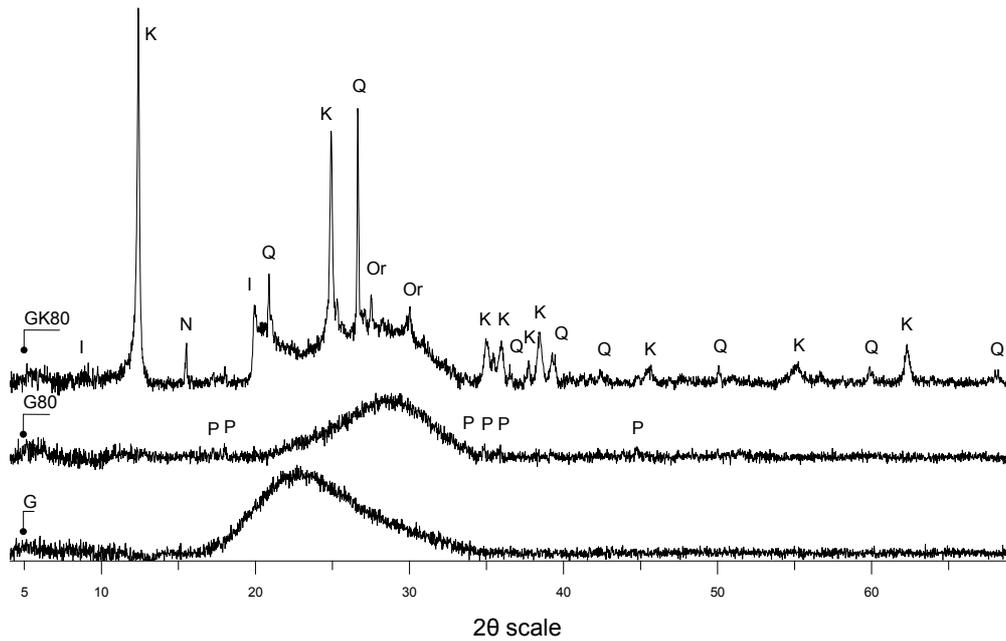


Figure 6. X-ray patterns of raw glass (G), pure glass inorganic polymer (G80) and glass-kaolinite (GK80) inorganic polymer produced under various conditions (Q: Quartz, K: Kaolinite, I: Illite, Or: Orthoclase, N: Natrolite, P: Pirssonite)

3.3 SEM analysis

Slag-glass specimens exhibiting high compressive strength were examined under the microscope in order to identify their microstructure. A backscattered electron image (BSI) displaying the microstructure of a 50% w/w slag-glass inorganic polymer is shown in Figure 7. It is seen in this micrograph that the matrix is quite heterogenous; slag and glass grains are pointed out (slag grains are darker). The binder formed by the geopolymeric gel is seen between slag and glass grains.

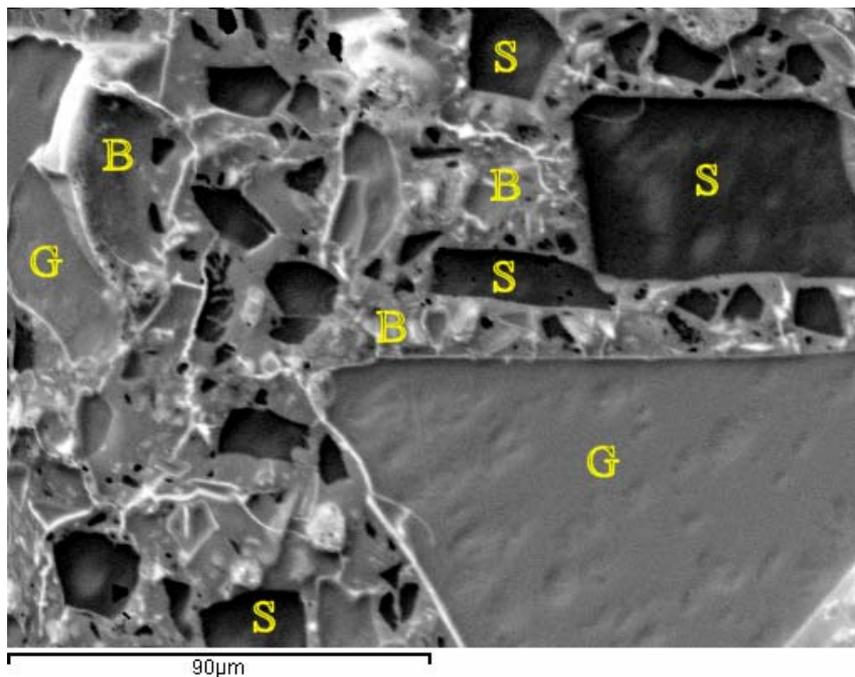


Figure 7. Backscattered image of slag-glass inorganic polymer (S: slag grains, G: glass grains, B: binder)

The element spectra for slag and glass grains as well as for the binder show that the ratio of Si/Al in slag, which also contains calcium and chromium, is ~2.5. Glass grains consist mainly of silicon while some calcium and magnesium are also seen. The binder contains silicon and aluminum solubilised from the raw materials; silicon is also provided from the sodium silicate solution used during synthesis. The Si/Al ratio, which is affected by the potassium hydroxide concentration, is higher in the binder (~13) than the respective ratio in slag (~2.5) and lower than that in glass (~21.5) (Schneider *et al.*, 2001). Considering that Si and Ca are the main elements present in the binder (the content of Na and Al is much lower), it is believed that calcium silicate hydrates (CSH) are also formed (Zhang *et al.*, 2007) or calcium may participate in the formation of Ca polysialate-(di)siloxo structures (Davidovits, 1988). It is also noted that the ratio of Fe/Cr is almost identical in slag and the binder, 7.1 and 6.9 respectively, indicating that the solubilisation rate of iron and chromium phases present in the raw material is almost equal.

4. CONCLUSIONS

The present paper attempts to assess the effect of various additives on the compressive strength of inorganic polymers synthesised using low calcium electric arc ferronickel slag. Addition of kaolinite and pozzolan reduces to a lesser or higher degree the compressive strength over a temperature range varying between 40 and 80 °C. When fly ash or red mud is added a significant reduction of strength, up to 92%, is seen; similar behaviour is seen when CaO is added. On the contrary, addition of pulverised silica sand increases slightly the compressive strength. Superior strength, reaching 123 MPa, is acquired for pure glass inorganic polymers; addition of kaolinite in this case results in much lower strength.

XRD is used to identify new formed phases, the degree of amorphicity and provide insights for the elucidation of mechanisms involved. Analysis of slag-based inorganic polymers reveals the presence of quartz, magnetite, maghemite and the formation of calcite. The presence of remaining kaolinite indicates that the initially used quantity has not fully reacted during synthesis. The morphology of slag-glass inorganic polymers was also investigated using backscattered SEM; unreacted particles present in the raw materials as well as calcium rich phases were identified.

Additional studies are required to elucidate inorganic polymer mechanisms, identify optimum synthesis conditions in each case, shed light on the degree, efficiency and chemical/physical nature of immobilisation of metals in the geopolymer matrix and assess the potential of this innovative technology for utilisation of mining and metallurgical wastes towards sustainable development of the broader minerals sector.

ACKNOWLEDGEMENTS

The financial support of the Research Committee of the Technical University of Crete for the basic research project "Elucidation of inorganic polymer mechanisms" is greatly acknowledged. The authors would also like to thank the assistance of the laboratories of Rock Mechanics and Ore Processing of the Department Mineral Resources Engineering of Technical University Crete, in various stages of this study, as well as LARCO S.A for providing the slag.

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