Effect of synthesis parameters on the compressive strength of low-calcium ferronickel slag inorganic polymers

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ABSTRACT

The wide range of physical and chemical properties of inorganic polymers, also known as geopolymers, commonly formed by alkali activation of aluminosilicates, makes these materials useful for a variety of applications.

In the present experimental study inorganic polymers are synthesised from low-Ca electric arc ferronickel slag. The effect of experimental conditions on the compressive strength of the final products is assessed.

A number of techniques, namely XRD, FTIR and TG–DTG were used to identify new phases and subsequently elucidate to some degree the mechanisms involved.

Finally, the paper discusses briefly the potential of inorganic polymer technology as a feasible option for the utilisation of certain potentially hazardous mining and metallurgical wastes towards an increased sustainability of the wider minerals sector.

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1. Introduction

Glukhovsky was the first who attempted to model cementitious systems in accordance with low temperature and pressure transformation of rocks into zeolites. These systems, formed by alkali activation of aluminosilicates present in industrial materials or wastes, were first called soil silicates [1].

Inorganic polymers (geopolymers) are amorphous tridimensional aluminosilicates, synthesised at ambient temperature and short time when aluminosilicate powder reacts with a caustic concentrated alkali metal silicate solution [2,3]. Such novel materials, exhibiting excellent physical and chemical properties [4,5] may be also obtained under specific conditions from utilisation of mining and metallurgical wastes [6]. Nowadays, several other names are used to describe these materials, including alkali-bounded-ceramics, hydroceramics and alkali-activated-cements, creating thus some confusion; however, in all cases alkali-activation is essentially involved [7].

The formation of these cementitious materials (M_2O–Al_2O_3–SiO_2–H_2O) is in general complex and involves destruction of primary solid phases, formation of certain units of unstable structure as well as contact interactions between the units; these mechanisms result in the formation of hydrated products having coagulated thixotropic and condensed/crystalline structures [8,9]. De Silva and Sagoe-Crenstil [10] 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 favour the formation of zeolitic products usually possess lower strength.

Inorganic polymers are similar to zeolites in chemical composition but they are characterised by higher density and amorphous to semi-crystalline three-dimensional alumino-silicate microstructure [11]. The factors affecting the synthesis of zeolites such as temperature, pH and presence of specific cations seem also to affect the synthesis of inorganic polymers [12,13].

The amorphous inorganic polymer structure is due to aluminosilicate precursor gels from which zeolites are hydrothermally generated [14,15]. It is worth mentioning that zeolitic materials are often detected in geopolymeric systems [11,16]; high-resolution microscopic techniques may be used to determine relations between inorganic polymer and zeolite synthesis [14].

A wide range of natural Al–Si minerals, wastes such as fly ash and various types of slags could serve as potential source materials for the synthesis of inorganic polymers characterised by less porous microstructure, advanced mechanical and thermal properties, good resistance to attack by aggressive solutions as well as by high added value [17–25].

Reactivity and solubility of the source materials, water content as well as the type of metal silicate used during synthesis of

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Table 1
Chemical analysis of ferronickel slag

	%
$Fe_2O_{3(total)}$	43.83
SiO_2	32.74
Al_2O_3	8.32
CaO	3.73
Cr_2O_3	3.07
MgO	2.76
Mn_3O_4	0.44
S	0.18
C	0.11
Ni	0.1
Co	0.02

waste-based inorganic polymers define to a significant degree the properties of the final products [26]. Varying waste properties and reactivity between different sources or even between batches of the same source requires full understanding of the effect of composition, synthesis and post-synthesis parameters on the nature, strength and performance of the final products [27].

Compressive strength measurements are used widely as an indicator to assess the success of inorganic polymer technology. This is due to the low cost, simplicity as well as due to the fact that strength development is a primary measure of the utility of these materials in various applications [14].

In the present experimental study, ferronickel slag-based inorganic polymers were produced by mixing slag with sodium silicate solution, sodium or potassium hydroxide and water. The effect of additives such as kaolin or metakaolin and pre-curing period on the final compressive strength was also evaluated. XRD, DTG and FTIR studies were carried out to identify new phases and subsequently elucidate to some extent the main mechanisms involved.

2. Materials and methodology

The raw material used is electric arc slag produced at the LARCO S.A 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. Table 1 shows its chemical composition in the form of oxides and trace elements, while Fig. 1 presents the main mineralogical phases, namely fayalite, anorthite, quartz, tridymite, cristobalite, magnetite, forsterite and chromite. From the XRD pattern seen in Fig. 1 it is estimated that the amorphous content exceeds 50%.

The particle size of the as received brittle slag varies between 0.075 and 4 mm (most of it is seen in the 0.1–1.5 mm fraction). Based on previous studies [28,29] and in order to achieve higher compressive strength, pulverised slag (91%–50 μm, 47%–10 μm) using a FRITSCH pulverizer was used.

The inorganic polymer liquor was prepared by dissolving sodium or potassium hydroxide anhydrous pellets (ACS-ISO for analysis) in deionised water and then mixing the resulting solution with a sodium silicate solution (Merck, Na_2O:SiO_2 = 0.3, Na_2O = 7.5–8.5%, SiO_2 = 25.5–28.5%). Slag and additives, such as kaolin (Fluka) or metakaolin (derived by calcining kaolin at 600 °C for 4 h) were then slowly added in the liquor under continuous mechanical mixing so that a reactive and homogeneous paste was obtained.

The wt% of the raw materials/additives involved varies and depends on the reagents used in each case to produce a workable paste. The additives were used to trigger chemical reactions between alumino-silicates and alkali metal silicate solutions under highly alkaline conditions so that amorphous or semi-crystalline three-dimensional structures consisting of Si–O–Al–O bonds are formed.

The cement like paste was cast in high-resistance plastic cubic moulds (50 mm each side) which were vibrated for a few minutes to remove air trapped within the paste. The moulds were cured at room temperature for 48 h and then heated in a laboratory oven (MMM GmbH) at the required temperature for a specific time. Aging took place at room temperature in order to enhance the development of structural bonds. The compressive strength of the final products was measured using a MTS 1600 load frame. All experiments were carried out in duplicate. Only in a few cases, when deviation in the experimental data was higher than 10%, additional specimens were prepared.

XRD analysis was performed by a Siemens D500 diffractometer using a Cu tube and a scanning range from 3° to 70° 2θ, with a step 0.03° and 4 s/step measuring time. The qualitative analysis was carried out using the Diffrac^{plus} Software (Bruker AXS) and the PDF database. FTIR analysis was carried out by the FTIR Spectrometer Model 1000 (Perkin-Elmer) using the KBr pellet technique (1.5 mg powder sample mixed with 150 mg of KBr). TG and DTG analysis was performed using a Perkin Elmer Thermogravimetric Analyser TGA 6 (maximum heating temperature was 950 °C at a rate of 10 °C min^{-1} using a nitrogen purge rate of 60 mL min^{-1}). Table 2 shows the composition as well as the experimental conditions of inorganic polymers used for mineralogical analyses.

3. Effect of synthesis conditions

3.1. Alkali cation

In order to study the effect of alkali addition inorganic polymers were synthesised and heated at 40, 60 and 80 °C for 24 or 48 h.
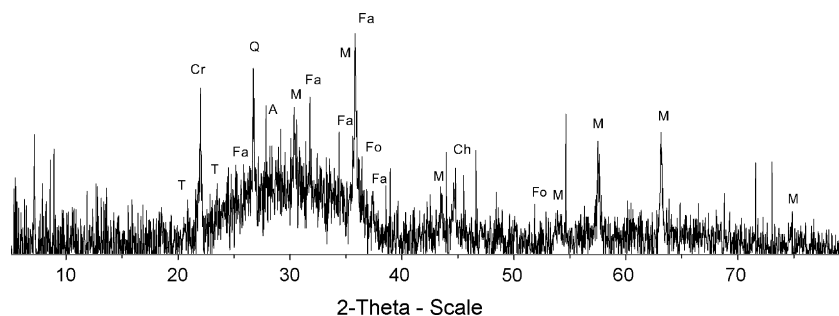

Fig. 1. X-ray pattern of slag (Fa: fayalite, A: anorthite, Q: quartz, T: tridymite, Cr: cristobalite, M: magnetite, Fo: forsterite and Ch: chromite).

Table 2
Synthesis conditions of inorganic polymers T1, T2, T3 and T4

Inorganic polymer	Composition	Experimental conditions
T1	Slag, metakaolin, NaOH, sodium silicate solution, H_2O	60 °C, 24 h, 7 days
T2	Slag, kaolin, NaOH, sodium silicate solution, H_2O	60 °C, 48 h, 7 days
T3	Slag, kaolin, KOH, sodium silicate solution, H_2O	60 °C, 24 h, 28 days
T4	Slag, metakaolin, KOH, sodium silicate solution, H_2O	80 °C, 48 h, 7 days

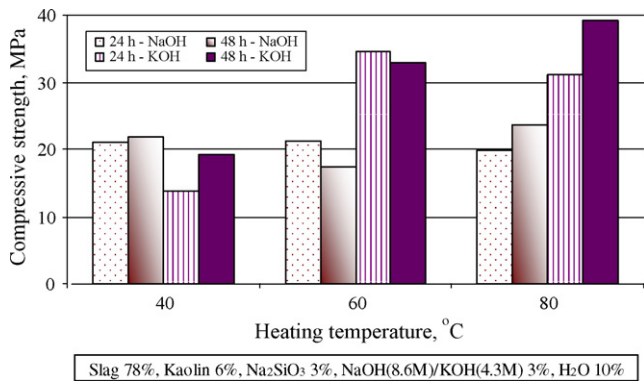Slag 78%, Kaolin 6%, Na_2SiO_3 3%, NaOH(8.6M)/KOH(4.3M) 3%, H_2O 10%

Fig. 2. Compressive strength evolution vs. heating temperature (heating period 24 or 48 h, use of NaOH or KOH).

Curing took place at room temperature for 7 or 28 days in order to enhance structural bonding and then the hardened products were subjected to compressive strength testing (Fig. 2).

The experimental results show that almost no increase in the compressive strength, varying between 20 and 24 MPa, is seen when 8.6 M NaOH is used over the entire temperature range and duration of heating studied. On the other hand, when 4.3 M KOH is used, the compressive strength of the final inorganic polymers increases substantially with temperature and slightly with heating time and reaches 40 MPa at 80 °C after 48 h.

In order to examine the effect of KOH or NaOH concentration on the compressive strength, slag-based inorganic polymers (without addition of kaolin) were prepared using various alkali hydroxide concentrations and heated for 48 h at 80 °C; the results are shown in Fig. 3.

It is seen from this figure that use of KOH up to 8 M results in much higher compressive strength, reaching 50 MPa. Use of excess KOH (e.g. 10 M) results in decreased final strength; this is mainly due to the fact that this additional quantity does not react with the
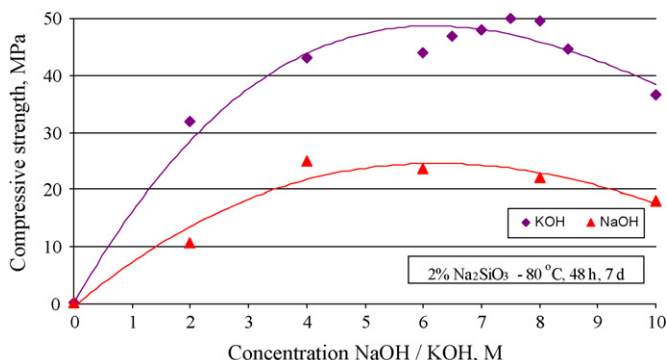

2% Na_2SiO_3 - 80 °C, 48 h, 7 d

Fig. 3. Compressive strength evolution vs. alkali hydroxide concentration.

Slag 77%, Kaolin 5%, Na_2SiO_3 3%, NaOH 1.5% (3 M), KOH (2 M) 1.5%, H_2O 12%
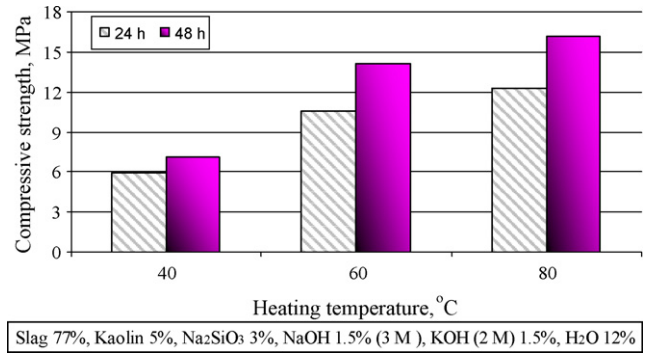
Fig. 4. Compressive strength evolution vs. temperature when both NaOH and KOH are used (heating period 24 or 48 h).

raw materials. On the other hand, use of NaOH between 4 and 8 M, results in compressive strength not exceeding 25 MPa. It is underlined that when no alkali solution is used the paste exhibits high viscosity, cannot solidify and under the same synthesis conditions acquires practically no strength (0.22 MPa).

KOH provides more inorganic polymer precursors since the larger size of K^+ favours the formation of larger silicate oligomers with which $Al(OH)_4^-$ prefers to bind; thus better setting and higher compressive strength is obtained.

It is seen therefore that the presence of alkali metal cation plays a catalytic role, controls all stages of inorganic polymer formation, in particular gel hardening and crystallisation and enables an appropriate structure formation [17,30–32].

When a mixed KOH/NaOH solution is used (1:1 ratio, 2.2 M and 3.1 M respectively) the results are discouraging; the maximum compressive strength attained at 80 °C does not exceed 16 MPa (Fig. 4). This is not the case for inorganic polymers made of pure metakaolin and mixed-alkali solution (Si/Al ≥ 1.90), where the final compressive strength after 28 days reached almost 85 MPa [33].

Another factor that plays an important role during inorganic polymer synthesis is the available calcium content of the raw materials. It is believed that at high alkalinity, calcium plays a lesser role in affecting the nature of the final binder, as it probably forms precipitates rather than hydrated gels. Indeed, when in the present study additional crystalline CaO was added in the initial mixture, varying between 5 and 20% (w/w), the compressive strength decreased gradually to 24 and 5 MPa, respectively; similar results were also reported in previous studies [34,35]. On the other hand, the presence of calcium provides extra nucleation sites for precipitation of dissolved species, which may be used to tailor setting times and material properties [27]. When the content of CaO in the source material is high an amorphous Ca–Al–Si gel structure with a decreased microstructural porosity is formed and therefore the final strength is high [16,18,36]. Finally, it is underlined that the role of available calcium during inorganic polymer synthesis requires further elucidation.

3.2. Alkali activator

The effect of sodium silicate, used as alkali activator in the present study, on the compressive strength was examined for slag-based inorganic polymers synthesised using admixture percentages of Na_2SiO_3 varying from 0 to 14%; in each case, water percentage was adjusted accordingly so that a workable paste was obtained. Mixing percentages for all specimens synthesised are shown in Table 3. Fig. 5 presents the evolution of the compressive strength in relation to sodium silicate percentage, when KOH or NaOH are used, respectively.

Table 3
Mixing percentages of slag-based inorganic polymers using various % (w/w) of Na_2SiO_3

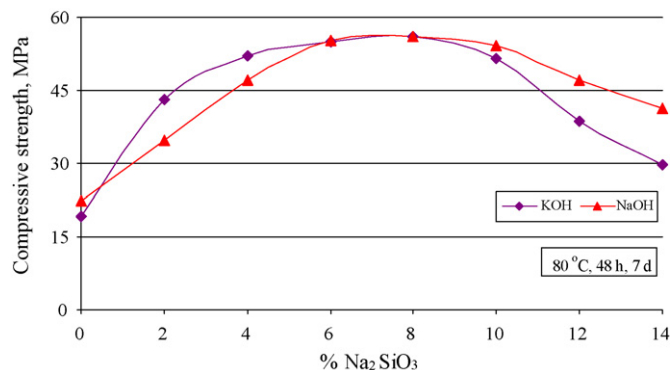| % Slag	83.5	83.5	83.5	83.5	83.5	83.5	83.5	83.5
% KOH	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
% Na_2SiO_3	0	2	4	6	8	10	12	14
% H_2O	14	12	10	8	6	4	2	0

Fig. 5. Compressive strength evolution vs. % Na_2SiO_3 when KOH or NaOH is used.

It is seen from this figure that the optimum addition percentage for sodium silicate is close to 8% (w/w) in both cases. The maximum compressive strength acquired is 56.2 MPa which decreases when higher percentages of alkali activator are used. It is worth mentioning that KOH has a more beneficial effect until the maximum compressive strength is reached, whereas after that point this trend reverses.

Alkali activator acts as binder, dispersant or plasticizer, affects inorganic polymer bonding and therefore results in denser structures that improve substantially the mechanical strength of the produced specimens; similar results are also seen in previous studies [37–43].

As seen from Figs. 3 and 5, the properties of the final inorganic polymers depend on the composition of the starting mixture, the concentration of KOH/NaOH solution as well as on the % (w/w) of sodium silicate addition.

3.3. Pre-curing period

In order to study the effect of pre-curing period inorganic polymers were synthesised, left for up to 2 days at room temperature and then heated at 80 °C for 48 h. Thereafter, aging took place at room temperature for 7 days.

The composition of the control specimen C is seen in Table 4; in all other specimens the w/w % of kaolin, KOH and Na_2SiO_3 was modified accordingly. The water content was also slightly modified in each case to obtain a workable paste, but remained close to the optimum value of 12% that resulted in the highest compressive strength of 43 MPa. It is seen in Fig. 6 that low percentage of the three additives does not result in acceptable compressive strength values while excess of these additives has practically no further

Table 4
Mixing compositions of slag–kaolin inorganic polymers for various w/w % of kaolin, KOH and Na_2SiO_3

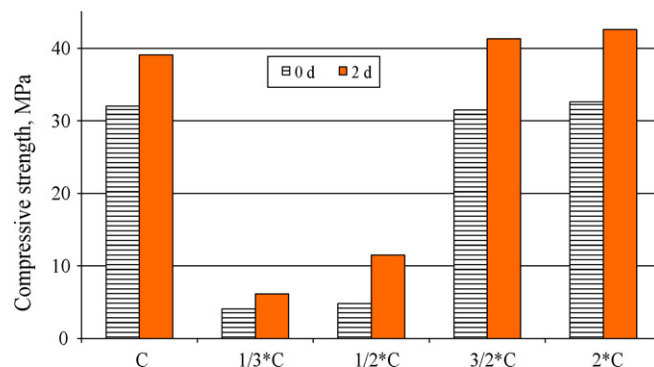| %	C	(1/3) C	(1/2) C	(3/2) C	2 C
Slag	76.6	83.09	81.52	71.78	67.10
H_2O	12.45	13.27	13.00	11.80	11.00
Kaolin	5.43	1.8	2.72	8.14	10.86
KOH	2.97	0.98	1.48	4.46	5.94
Na_2SiO_3	2.55	0.85	1.28	3.82	5.10

Fig. 6. Effect of pre-curing period (0 or 2 days) on the compressive strength.

beneficial effect. It is also seen that pre-curing for 2 days increases the compressive strength of almost all specimens by almost 30%. Pre-curing is considered as an important factor during inorganic polymer synthesis; increase of the pre-curing period from 2 to 4 days (data not shown) results in no further increase of the compressive strength.

Pre-curing for a specific period allows reaction of water with the raw materials present in the paste and therefore enhances the development of structural bonding; the specimens produced in the laboratory were perfectly cubic and no surface cracks were seen. Pre-curing did not seem to improve the final compressive strength when temperatures higher than 80 °C were considered; in this case (e.g. 120 °C) accelerated evaporation of the water takes place resulting thus in the development of pores and cracks and therefore in decreased compressive strength [20,44,45]. It is also mentioned that the formation of cracks is affected by the rate of heating that obviously affects the water evaporation rate.

Similar results were obtained in earlier studies using high calcium slag or fly ash as raw materials [3,46–49]. High temperature may increase the lability of inorganic polymer gel resulting thus in structural reorganisation and densification. The structural transition from amorphous to crystalline at low or mild temperatures implies that synthesis temperature and aging period are critical factors during inorganic polymer synthesis [3].

3.4. Kaolin/metakaolin

Fillers such as kaolin or metakaolin, may be used for the supply of Al^{3+} ions in the inorganic polymer paste. Kaolin $(Al_2Si_2O_5(OH)_4)$ is a well crystalline material, while metakaolin was obtained in the present study under calcination of kaolin at 600 °C for 4 h; it is known that calcination alters the original crystalline structure. Briefly, the decomposition process starts with dehydration at around 100–120 °C and proceeds with dehydroxylation of the structure (loss of water from the condensation of interlayer hydroxyl groups) yielding metakaolin at around 590 °C [50,51]. Crystallinity loss due to calcination weakens the bonds between crystals and the amorphous phase; the amorphicity of metakaolin is seen in the XRD pattern presented in the following section.

In order to study the effect of kaolin and metakaolin addition several experiments were carried out and the respective percentage varied between 0% (control specimen) and 12%. Fig. 7 shows that increased percentages of kaolin result in decreased compressive strength values which drop to 17 MPa when kaolin addition is 12% (w/w). When metakaolin is used, at the same percentages as kaolin, a more noticeable decrease in the compressive strength is observed. Addition of only 3% metakaolin results in compressive strength not exceeding 25 MPa; when the addition is 12% the compressive strength reaches the lowest value, 3 MPa.
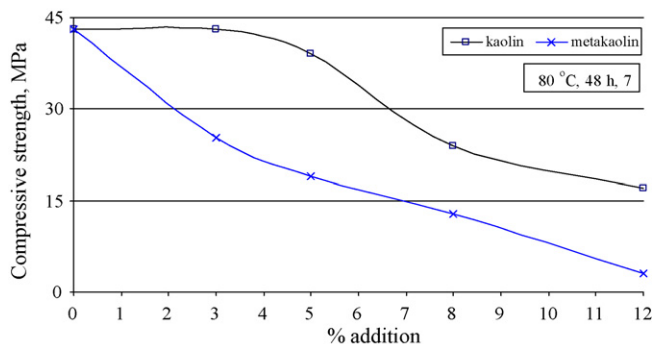
Fig. 7. Variation in compressive strength of inorganic polymers vs. kaolin/metakaolin addition.
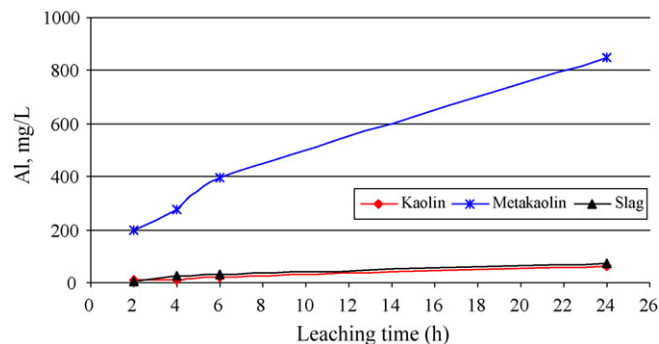

Fig. 8. Al dissolution from kaolin, metakaolin and slag.

It is deduced from this experimental data that sufficient available quantities of Si and Al are provided from sodium silicate solution (mainly) or slag, therefore the addition of kaolin does not further contribute to the formation of strong inorganic polymer bonds; on the contrary most Si and Al dissolved from kaolin remains practically un-reacted, therefore limited strength is obtained. Similar results have been reported for fly ash-based inorganic polymers [52]. Finally, it should be mentioned that the high Fe_2O_3 content of slag although it does not take part in the formation of gel, seems to play some role during inorganic polymers synthesis.

The noticeable decrease in the compressive strength of slag-metakaolin inorganic polymers may be due to the thermal processing of kaolin which results in a totally different final structure, due to dissolution–migration–polymerisation phenomena. It is known that the presence of metakaolin increases porosity and therefore the specimens may require too much water as also mentioned in a recent study [3]. De Silva et al. [53] also state that when the paste has a high Al_2O_3 content (i.e. low SiO_2/Al_2O_3 ratio) the resulting products acquire low strength. In addition, the plate-like structure of residual metakaolin particles does not provide sufficient moisture escape routes at elevated temperatures causing thus substantial damage to the matrix [54].

On the other hand it is known that calcination of kaolin transforms the octahedral coordinated Al layers into the more reactive tetrahedral form; it would then be expected that since Al ions dissolve more readily from metakaolin than from un-calcined kaolin, inorganic polymers containing metakaolin would exhibit higher compressive strength [15,18]. The fact that this is not the case in this as well as in other similar studies implies that synthesis does not entirely depend on dissolution and migration of ions dissolved from mineral surfaces [55].

In order to further elucidate this issue, slag, kaolin and metakaolin were leached in 1N KOH solution using a solid to liquid ratio of 1:20 and the results are presented in Fig. 8. It is seen from this figure that while leaching of metakaolin is a first order reaction and after 24 h enriches the solution with almost 850 mg/L of Al, very little Al is dissolved from slag and kaolin. This Al excess cannot react in the system and therefore the final specimen acquires low strength. It is underlined that Si dissolution exhibits a similar trend (data are not shown); concentration of Si though is much lower than that of Al.

4. Mineralogical studies

4.1. XRD

X-ray patterns of slag-metakaolin (T1 and T4) and slag–kaolin inorganic polymers (T1 and T2) synthesised under the experimental conditions shown in Table 2 are seen in Fig. 9. XRD analysis reveals the presence of quartz, kaolin, fayalite, magnetite and the formation of new phases, such as hydroxysodalite, maghemite and calcite.

The presence of remaining kaolin in specimens T2 and T3 indicates that the initially used quantity has not fully reacted during inorganic polymer synthesis [6,55]. Furthermore, the broad peak seen between 25° and 40° 2θ indicates that specimens T1 and T4 are characterized by a certain degree of amorphicity.

Sodalite, $Na_4Al_3(SiO_4)_3Cl$, with a Mohs hardness of 5.5–6, is a member of the feldspathoid group and belongs to rock forming minerals. Hydroxysodalite is detected in T2 and T3 slag–kaolin inorganic polymers exhibiting maximum strength [25], while no hydroxysodalite was detected in specimens T1 and T4 where metakaolin was used. Hydroxysodalite, $Na_8Al_6Si_6O_{24}(OH)_2(H_2O)_2$, is produced by replacing Cl^- with OH^- when NaOH reacts with kaolin according to the following reaction:

$$3Al_2(Si_2O_5)(OH)_4 + 8NaOH$$
$$\rightarrow Na_8Al_6Si_6O_{24}(OH)_2(H_2O)_2 + 7H_2O \qquad (1)$$
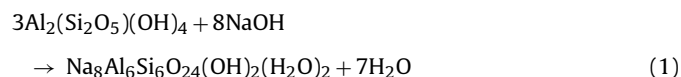
Kaolin provides OH^- and accelerates reaction (1) whereas the use of metakaolin which is a dehydroxylation product does not contribute to hydroxysodalite formation. However, Barrer and Mainwaring [56,57] who studied low-temperature hydrothermal behaviour of metakaolin using NaOH or KOH found that zeolitisation reactions were dominant and sodalite phases were also formed. In the framework of sodalite, when aluminum is substituted by silicon, the one minus charge generated can be balanced
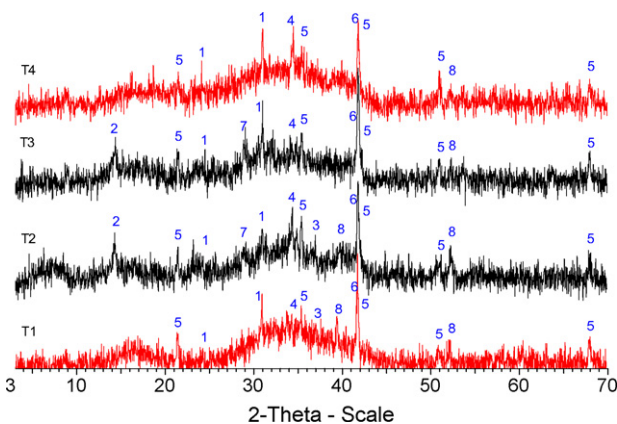

Fig. 9. X-ray patterns of inorganic polymers produced under various conditions (1: quartz, 2: kaolin, 3: fayalite, 4: calcite, 5: magnetite, 6: maghemite, 7: hydroxysodalite and 8: trona).

by the incorporation of an alkali cation which is strongly attracted by electrostatic interaction with negatively charged Al sites [58].

Engelhardt et al. [59] prepared hydrosodalite from kaolin and aqueous NaOH solution using different hydrothermal synthesis conditions. Dombrowski et al. [60] reported that the formation of hydrosodalite is feasible when kaolin or other phyllosilicates (montmorillonite, halloysite) react with a concentrated NaOH solution at 100 °C. The concentration of caustic soda may also affect the formation of hydroxysodalite in fly ash-based inorganic polymers [9].

The formation of hydroxysodalite in inorganic polymer T3, where KOH instead of NaOH was used, may be due to the presence of sodium silicate solution. According to Ogura et al. [58], when a potassium nitrate solution is heated at 80 °C for 24 h, partial potassium doping of sodalite, designated as K/sodalite, may take place through ion exchange; K/sodalite may be therefore present in limited amounts in inorganic polymer T3.

The olivine group comprises easily weathered silicates and therefore the remaining quantity of fayalite, Fe_2SiO_4, seen in the XRD patterns of T1 and T2 specimens, synthesised with the use of NaOH solution, is significantly less than the quantity initially present in the slag.

Calcite, $CaCO_3$, is formed when calcium hydroxide reacts with atmospheric carbon dioxide; it is well known that the solubility of calcium decreases at elevated pH values due to the formation of unstable calcium hydroxide. Excess of calcium hydroxide in the inorganic polymer paste induces carbonation and thus the strength of the final product is reduced [9,25].

Maghemite, γ-Fe_2O_3, may be formed during low-temperature oxidation of ferrous iron phases present in the raw slag [61].

It has to be mentioned that traces of a salt like phase seen on the surface of some specimens consist of synthetic thermonatrite, trona, calcite, hydroxysodalite and quartz; thermonatrite $Na_2CO_3 \cdot H_2O$ and trona $Na_3(CO_3)(HCO_3) \cdot 2(H_2O)$ belong to soda minerals group.

4.2. TG–DTG

Thermogravimetric analysis (TG) and derivative thermogravimetry (DTG) may be used to assess the rates of water evaporation in a system or identify the mechanism by which a material loses weight as a result of controlled heating [62]. TG curves for specimens T1, T2, T3 and T4 are shown in Fig. 10. Each specimen lost in total 4, 7, 6.5 and 5% water, of which approximately 2, 5, 4.5 and 3.5%, respectively, is absorbed water lost at temperatures lower than 200 °C. The water loss at around 550 °C is probably due to dehydroxylation of kaolin. The remaining water is less able to
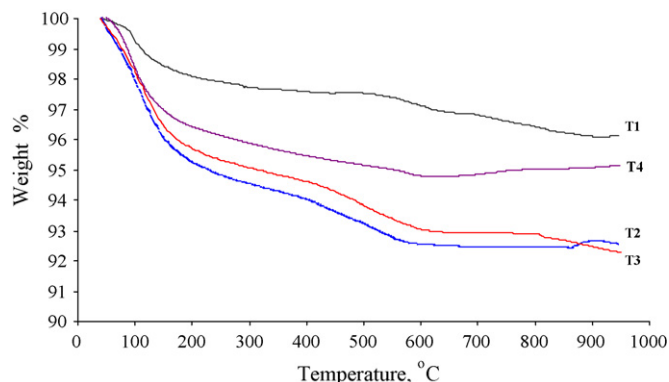

Fig. 10. TG plot of weight % vs. temperature for inorganic polymers T1, T2, T3 and T4.
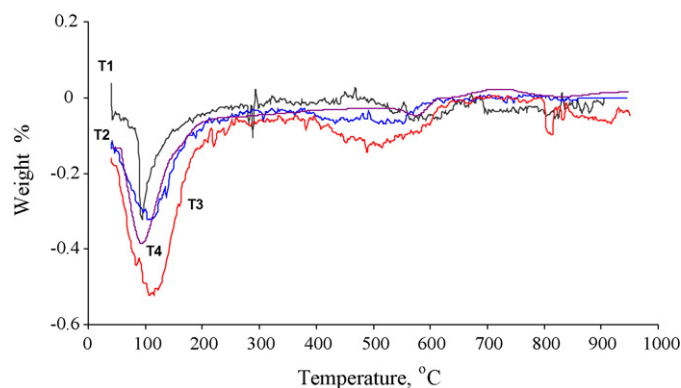

Fig. 11. DTG plot of weight % vs. temperature for inorganic polymers T1, T2, T3 and T4.

diffuse to the surface or bound tightly [63] and continues to evaporate slowly at temperatures higher than 200 °C. The continuous mass loss up to about 550 °C is due to the loss of hygroscopic water or water residing in the channels [64]. As it has been mentioned earlier an optimum water content should be present in the initial paste so that an adequate compressive strength is acquired; specimen T3 reaches 53 MPa, while specimen T1 only 1.5 MPa.

DTG thermograms are presented in Fig. 11 where all curves are typical of poly(sialate-siloxo) inorganic polymers. The endotherms seen at approximately 110 °C can be attributed to evaporation of free pore water [65]; this may cause a slight increase in porosity [47]. The appearance of a distinct minimum in the dehydration endotherm for all specimens implies that more water evaporates over this narrow temperature range; this observation confirms the weight loss seen in Fig. 10. Moreover, the greater temperature span of the endotherms may suggest that T2 and T3 specimens contain water that is more tightly bound within the inorganic polymer gel due to the presence of zeolitic phases that incorporate water into their cage-like structure [65]. The broad endothermic peak between 400 and 600 °C seen in inorganic polymers T2 and T3 is due to dehydroxylation of kaolin.

4.3. FTIR

FTIR analysis shows increased sensitivity for structures of short-range structural order and is considered as an appropriate technique for studying the structural evolution of amorphous aluminosilicates exhibiting high heterogeneity [66]. Infrared absorption bands enable identification of specific molecular components and structures. The difference in absorption frequencies between slag and final products predicts transformations taking place during inorganic polymers synthesis. The FTIR spectra of slag and specimens T1, T2, T3 and T4 are seen in Fig. 12.

The bands at 460–465 cm^{-1} seen for specimens T2, T3 and T4 are due to in plane Si–O bending and Al–O linkages originating from within individual tetrahedra [26]. The small band seen at $\sim$530 cm^{-1} only for T2 and T3 specimens is mainly due to out of plane Si–O bending; it may be also overlapped by hematite absorption which demonstrates a strong peak between 520 and 610 cm^{-1} [67]. The bands at approximately 680 cm^{-1} represent the functional group of AlO_2.

The very small peak seen at 864 cm^{-1} for inorganic polymers T2, T3 and T4 corresponds to dissolved silicate and/or aluminosilicate species and indicates that dissolution of raw material takes place [68,69]. The band at around 850 cm^{-1} is assigned to T–OH stretching modes [70].
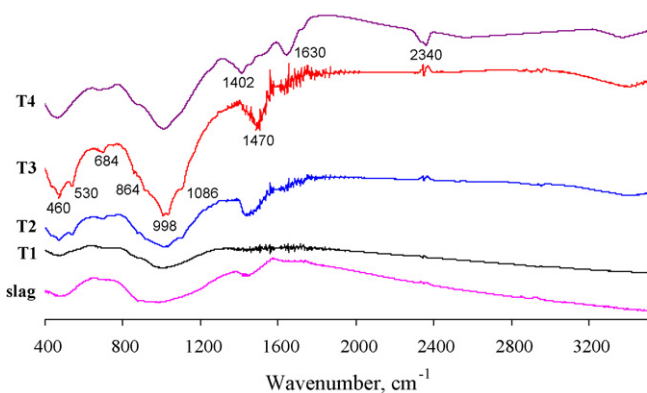
Fig. 12. FTIR spectra of slag and inorganic polymers T1, T2, T3 and T4.

The broad band of slag at around 965 cm^{-1} has been shifted in inorganic polymers to around 990 cm^{-1} where maximum absorbance is seen. This band may be due to T–O–Si (T:Si or Al) asymmetric stretching vibration (950–1200 cm^{-1}) as a result of TO$_4$ reorganisation that takes place during synthesis [61,69]. The position of the main T–O–Si stretching band indicates the length as well as the angle of the bonds in a silicate network [69]; shifting to lower wavenumbers hints lengthening of T–O–Si bonds, reduction in the bond angle and therefore decrease of the molecular vibrational force constant [71–73].

The only significant band for T1 specimen is the one seen at 987 cm^{-1}. All bands at around 1088 cm^{-1} are a major fingerprint of the inorganic polymer matrix and define the extent of polysialation or aluminium incorporation; they are either due to asymmetric stretching of Al–O and Si–O bonds originating from within individual tetrahedra [74] or due to the presence of quartz in the reactive paste [61].

Atmospheric carbonation is seen in the infrared spectral region 1410–1570 cm^{-1} [75,76]; a percentage of the excess Na is carried to the surface where it reacts [77]. The band seen at 1630 cm^{-1} for specimen T4 is attributed to bending vibrations (H–O–H) and is typical for polymer structures including aluminosilicate networks [70]. The small bands seen at around 2504 cm^{-1} are probably due to the infrared band position of HCO$_3$$^-$ ions [67]. Finally, it is mentioned that the noise seen in some parts of the curves is due to instrumental difficulties.

5. Conclusions

The main factors affecting synthesis of ferronickel slag inorganic polymers include mineralogy of raw materials, types of additives used, initial water content, alkali concentration and activator, precuring period as well as heating temperature, heating and aging period.

The presence of alkali metal cations plays a catalytic role, controls all stages of inorganic polymer synthesis in particular gel hardening and crystallisation and contributes to strong structure formation. KOH provides more inorganic polymer precursors compared to NaOH since the larger size of K$^+$ favours the formation of larger silicate oligomers with which Al(OH)$_4$$^-$ prefers to bind; thus better setting and higher compressive strength is acquired. Inorganic polymers acquire the highest compressive strength value of almost 60 MPa when 8 M KOH and 8% Na$_2$SiO$_3$ are used.

The presence of kaolin in the initial paste results in decreased compressive strength values. In the presence of metakaolin, derived from calcination of kaolin, the final compressive strength decreases

further; this is probably due to the increased porosity of the new structure as a result of thermal processing.

Pre-curing for a short period (e.g. 2 days) favours reactions between water and raw materials/additives so that an appropriate structural bonding is developed. Pre-curing for longer periods or prior to heating at temperatures higher than 80 °C does not further improve the final compressive strength.

XRD, TG–DTG and FTIR analyses of inorganic polymers may elucidate to some extent mechanisms involved during synthesis and predict the degree of amorphicity of the final products. Hydroxysodalite is identified in slag–kaolin inorganic polymers exhibiting high compressive strength. Thermogravimetric analysis shows that the presence of an optimum water content in the initial reactive paste affects positively the final compressive strength; DTG thermograms may be used to identify the formation of poly(sialatesiloxo) inorganic polymers. FTIR spectra reveal the transformations taking place during inorganic polymer synthesis corresponding mainly to Si–O bending and Al–O bonds.

Further research is required to overcome the industrial barriers and establish inorganic polymer technology as a feasible option for the management of potentially hazardous mining and metallurgical wastes. Industrial barriers involve mainly the entrenched position of OPC concrete and the conservative nature of the industry in adopting innovative technologies as well as in accepting new products. Such developments will contribute to considerable savings in disposal costs, recycling of wastes, substantial reduction of greenhouse gas emissions, higher degree of social acceptance of the industry and ultimately increase of sustainability of the wider minerals sector.

Acknowledgments

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