

# EFFECTS OF BLAST-FURNACE SLAG ON NATURAL POZZOLAN-BASED GEOPOLYMER CEMENT

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*A number of geopolymer cement mixes were designed and produced by alkali-activation of a pumice-type natural pozzolan. Effects of blast-furnace slag on basic engineering properties of the mixes were studied. Different engineering properties of the mixes such as setting times and 28-day compressive strength were studied at different amounts of blast-furnace slag, sodium oxide content, and water-to-cement ratio. The mix comprising of 5 wt.% blast-furnace slag and 8 wt.% Na<sub>2</sub>O with a water-to-dry binder ratio of 0.30 exhibits the highest 28-day compressive strength, i.e. 36 MPa. Mixes containing 5 wt.% of ground granulated blast furnace slag showed the least efflorescence or best soundness. Laboratory techniques of X-ray diffractometry (XRD), fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were utilized for characterizing a number of mixes and studying their molecular and micro-structure. Investigations done by scanning electron microscopy confirm that smaller blast-furnace slag particles react totally while the larger ones react partially with alkaline activators and contribute to the formation of a composite microstructure.*

## INTRODUCTION

Geopolymer cements are a group of alkali-activated materials exhibiting superior engineering properties compared to Portland cements. Synthesis of geopolymers is based on the activation of aluminosilicate materials by an alkali metal hydroxide and an alkali metal salt [1,2]. The aluminosilicate network consists of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedral structural units connected to each other by sharing their oxygen atoms. The presence of positive ions such as Na<sup>+</sup>, K<sup>+</sup> is necessary to balance the negative charge of aluminum [2-4].

In recent years, many research works have been carried out to investigate the possibility of utilizing industrial waste materials as raw material in the production of geopolymer cements. The use of granulated blast-furnace slag and fly ash has been reported in many research works [5,6]. Ground granulated blast-furnace slag (GGBFS) has latent hydraulic properties that could be activated using suitable activators [4]. The activation of blast-furnace slag with alkaline liquids (e.g., NaOH or water glass) to produce alkali-activated slag cement has been studied during the past few decades. Natural pozzolans can also be utilized as a suitable raw material for production of geopolymer cements [7-11]. Activation of mixtures of suitable raw materials however to produce geopolymer cement is almost a new approach.

This work however investigates the effects of ground granulated blast-furnace slag on a pumice-type natural pozzolan-based geopolymer cement. Using natural pozzolan, blast-furnace slag, and different alkali-activators based on combinations of Na<sub>2</sub>SiO<sub>3</sub> and NaOH, a number of slag-blended natural pozzolan-based geopolymer cements were designed and prepared and tested for investigating the effects of sodium oxide content, percentage of natural pozzolan replaced by ground granulated blast-furnace slag, and water-to-dry binder ratio on set and strength behaviors of natural pozzolan-based geopolymer cement. Laboratory techniques of X-ray diffractometry (XRD), fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were utilized in characterizing the material and studying the effects of blast-furnace slag on molecular and micro-structure of the natural pozzolan-based geopolymer cement.

## EXPERIMENTAL

### Raw Materials

Natural pozzolan, used in this work, was pumice obtained from Taftan Mountain, located at the south east of Iran. The obtained pozzolan was characterized for its chemical and mineralogical compositions and also

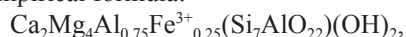
its pozzolanic activity. The results of chemical analysis determined according to ASTM standard C311 [12] are shown in Table 1.

The mineralogical phase composition of the pozzolan was determined by the use of powder X-ray diffraction (JEOL JDX-8030, Cu-K $\alpha$  radiation). Figure 1 shows the X-ray diffraction pattern of Taftan pozzolan. The crystalline mineral phases present in Taftan pozzolan therefore include:

Anorthite with empirical formula:



Hornblende with empirical formula:



Biotite with empirical formula:



The pozzolanic activity of Taftan pozzolan was also evaluated by determining its strength activity index with Portland cement at 7 and 28 days (ASTM C311) [12]. The results obtained, i.e. 83.2 and 86.8 % of control respectively for 7 and 28 days, show a relatively good pozzolanic activity in accordance with ASTM standard C618 [13].

Knowing that particle size distribution of pozzolan powder could effectively affect both wet and dry properties of natural pozzolan cement, the pozzolan was ground in an industrial closed mill to obtain a relatively highly fine powder with a suitable particle size distribution. The particle size distribution of pozzolan powder was determined by a laser particle size analyzer (Sympatec, GmbH, HDD). The Particle size distribution curve of pozzolan powder is presented in Figure 2. The slope of the curve and the mean particle size of the ground natural pozzolan are 0.95 and 22.63  $\mu\text{m}$ , respectively.

The value of specific surface area determined by Blaine air-permeability apparatus are shown in Table 1.

Granulated blast-furnace slag was prepared from Isfahan steel complex located in Isfahan province, Iran. The prepared slag was firstly ground in a laboratory ball mill to attain a Blaine specific surface area of 340  $\text{m}^2/\text{kg}$ . The chemical composition and the specific surface area of the blast-furnace slag are given in Table 1 and Figure 3 shows its X-ray diffraction pattern. As seen in Figure 3, the blast-furnace slag is not well amorphous and is mostly composed of akermanite and calcite crystalline mineral phases. The abnormal crystallinity of the slag must be due to improper quenching or cooling stage in the production process. According to the information taken from the producer, the slag was not quickly quenched in water or air, but for a while and during transportation stage was slowly cooled in the ambient temperature and then quenched in water.

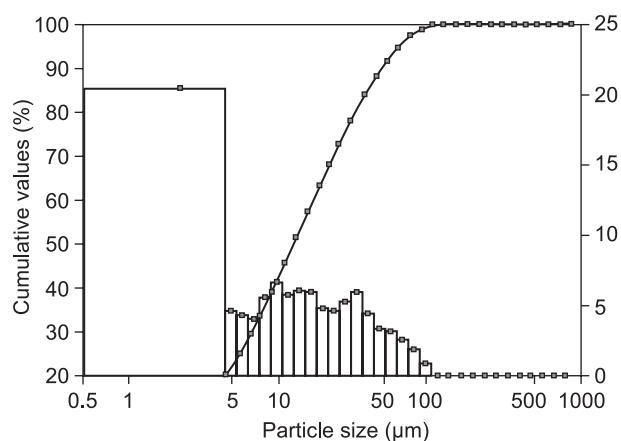


Figure 2. Particle size distribution of ground Taftan pozzolan.

Table 1. Chemical composition (wt.%) and Blaine fineness of ground pozzolan and blast-furnace slag.

Oxide	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Cl	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	MnO	Blaine (m <sup>2</sup> /kg)
Pozzolan	61.57	18.00	4.93	6.69	2.63	0.10	0.04	1.95	1.65	-	-	309
Slag	36.06	9.16	0.70	36.91	10.21	1.15	-	0.70	0.48	3.50	1.46	340

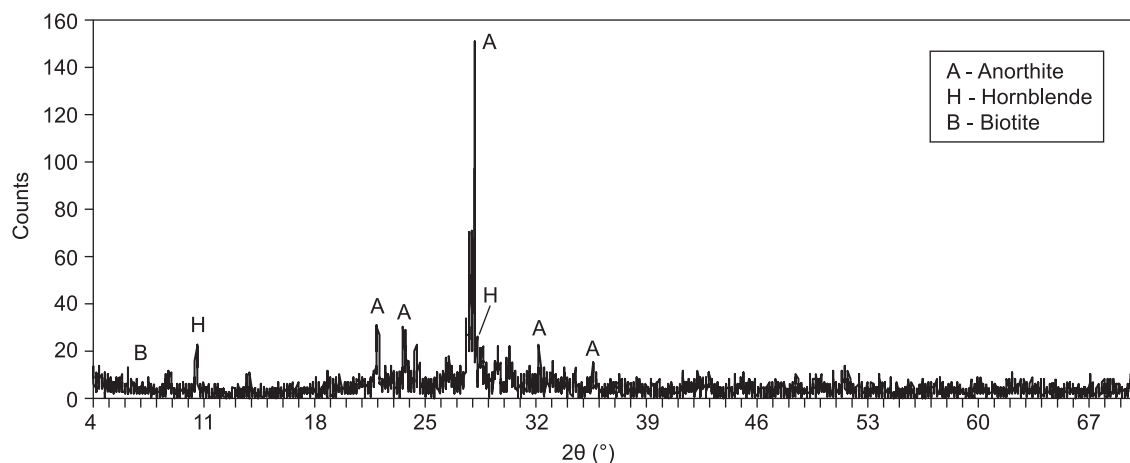


Figure 1. X-ray diffraction pattern of Taftan pozzolan.

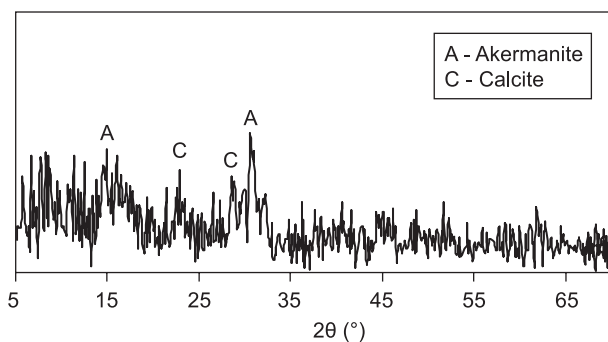


Figure 3. X-ray diffraction pattern of blast-furnace slag.

### Specimens Preparation

Commercial water-glass was used for preparing alkali-activators. The silica modulus ( $M_s$  = weight ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$ ) and  $\text{SiO}_2$  content of water glass are 0.86 and 34.32 w.t%, respectively. Enough sodium hydroxide was added to water-glass for preparing an alkali-activator having silica modulus of 0.60.

According to our previous work and recently published results [7], a silica modulus of 0.60 is the amount resulting the highest compressive strength. The sodium oxide contents of the designed geopolymer cement mixes coming from both sources of sodium hydroxide and sodium silicate of the activator were adjusted at three different levels of 4, 6, and 8% (by weight of dry binder). The water-to-dry binder ratio (W/C-ratio) was adjusted at four different values of 0.26, 0.28, 0.30 and 0.32. To calculate the W/C-ratio, we considered the total amount of water present in the mix including not only the water added individually, but also water coming from both sodium silicate and sodium hydroxide. Also four levels of slag weight percent including 0, 5, 15 and 25 were chosen for investigating the effects of which on set and strength behaviors of the mixes. After adding activators to the dry binders and mixing for 10 min manually, the pastes were cast into molds of  $2 \times 2 \times 2$  cm in size. The molds were held at ambient conditions ( $25^\circ\text{C}$  and 40% relative humidity) until the specimens were enough hardened to be removed (24 hr). After opening the molds, the specimens were stored and cured at ambient conditions until the time of testing.

### Test Procedure

The effects of sodium oxide content, W/C-ratio, and amount of blast-furnace slag on set and strength behaviors and soundness of the mixes were investigated by measuring their initial and final setting times, 28-day compressive strengths and inspecting any possible efflorescence. The setting times were measured using Vicat needle and in accordance with ASTM standard

C191-82 [14]. At the age of 28 days, the specimens were used to determine their compressive strengths. For each mix, three specimens were used and the average of the three values was reported as the result of 28-day compressive strength. To investigate any possible efflorescence, from each mix a 28-day hardened specimen was placed in a given volume of water, i.e. 40 ml, and kept in an open-air atmosphere at ambient temperature, i.e.  $25^\circ\text{C}$ , until the water was dried completely. The required time for 40 ml of water to completely dry was almost 2 weeks, but the specimens were held at the same conditions for 2 more weeks to be sure for complete drying at open air atmosphere. Dissolution properties of the used blast furnace slag and natural pozzolan were conducted by mixing 1.0 ( $\pm 0.0001$ ) g of solid with 20 ml of 10 molar NaOH solution for certain time (24 hr). Liquor portion was collected by a centrifugal separator at 5000 rpm for 10 min. Thus, concentrations of metallic ions leached out of the samples into the liquor were determined on  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  species by ICP technique, employing a Varian 720-ES analyzer. Mixes exhibiting the highest 28-day compressive strength were characterized by X-ray diffractometry (JEOL JDX-8030, Cu-K $\alpha$  radiation and Ni-filter), Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 740), and Scanning electron microscopy (SEM, Philips XL30).

## RESULTS AND DISCUSSION

### Effects of $\text{Na}_2\text{O}$ content, W/C-Ratio and blast-furnace slag on setting times

Since all the mixes exhibit relatively long setting times, the pastes were stored at an atmosphere of more than 95 % relative humidity at  $25^\circ\text{C}$  to prevent any setting due to drying and to measure the actual setting times. Figures 4 to 11 presents the results obtained for the effects of  $\text{Na}_2\text{O}$  content, W/C-ratio, and blast-furnace slag on initial and final setting times of mixes. As seen, all mixes exhibit relatively too long setting times, except those containing relatively higher contents of  $\text{Na}_2\text{O}$  and prepared at relatively lower W/C-ratios. Such long setting times could strongly restrict the applications of the material. In practice, before any actual setting due to geopolymerization reactions, the material will lose water and dry soon unless being kept in an atmosphere of more than 95% relative humidity. A relatively long setting time proves that geopolymerization reactions proceed very slowly at ambient temperature. It is seen that initial and final setting times are strongly affected by both  $\text{Na}_2\text{O}$  content and W/C-ratio. Increasing the  $\text{Na}_2\text{O}$  content could effectively accelerate the geopolymerization reactions which in turn results in a significant decrease in both initial and final setting times. A comparison of figures, however, clearly shows that incorporation of slag does not considerably affect the initial and final setting times.

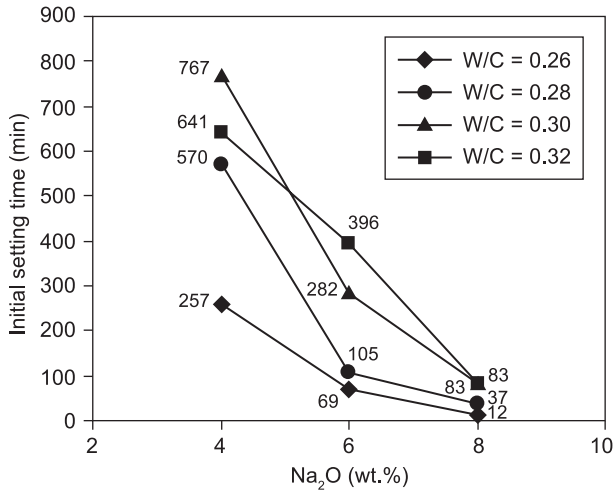


Figure 4. Effect of Na<sub>2</sub>O content on initial setting time of mixes containing 0 wt.% slag.

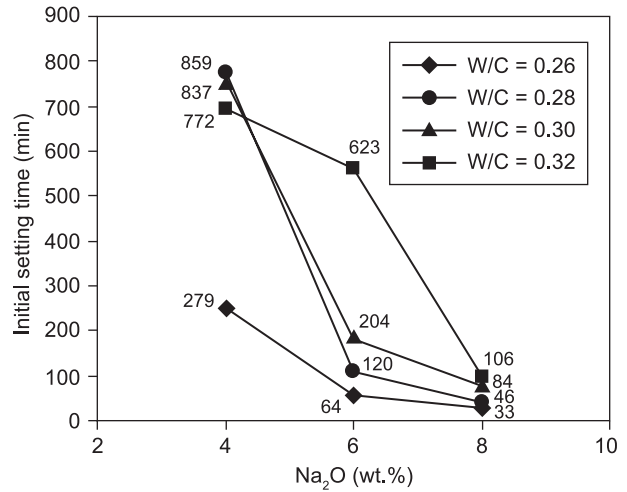


Figure 7. Effect of Na<sub>2</sub>O content on initial setting time of mixes containing 25 wt.% slag.

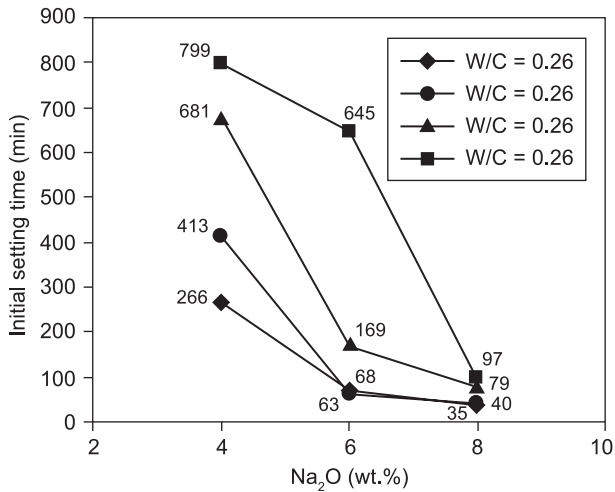


Figure 5. Effect of Na<sub>2</sub>O content on initial setting time of mixes containing 5 wt.% slag.

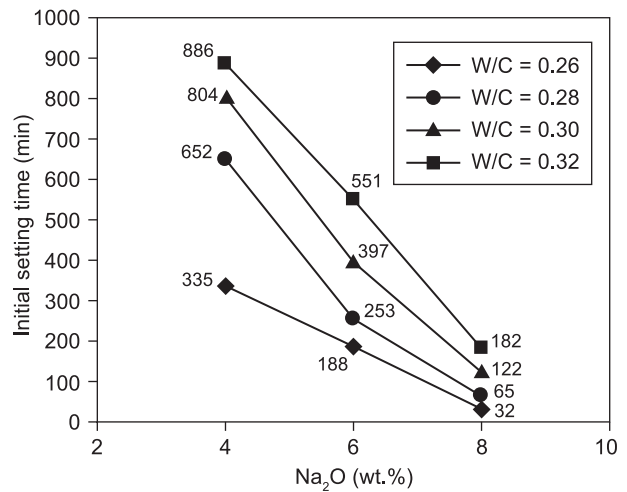


Figure 8. Effect of Na<sub>2</sub>O content on final setting time of mixes containing 0 wt.% slag.

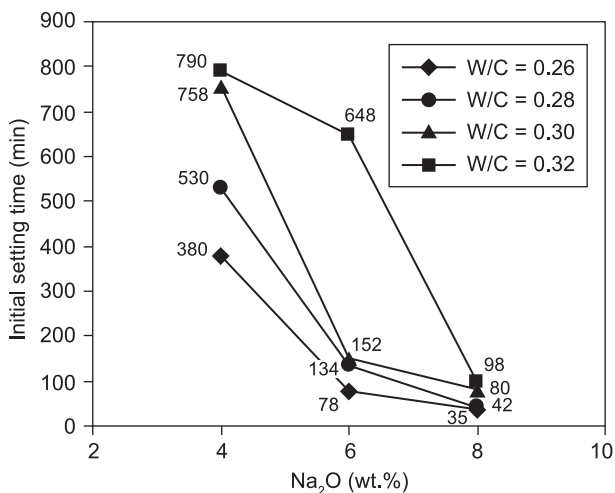


Figure 6. Effect of Na<sub>2</sub>O content on initial setting time of mixes containing 15 wt.% slag.

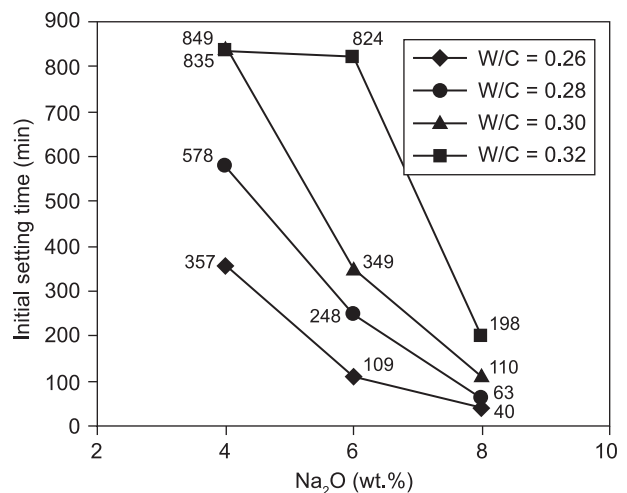


Figure 9. Effect of Na<sub>2</sub>O content on final setting time of mixes containing 5 wt.% slag.

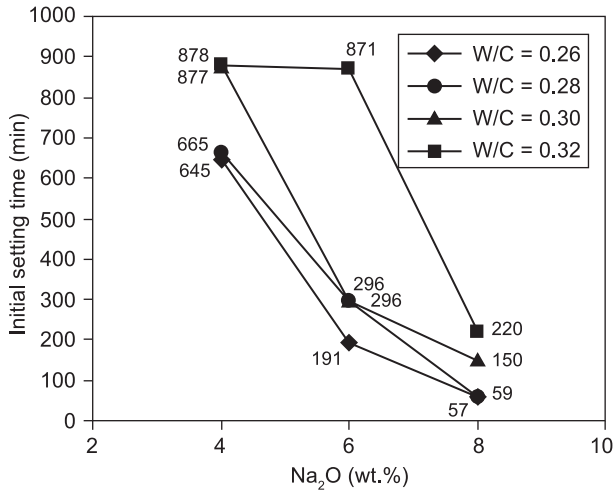


Figure 10. Effect of Na<sub>2</sub>O content on final setting time of mixes containing 15 wt.% slag.

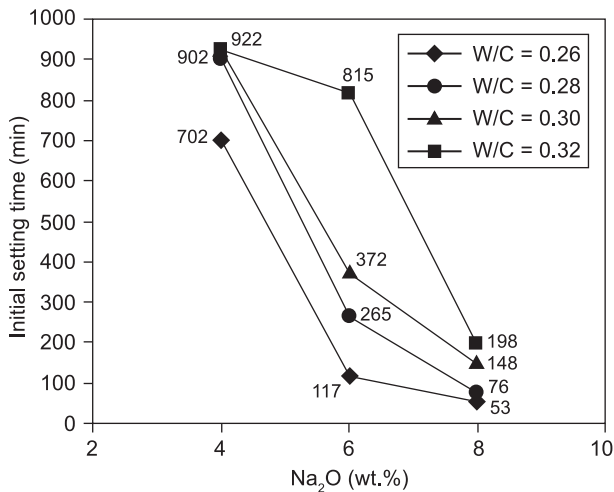


Figure 11. Effect of Na<sub>2</sub>O content on final setting time of mixes containing 25 wt.% slag.

#### Effects of sodium oxide content and W/C-ratio on 28-day compressive strength

Results obtained for the effects of sodium oxide content and W/C-ratio on 28-day compressive strength are presented in Figures 12 to 15. As seen, in general any increase in the content of sodium oxide, results in an increase in 28-day compressive strength. Considering the key role of sodium ion in the mechanism of geopolymerization reaction, i.e. dissolution of the aluminosilicates in the very first stage and charge balance of the 3-dimensional network in the last stage [2], one can conclude that increasing the sodium oxide content of the mix results in the acceleration of the geopolymerization reactions and causes the reactions to proceed to a higher extent. This in turn leads to an improvement in the strength behavior of the geopolymer

cement system. However, it must be considered that there should be an optimum for sodium oxide content. Increasing the sodium oxide content of the mix to values higher than optimum, probably results in a decrease in 28-day compressive strength due to the presence of excess sodium hydroxide. As mentioned before [2, 15, 16], in the process of alkali-activation of the aluminosilicate materials, the main roles of alkali metal cation in the form of sodium and/or potassium hydroxide is to prepare a medium for dissolution of the materials and also charge balancing of the tetrahedral Al<sup>3+</sup> in the geopolymer network. If the amount of sodium hydroxide coming from alkali activator is higher than the required amount of sodium cation for charge balancing of the Al<sup>3+</sup>, some of it will remain unreacted which we named it excess sodium hydroxide.

A significant difference can also be observed between the compressive strength of mixes with less than 6 wt.% sodium oxide content and those with 8 wt.% prepared at higher W/C-ratios. This difference is probably due to a fundamental change happening in the

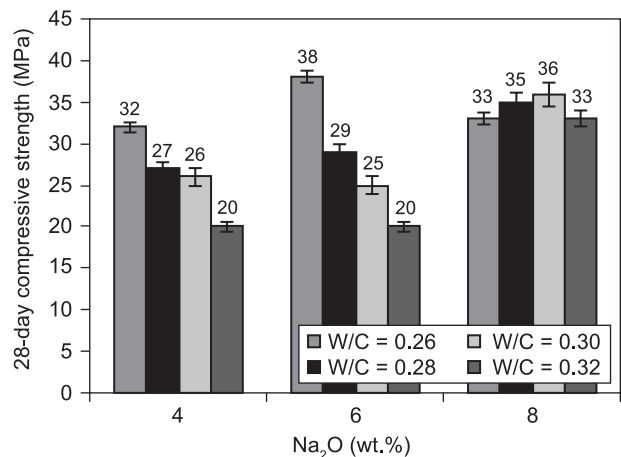


Figure 12. Effect of Na<sub>2</sub>O content on 28-day compressive strength of mixes containing no slag.

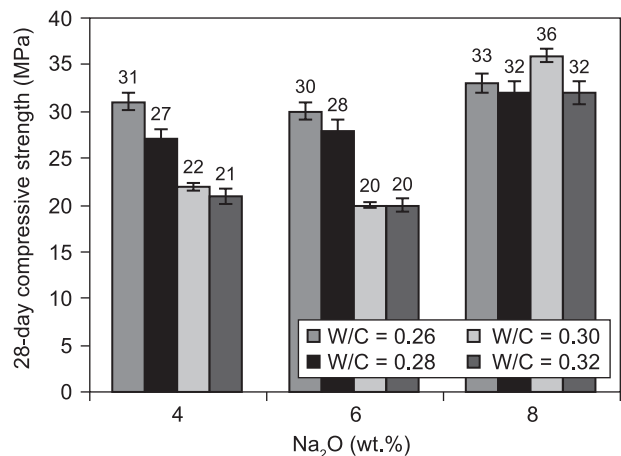


Figure 13. Effect of Na<sub>2</sub>O content on 28-day compressive strength of mixes containing 5 wt.% slag.

geopolymerization reactions. Higher alkalinity along with a better contact of reacting materials caused by a more effective mixing at relatively higher W/C-ratios probably enhances the reactivity of the materials. In other words, such conditions could probably result in a higher degree of dissolution of the pozzolan in the alkaline medium producing a higher amount of geopolymer gel. This scientific reasoning, however, requires detailed investigations with suitable laboratory techniques to be scientifically confirmed.

The effects of W/C-ratio on 28-day compressive strength of mixes could also be observed in the same figures. As seen, in all the cases except mixes containing 8 wt.% Na<sub>2</sub>O, any increase in W/C-ratio results in a decrease in 28-day compressive strength. Usually W/C-ratio is increased for increasing the workability of inorganic binders in the form of paste, mortar, and concrete. However, it should be noted that in most cases any increase in W/C-ratio results in an increase in the total pore volume which in turn weakens the strength behavior of the material. In some cases a relatively high

W/C-ratio could also result in a relatively high drying shrinkage which may itself lead to shrinkage cracks working as macro-defect points.

For mixes containing 8 wt.% Na<sub>2</sub>O, however, the effect of W/C-ratio is quite different. An increase in W/C-ratio, up to 0.30, results in a small increase in 28-day compressive strength. More increase in W/C-ratio from 0.30 to 0.32 results in a small decrease in 28-day compressive strength. The small increase in 28-day compressive strength, when increasing the W/C-ratio from 0.26 to 0.30 is probably due to better ionization of sodium oxide. At relatively higher contents of sodium oxide, e.g. 8 wt.%, a small increase in water could result in a better ionization of sodium oxide along with a more uniform distribution of sodium cations. These in turn provide better conditions for geopolymerization reactions and therefore enhancing the strength behavior of the material.

Effects of blast-furnace slag on 28-day compressive strength

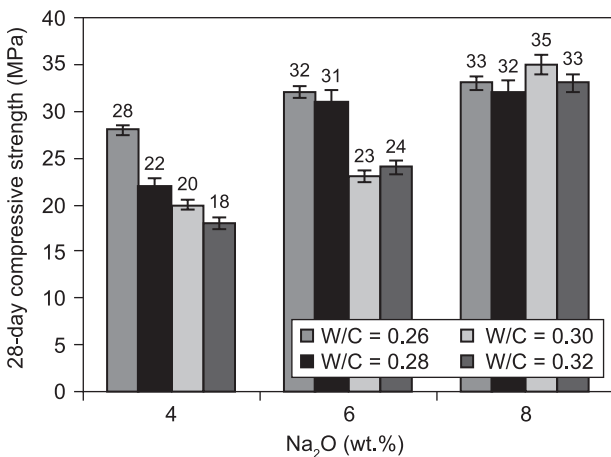


Figure 14. Effect of Na<sub>2</sub>O content on 28-day compressive strength of mixes containing 15 wt.% slag.

Results obtained for the effects of slag on 28-day compressive strength at W/C-ratios of 0.26 and 0.32 are presented in Figures 16 and 17, respectively. As seen, incorporation of the used blast-furnace slag does not provide any improvement in strength behavior of the studied natural pozzolan-based geopolymer cement and at relatively higher replacement percentages up to 25 wt.%, it causes a decrease in 28-day compressive strength.

Utilization of blast-furnace slag in production of alkali-activated cement has been reported in many research works. Since blast-furnace slag is a material with latent hydraulic properties and very suitable for alkali-activation, the alkali-activated blast-furnace slag cements usually exhibit very good strength behavior [4, 17-19]. The negative effect of slag on 28-day com-

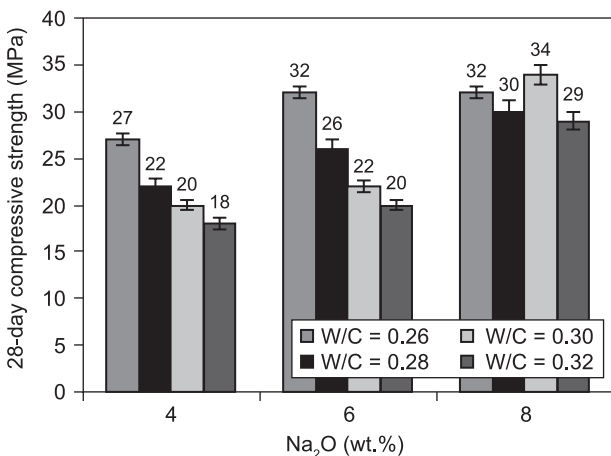


Figure 15. Effect of Na<sub>2</sub>O content on 28-day compressive strength of mixes containing 25 wt.% slag.

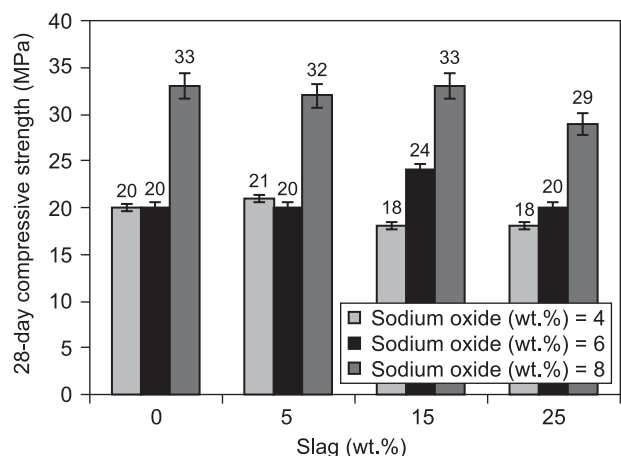


Figure 16. Effect of slag on 28-day compressive strength at W/C of 0.26.

pressive strength of natural pozzolan-based geopolymer cement in this study, however, could be attributed to the changes made in chemical composition of the dry binder. It is reported that a decrease in Si/Al-ratio of the dry binder could result in an improvement in the strength behavior of geopolymer cement [4]. As seen in Figure 18, incorporation of slag increases the Si/Al-ratio of the dry binder to values higher than 3.6. This could be the reason for weakening the strength behavior at relatively high percentages of replacement.

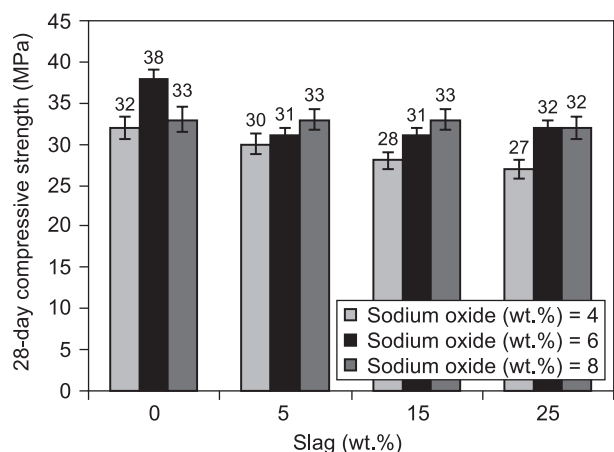


Figure 17. Effect of slag on 28-day compressive strength at W/C of 0.32.

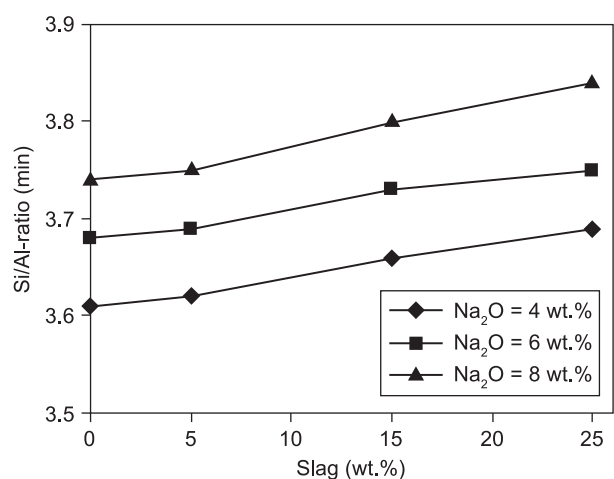


Figure 18. Variation of Si/Al-ratio of dry binder with slag.

Effects of Na<sub>2</sub>O content, W/C-ratio and blast-furnace slag on efflorescence

From each mix, a 28-day hardened paste specimen was tested to investigate any possible efflorescence. The results of efflorescence were obtained qualitatively by just comparing the specimens visually. Table 2 presents the results obtained. The severity of the efflorescence has been differentiated by letters A, B and C. Mixes exhibiting no efflorescence are shown by letter A. Those

showing slight and severe efflorescence are distinguished by letters B and C, respectively. Figure 19 shows three specimens exhibiting no, slight, and severe efflorescence. As seen in Table 2, most of the mixes containing 4 wt.% Na<sub>2</sub>O do not show any efflorescence. An increase of 2 wt.% in Na<sub>2</sub>O content however results in appearance of efflorescence. Most of mixes containing 8 wt.% sodium oxide exhibit severe efflorescence.

Table 2. Effects of Na<sub>2</sub>O content, W/C-ratio, and blast-furnace slag on severity of efflorescence.

Mix No.	Na <sub>2</sub> O (wt.%)	W/C	Slag (wt.%)	Efflorescence severity
1	4	0.26	0	B
2	4	0.26	5	A
3	4	0.26	15	A
4	4	0.26	25	A
5	4	0.28	0	A
6	4	0.28	5	A
7	4	0.28	15	A
8	4	0.28	25	B
9	4	0.30	0	A
10	4	0.30	5	A
11	4	0.30	15	B
12	4	0.30	25	B
13	4	0.32	0	A
14	4	0.32	5	A
15	4	0.32	15	B
16	4	0.32	25	B
17	6	0.26	0	B
18	6	0.26	5	B
19	6	0.26	15	B
20	6	0.26	25	B
21	6	0.28	0	B
22	6	0.28	5	B
23	6	0.28	15	B
24	6	0.28	25	C
25	6	0.30	0	C
26	6	0.30	5	B
27	6	0.30	15	C
28	6	0.30	25	B
29	6	0.32	0	B
30	6	0.32	5	B
31	6	0.32	15	B
32	6	0.32	25	B
33	8	0.26	0	C
34	8	0.26	5	B
35	8	0.26	15	B
36	8	0.26	25	B
37	8	0.28	0	C
38	8	0.28	5	C
39	8	0.28	15	C
40	8	0.28	25	C
41	8	0.30	0	B
42	8	0.30	5	A
43	8	0.30	15	B
44	8	0.30	25	A
45	8	0.32	0	B
46	8	0.32	5	B
47	8	0.32	15	B
48	8	0.32	25	C

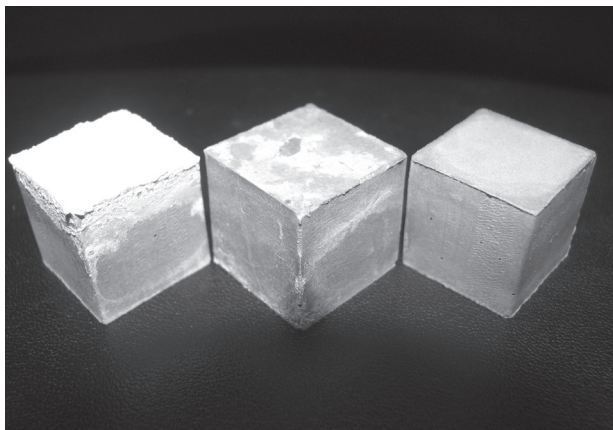


Figure 19. Specimens exhibiting no, slight, and severe efflorescence (from right).

A comparison of the results of 28-day compressive strength and efflorescence reveal that a relatively high compressive strength attainable at higher  $\text{Na}_2\text{O}$  contents does not necessarily mean soundness and durability. On the other hand, mixes showing no efflorescence do not exhibit good 28-day compressive strength. Previous investigations have proved that the appearance of efflorescence is due to leaching of non-reacted sodium hydroxide which later in a secondary reaction reacts with atmospheric carbon dioxide producing sodium carbonate [20, 21]. An optimum  $\text{Na}_2\text{O}$  content along with hydrothermal treatment of paste specimens probably could result in development of a suitable geopolymer cement system. As seen, all the specimens containing slag show an improvement in severity of efflorescence compared to those with no slag. A comparison of the results, however, shows that a 5 wt.% replacement of natural pozzolan by slag is the optimum amount considering the relative reduction in severity of the efflorescence. It seems that higher percentages of replacement do not result in any more reduction in the efflorescence.

#### Dissolution Properties

Table 3 represents the extent of dissolution of Al and Si in relation to the used blast furnace slag and natural pozzolan in 10 molar NaOH solution for 24 hr. As seen, natural pozzolan released higher amounts of Si and Al than blast furnace slag confirming a higher extent of dissolution for natural pozzolan. The process of geopolymerization starts with dissolution of Al and Si from aluminosilicate materials in alkaline solution forming the alkali aluminosilicate gel, which result in subsequent setting and hardening [22]. Consequently, an understanding of the extent of dissolution of the used aluminosilicates is imperative for an understanding of geopolymerization reactions and the effect of slag on the properties of natural pozzolan based geopolymer. As

observed previously, replacement of natural pozzolan with blast furnace slag results in reduced compressive strengths except limited increase at relatively lower levels of replacement, i.e. 5 wt.%. The lower extent of dissolution of blast furnace slag in alkaline activating media lowers the amount of total geopolymer gel formed in the first stages of the geopolymerization reactions. This reduces the extent of geopolymerization reactions which in turn lowers the compressive strength of the material. The very limited increase in compressive strength at relatively lower levels of replacement, i.e. 5 wt.%, can be attributed to a probable dense packing and/or reinforcement effects brought about by the particles of blast furnace slag.

Table 3. Extent of Al and Si dissolution in 10 molar NaOH solution for 24 hr.

Material	Extent of dissolution (ppm)	
	Si	Al
Natural Pozzolan	216.72	52.64
Blast furnace slag	181.70	46.25

#### X-Ray Diffraction

X-ray diffraction patterns of 28-day hardened paste of geopolymer cement system containing 5 wt.% slag prepared at  $\text{Na}_2\text{O}$  content of 8 wt.% and W/C-ratio of 0.30, and 28-day hardened paste of geopolymer cement system containing no slag prepared at  $\text{Na}_2\text{O}$  content of 8 wt.% and W/C-ratio of 0.30 are presented in Figures 20 and 21, respectively.

As mentioned above, the geopolymer cement mix comprising of 5 wt.% blast-furnace slag and 8 wt.%  $\text{Na}_2\text{O}$  with a W/C-ratio of 0.30 exhibits the highest 28-day compressive strength, i.e. 36 MPa, along with almost acceptable initial and final setting times compared to Portland cement and shows the least efflorescence. As seen in Figure 1 and discussed earlier, the pumice-type natural pozzolan used in this work contains a number of crystalline phases including anorthite, hornblende, and biotite. The blast-furnace slag is mainly amorphous in view of the large diffuse diffraction peak centered at  $30^\circ$  ( $2\theta$ ) as seen in Figure 3. The interesting point is the presence of crystalline phases in both geopolymer cement systems. In addition to the diffuse halo diffraction peaks, centered around  $30^\circ$  ( $2\theta$ ) and implying that the materials are partially amorphous, the two X-ray diffraction patterns also show a number of sharp peaks corresponding to Albite (empirical formula;  $\text{Na}_{0.95}\text{Ca}_{0.05}\text{Al}_{1.05}\text{Si}_{2.95}\text{O}_8$ , and chemical formula;  $\text{NaAlSi}_3\text{O}_8$ ) as the main crystalline phase and Actinolite (empirical formula;  $\text{Na}_{0.05}\text{Ca}_{0.95}\text{Al}_{1.95}\text{Si}_{2.05}\text{O}_8$ , and chemical formula;  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) and Termolite (empirical formula;  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ ) as the minor crystalline phases.



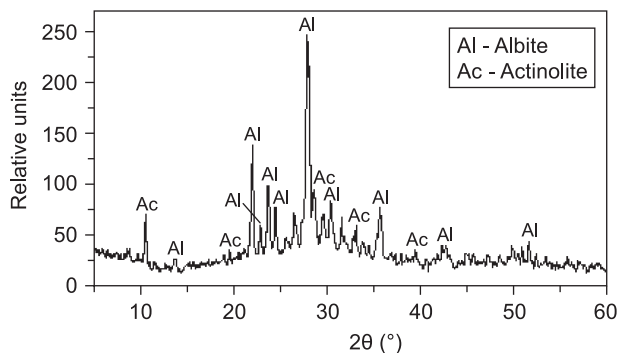


Figure 20. X-ray diffraction pattern of 28-day hardened paste of geopolymer cement mix containing 5 wt.% slag prepared at  $\text{Na}_2\text{O}$  content of 8 wt.% and W/C-ratio of 0.30.

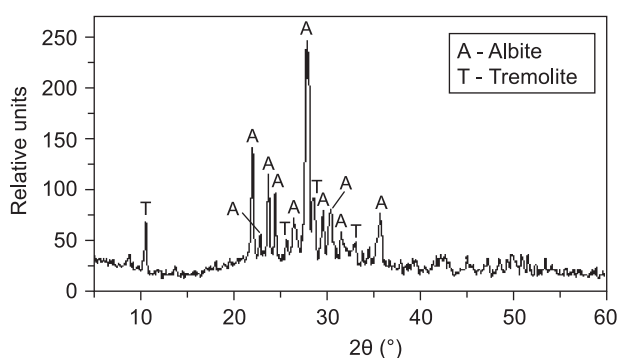


Figure 21. X-ray diffraction pattern of 28-day hardened paste of geopolymer cement mix containing no slag prepared at  $\text{Na}_2\text{O}$  content of 8 wt.% and W/C-ratio of 0.30.

The main crystalline phases of Taftan pozzolan and geopolymer cement mixes, i.e. Anorthite and Albite respectively, are similar and belong to the same group of plagioclase with chemical formula of  $(\text{Na,Ca})(\text{Si,Al})_4\text{O}_8$ , differing in their cations and their  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  ratio. This shows that activation of natural pozzolan with  $\text{Na}_2\text{SiO}_3$  and  $\text{NaOH}$  could result in changes in mineralogical phase composition of the crystalline part of the material, i.e. conversion of Anorthite to Albite, in addition to the geopolymerization reactions in the amorphous part of the material. The absence of binding property in the plagioclase minerals implies that the strength behavior of the material is due to geopolymers produced in the amorphous part of the material.

#### Fourier transform infrared spectroscopy

Figure 22 displays infrared spectra of natural pozzolan, blast-furnace slag, 28-day hardened paste of geopolymer cement prepared at  $\text{Na}_2\text{O}$  content of 8 wt.% and W/C-ratio of 0.30 (sample a), and 28-day hardened paste of geopolymer cement mix containing 5 wt.% slag prepared at  $\text{Na}_2\text{O}$  content of 8 wt.% and W/C-ratio of 0.30 (sample b).

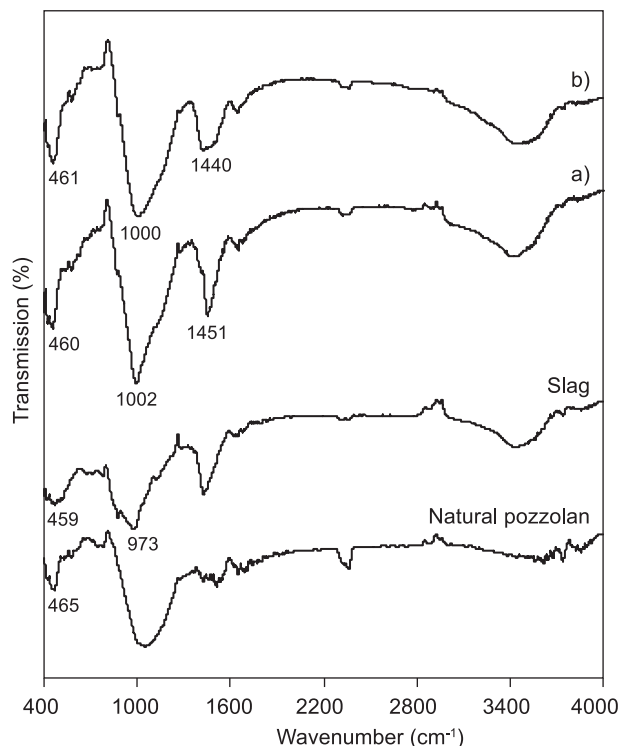


Figure 22. Infrared spectra of natural pozzolan, blast-furnace slag, 28-day hardened paste of geopolymer cement prepared at  $\text{Na}_2\text{O}$  content of 8 wt.% and W/C-ratio of 0.30 (a), and 28-day hardened paste of geopolymer cement containing 5 wt.% slag prepared at  $\text{Na}_2\text{O}$  content of 8 wt.% and W/C-ratio of 0.30 (b).

Infrared spectra of the samples are rather similar, presenting analogous absorption bands. All show bands at 3440 and 1650  $\text{cm}^{-1}$ , respectively, related to O–H stretching and bending modes of molecular water and also near 1000  $\text{cm}^{-1}$  and at 450  $\text{cm}^{-1}$  due to anti-symmetric Si–O(Al) stretching vibrations and to in-plane Si–O bending vibrations in  $\text{SiO}_4$  tetrahedra, respectively [23,24].

As seen in Figure 22, in spectra of samples a and b, there exist a main broad and strong absorption peak appearing at about 1000  $\text{cm}^{-1}$ , a fairly broad and relatively strong peak at about 460  $\text{cm}^{-1}$ , and a number of very weak peaks in the range 500 ~ 900  $\text{cm}^{-1}$ . The first of these bands that is the most intensive is usually a superposition of some bands situated close to each other. The principal band associated with the Si–O(Al) stretching vibrations in  $\text{SiO}_4$  tetrahedral near 1000  $\text{cm}^{-1}$  is very broad [5, 23, 24].

The Si–O stretching modes for the  $\text{SiQ}^n$  units show infrared absorption bands localized around 1100, 1000, 950, 900, and 850  $\text{cm}^{-1}$  for  $n=4, 3, 2, 1,$  and 0, respectively [23]. These values shift to lower wavenumbers when the degree of silicon substitution by aluminium in the second coordination sphere increases, as a consequence of the weaker Al–O bonds. In Figure 22, it appears that this Si–O stretching band shifts progressively towards greater

wavenumbers from  $1000\text{ cm}^{-1}$  for sample b to  $1002\text{ cm}^{-1}$  for sample a. These results indicate a distribution of the  $Q^n$  units centered around  $Q^2$  and  $Q^3$  units for sample b), while the shift to higher wavenumbers points out the presence of more polymerised units such as  $Q^3$  and  $Q^4$  units for sample a).

The main peaks of interest in geopolymer materials are peaks at  $\sim 460\text{ cm}^{-1}$  assigned to the in-plane bending of Al–O and Si–O linkages, while the peaks at around  $1000\text{ cm}^{-1}$  have been attributed to asymmetric stretching of Al–O and Si–O bonds originating from individual tetrahedral [24]. The peaks at  $\sim 1000\text{ cm}^{-1}$  are a major fingerprint for geopolymer materials representing the fusion of both Al–O and Si–O asymmetric stretching and can indicate the extent of aluminum incorporation with a lowering in the energy of the peak. Octahedrally coordinated aluminium if present can be detected by a peak at  $540\text{ cm}^{-1}$  [5] while tetrahedral aluminium shows a weak peak at about  $800\text{ cm}^{-1}$ , which is due to symmetric Al–O stretching.

Samples a and b contain carbonate species with different intensities pointed out by the presence of the large absorption band near  $1450\text{ cm}^{-1}$ , related to anti-symmetric stretching and out of plane bending modes of  $\text{CO}_3^{2-}$  ions [25, 26].

#### Scanning Electron Microscopy

Investigations done by scanning electron microscopy (SEM) on 28-day hardened paste of geopolymer cement mix containing 5 wt.% slag prepared at  $\text{Na}_2\text{O}$  content of 8 wt.% and W/C-ratio of 0.30 clearly confirm the presence

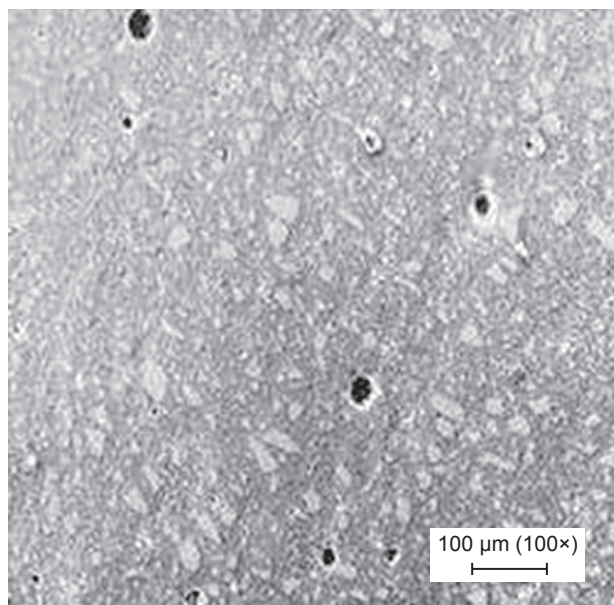


Figure 23. SEM image from microstructure of 28-day hardened paste of geopolymer cement containing 5 wt.% slag prepared at  $\text{Na}_2\text{O}$  content of 8 wt.% and W/C-ratio of 0.30.

of an amorphous matrix in which particles of various shapes and sizes are embedded (Figure 23). Elemental point analyses were done by EDX on embedded particles. The results are listed in Table 4, where each value is the average of the measurements.

Table 4. Extent of Al and Si dissolution in 10 molar NaOH solution for 24 hr.

Elements	Relatively small particles	Relatively large particles
Si	33.59	29.41
Al	10.45	8.75
Na	3.05	–
Ca	–	48.93
Mg	–	9.65

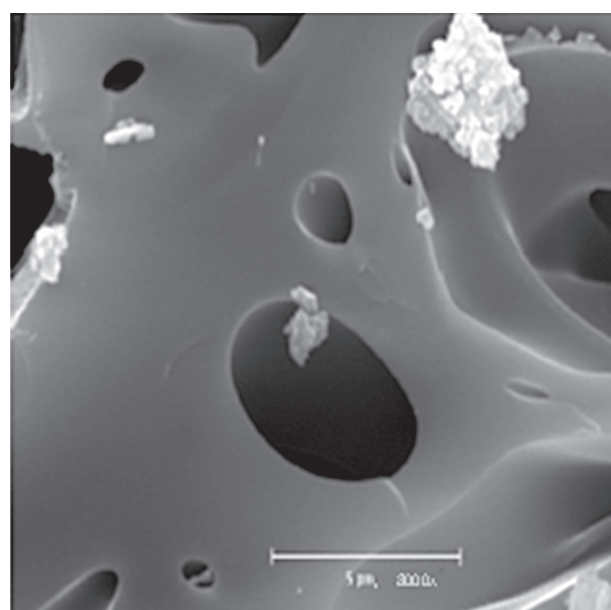
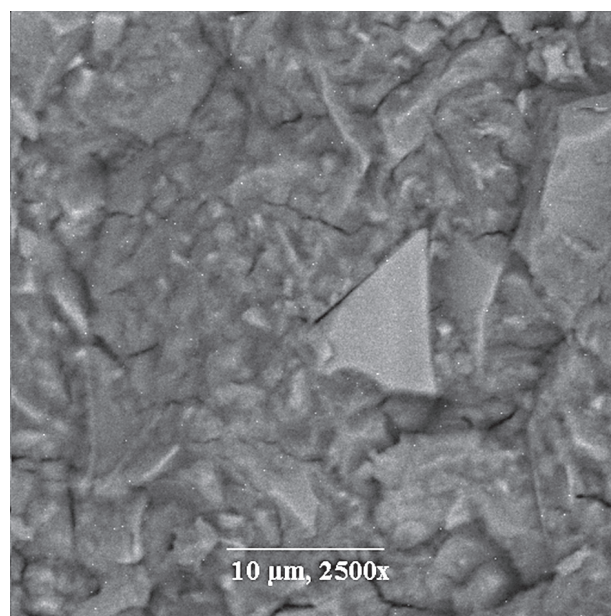


Figure 24. SEM images from the matrix of the microstructure of the geopolymer cement mix at two different magnifications.

In the view of chemical composition, relatively small particles are crystals of Albite that is the main crystalline phase of the material and relatively large particles are grains of blast-furnace slag. This conclusion confirms previous results suggesting that smaller blast-furnace slag particles react totally while the larger ones react partially with alkaline activators and contribute to the formation of the binding matrix of the composite [27]. Figure 24 shows micrographs from the microstructures of the material at two different magnifications. A slag particle embedded in the amorphous matrix is displayed in the left-side micrograph and the amorphous matrix itself is shown in the right-side micrograph.

### CONCLUSION

1. Incorporation of the used blast-furnace slag does not provide any improvement in set and strength behaviors of the studied natural pozzolan-based geopolymer cement. At relatively higher replacement percentages of slag up to 25 wt.%, it causes a decrease in 28-day compressive strength. This could be attributed to the lower extent of dissolution of blast furnace slag in alkaline activating media.
2. The paste specimens of the geopolymer cement mix based on natural pozzolan and comprising of 5 wt.% blast-furnace slag, activated with 8 wt.% Na<sub>2</sub>O, and produced at a W/C-ratio of 0.30 are sound with no efflorescence and exhibit the highest 28-day compressive strength, i.e. 36 MPa, along with almost acceptable initial and final setting times.
3. Activation of natural pozzolan with Na<sub>2</sub>SiO<sub>3</sub> and NaOH could result in changes in mineralogical phase composition of the crystalline part of the material, i.e. conversion of Anorthite to Albite, in addition to the geopolymerization reactions in the amorphous part of the material.
4. Smaller blast-furnace slag particles react totally while the larger ones react partially with alkaline activators and contribute to the formation of a composite microstructure composed of an amorphous matrix in which relatively large particles of slag and relatively small crystals of Albite are embedded.

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