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Effects of curing time and temperature on strength development of inorganic polymeric binder based on natural pozzolan

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Abstract This paper reports the results of a study on the influence of curing conditions on compressive strength development in inorganic polymeric binder prepared from natural pozzolan. Three mixes with different chemical formulations were prepared and cured hydrothermally at different temperatures and times. In particular, the effect of a precuring at an atmosphere of more than 95% relative humidity at room temperature on compressive strength development before the application of heat was studied. Different curing regimes including hydrothermal treatment in steam-saturated atmosphere at different temperatures of 45, 65, 85 °C and for different time periods of 5, 10, 15, and 20 h after 1 and 7 days of precuring were applied. The mix exhibiting the maximum compressive strength after hydrothermal treatment was selected and cured in autoclave at temperatures of 125, 150, 180, and 210 °C for different time periods of 20, 30, 40, and 50 h for investigating the effects of higher times and temperatures of curing on strength development and also to determine the maximum achievable compressive strength. Results show that relatively long precuring in humid atmosphere is very beneficial for compressive strength development. The highest compressive strength achieved for three different regimes of curing including 28 days at an atmosphere of more than 95% relative humidity at 25 °C, 20 h hydrothermal treatment at 85 °C after 1 day precuring, and 20 h hydrothermal treatment at 85 °C after 7 days precuring were 37.5, 37.5, and 57.5 MPa, respectively. The maximum achievable compressive strength under autoclave curing at 210 °C for 30 h after 7 days of precuring was 108.7 MPa.

Introduction

Inorganic polymeric binders, i.e., geopolymer cements, are a group of alkali-activated materials exhibiting superior engineering properties compared to Portland cement. Synthesis of geopolymers is based on the activation of suitable aluminosilicate materials by an alkali metal hydroxide and an alkali metal salt. According to Davidovits [1], a time period of curing at temperatures in the range between 25 and 90 °C completes the process necessary for geoplymerization reactions. Due to their inorganic framework, geopolymers are intrinsically fire resistant and have shown excellent thermal stability compared to Portland cements. Geopolymers have also been shown to exhibit superior mechanical properties to those of ordinary Portland cement (OPC) [2, 3]. However, compared to other material processing technologies, research focused on understanding the relationships between composition, processing, microstructure, and the properties (e.g., mechanical strength) of geopolymers needs more completion.

Several researchers have investigated the effects of different curing conditions on properties of geopolymer cements made of fly ash or metakaolin [4–9]. Bakharev [4] investigated the effect of different curing regimes and precuring at room temperature on the strength development and hydration products of Class F fly ash activated by sodium silicate and sodium hydroxide. The study by Swanepoel and Strydom [5] investigated utilization of fly ash and kaolinite clay in a geopolymeric material cured at temperatures up to 70 °C. Palomo et al. [6] presented a study of alkali-activated fly ashes cured at 65 and 85 °C at

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two liquid/solid ratios, i.e., 0.25 and 0.3 that indicate formation of an amorphous alkali aluminosilicate similar to that obtained in the alkali activation of metakaolin and exhibiting compressive strengths up to 60 MPa. Perera et al. [8] studied the curing of a metakaolinite-based geopolymer at ambient and controlled relative humidity (RH) with mild heating (40–60 °C) to obtain geopolymers free of cracks. They reported that curing at a lower RH (e.g., 30%) is preferable to that at a higher RH (e.g., 70%).

Van Jaarsveld et al. [9] have proved that curing for longer periods of time at elevated temperatures appears to weaken the structure, suggesting thus that small amounts of structural water need to be retained in order to eliminate cracking and maintain structural integrity. In addition, they [9] have claimed that initial curing at higher temperatures (above 50–80 °C) does not increase compressive strength substantially above that achieved by curing at room temperature. In general, adequate curing is required to achieve advanced mechanical and durability performance in geopolymeric materials.

In this work, three inorganic polymeric binders based on natural pozzolan with different chemical formulations were prepared and cured hydrothermally at 45, 65, 85, and 105 °C for different times of 5, 10, 15, and 20 h to determine the optimum time and temperature of steam curing at atmospheric pressure. In particular, the effect of storing at an atmosphere of more than 95% relative humidity at room temperature, before the application of heat, on compressive strength development was studied. For investigating the effects of higher times and temperatures of curing on strength development and to determine the maximum achievable compressive strength, autoclave curing at temperatures of 125, 150, 180, and 210 °C for different time periods of 20, 30, 40, and 50 h was applied on mixes exhibiting higher compressive strengths after hydrothermal curing at atmospheric pressure. X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) techniques were utilized for studying the effects of curing conditions on molecular and microstructure of the material.

Experimental

Raw materials

Natural pozzolan used in this work was pumice-type obtained from Taftan Mountain, located at the south east of Iran. The obtained pozzolan was firstly characterized for its chemical and mineralogical compositions and also its pozzolanic activity. The results of chemical analysis determined according to ASTM standard C311 are shown in Table 1. As seen, this natural pozzolan is a relatively high siliceous one. Figures 1 and 2 show the X-ray diffraction pattern and FTIR spectrum of the used pozzolan, respectively. As seen in Fig. 1, the crystalline mineral phases present in Taftan pozzolan include:

Feldspar (Anorthite with empirical formula; $Na_{0.05}Ca_{0.95}Al_{1.95}Si_{2.05}O_8$),
Amphibole (Hornblende with empirical formula; $Ca_2Mg_4Al_{0.75}Fe^{3+}_{0.25}(Si_7AlO_{22})(OH)_2$),
Mica (Biotite with empirical formula; $KMg_{2.5}Fe^{2+}_{0.5}AlSi_3O_{10}(OH)_{1.75}F_{0.25}$).

As seen in Fig. 2, the FTIR spectrum of the pozzolan shows two strong peaks. One at wavenumbers about 460 cm^{-1} and the other a broad peak at wavenumbers in the range between 1007 and 1050 cm^{-1}, which are both attributed to asymmetric stretching of Al–O and Si–O bonds of aluminosilicate structure.

The pozzolanic activity of Taftan pozzolan was also evaluated by determining its strength activity index with Portland cement at 7 and 28 days in accordance with ASTM C311. 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. The prepared sample of pozzolan, previously ground in an industrial closed mill to attain a Blaine specific surface area of 305 m^2/kg, was a relatively highly fine powder. The particle size distribution of which was determined by a laser particle size analyzer (Sympatec, GmbH, HDD) and the corresponding curve is presented in Fig. 3. The mean particle size of the ground natural pozzolan was 22.63 μm. Industrial sodium silicate solution (weight ratio of $SiO_2/Na_2O=0.92$ and $SiO_2=31.36$ wt%) and industrial-grade NaOH (99% purity) were used throughout all experiments.

Specimens preparation

Three inorganic polymeric binders based on natural pozzolan with different chemical formulations exhibiting suitable set and strength behavior were selected according to previous work [10, 11]. Chemical compositions of the selected mixes have been varied by changing SiO_2/Na_2O

Table 1 Chemical composition of pozzolan

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Cl^-	LOI
wt%	61.57	18.00	4.93	6.69	2.63	0.10	1.95	1.65	0.04	2.15

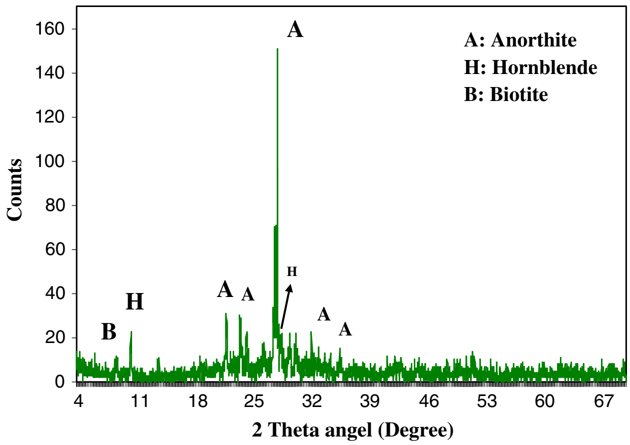

Fig. 1 X-ray diffraction pattern of pozzolan

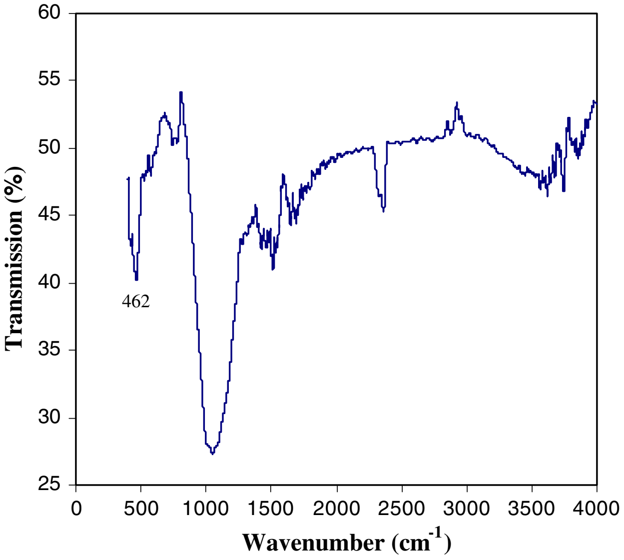

Fig. 2 FTIR spectrum of pozzolan

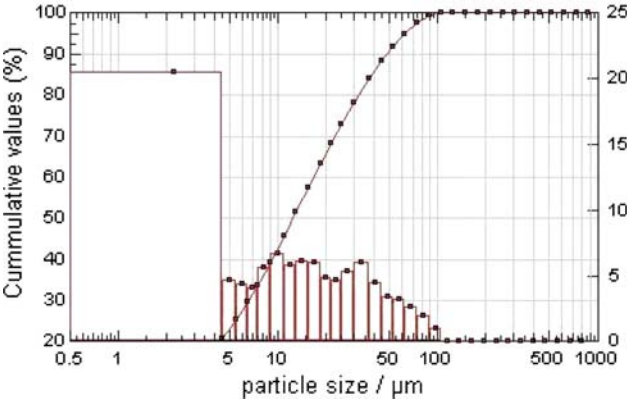

Fig. 3 Particle size distribution of ground pozzolan

Table 2 Chemical composition of cementing mixtures (at a constant total H_2O/Al_2O_3 molar ratio of 8.50)

Mix name	Activator SiO_2/Na_2O molar ratio (adjusted)	Total Na_2O/Al_2O_3 molar ratio (adjusted)	Total SiO_2/Al_2O_3 molar ratio (calculated)
IP1	0.75	0.92	6.00
IP2	0.6	1.08	5.90
IP3	0.6	1.23	5.98

(Si/Na) molar ratio of activator and Na_2O/Al_2O_3 (Na/Al) total molar ratio of cementing mixture. Enough sodium hydroxide was added to sodium silicate solution and the dosage of activator was so adjusted to prepare cementing mixtures, i.e., dry binder and activator together, having molar ratios of Si/Na and Na/Al adjusted at the values given in Table 2. The corresponding calculated values for total SiO_2/Al_2O_3 (Si/Al) molar ratio are also given in Table 2. The prepared paste was then cast into 2 × 2 × 2 cm^3 molds after enough mixing. Previous results [10] have shown that a simple curing regime of 28 days storing at an atmosphere of 95% relative humidity at 25 °C for the mixes named IP1, IP2, and IP3 could result in maximum compressive strengths up to 45, 37.5, and 33.75 MPa, respectively.

To investigate the effects of curing time and temperature on compressive strength development of the material, different hydrothermally curing regimes at atmospheric pressure were applied. The curing regimes applied include hydrothermal treatments in steam-saturated atmosphere at different temperatures of 45, 65, 85 °C and for different time periods of 5, 10, 15, and 20 h after 1 and 7 days of precuring.

The mix exhibiting the maximum compressive strength after hydrothermal treatment was selected and cured in autoclave at different temperatures of 125, 150, 180, and 210 °C and for different time periods of 20, 30, 40, and 50 h for investigating the effects of higher times and temperatures of curing on strength development and also to determine the maximum achievable compressive strength.

Test procedure

The cured specimens were allowed to cool to room temperature and then used to measure their compressive strength. For each measurement, three specimens were used and the average value was reported as the result. A Toni Technique (Toni Technic, Germany) compressive-strength-testing apparatus was used. Laboratory techniques of X-ray diffractometry (XRD; Philips Expert System), Fourier transform infrared spectroscopy (FTIR; Nicolet 740), and scanning electron microscopy (SEM; CamScan MV 2300, EDS; Oxford 7538) were used to characterize the effects of curing conditions on strength development. The X-ray diffraction patterns of the powdered samples were recorded on a Philips Expert diffractometer using CuKa radiation. The tests were run in a 2 h range of 4–70° at a scanning rate of 2°/min, with a deliverance slit of 1°, an anti-scatter slit of 1°, and a receiving slit of 0.01 mm. FTIR spectra were collected using a Nicolet 740 FTIR spectrometer in transmittance mode from 400 to 4000 cm^{-1} using standard KBr technique (0.5 mg sample with 250 mg KBr). All spectra were obtained with a sensitivity of 4 cm^{-1} and 64 scans per spectrum taken. For SEM studies, a number of specimens were cut into halves to expose internal regions. Suitable halves were then impregnated with epoxy resin, polished, and coated with carbon.

Results and discussion

Compressive strength

Before measuring compressive strength, the specimens were observed visually for any possible crack. They were quite sound and no crack was observed visually. Figures 4, 5, 6, 7, 8, 9 show the effects of time and temperature of hydrothermal curing at atmospheric pressure on compressive strength development of three inorganic polymeric binders based on natural pozzolan, i.e., IP1, IP2, and IP3 after 1 and 7 days of precuring in humid atmosphere and at room temperature. As seen, any increase in both time and temperature of hydrothermal curing causes an increase in compressive strength confirming the positive effect of hydrothermal curing compared to humid atmosphere curing. The strength development is significant at temperatures up to 85 °C. In both cases of precuring, the lowest temperature and the shortest time of hydrothermal treatment resulted in the least compressive strength. The highest compressive strengths were achieved in hydrothermal treatment at the highest temperature and for the longest time. A comparison of the results obtained for the two ages of precuring clearly show the positive effect of a 7 days precuring. The highest compressive strength obtained for mixes IP1, IP2, and IP3 after 1 day precuring are 35, 37.5, and 35 MPa, respectively, whereas the corresponding values for 7 days of precuring are 50, 57.5, and 50 MPa, respectively. This indicates that relatively long precuring in humid atmosphere, before the application of heat, is beneficial for compressive strength development.

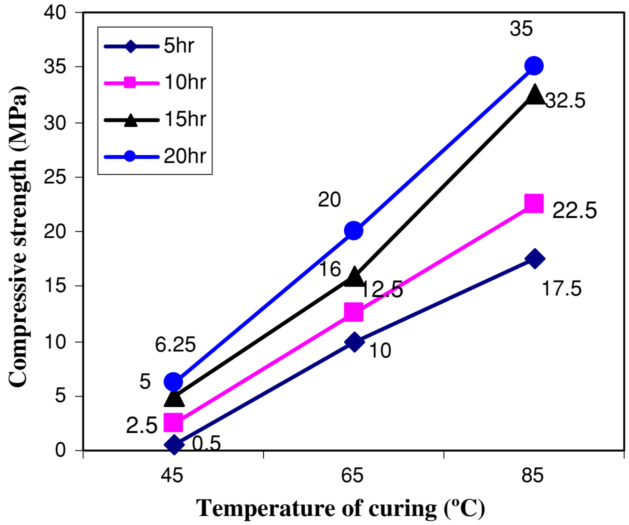

Fig. 4 Effects of temperature and time of hydrothermal curing on compressive strength development after 1 day of precuring for mix IP1

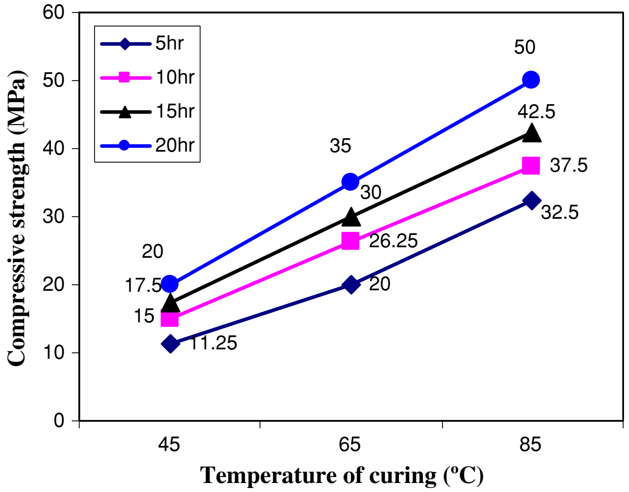

Fig. 5 Effects of temperature and time of hydrothermal curing on compressive strength development after 7 days of precuring for mix IP1

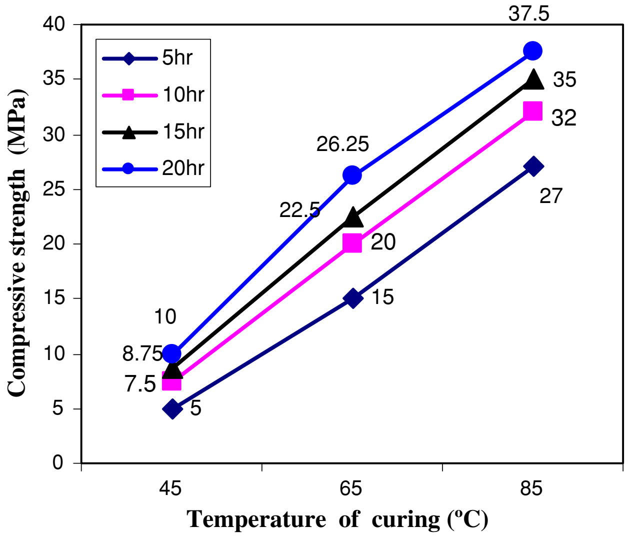

Fig. 6 Effects of temperature and time of hydrothermal curing on compressive strength development after 1 day of precuring for mix IP2

Figures 10 and 11 show the results obtained from mixes with different chemical compositions at different temperatures

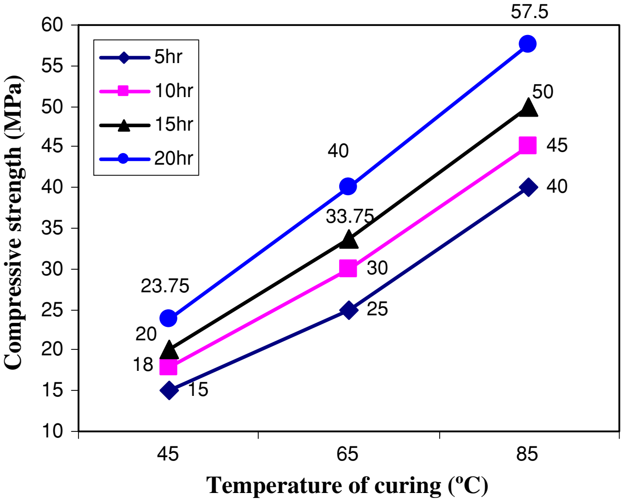

Fig. 7 Effects of temperature and time of hydrothermal curing on compressive strength development after 7 days of precuring for mix IP2

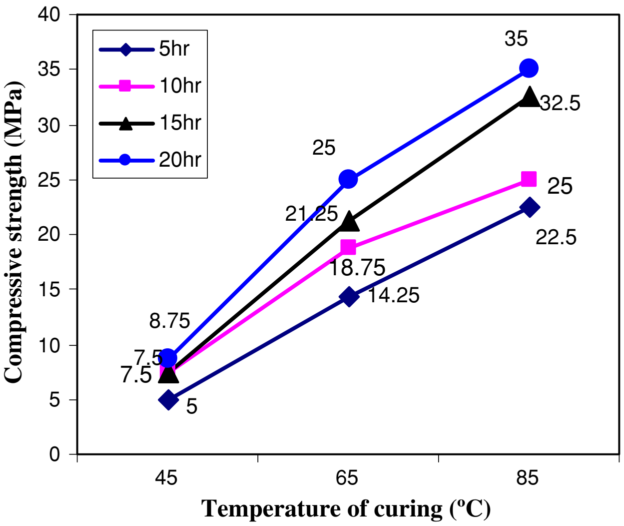

Fig. 8 Effects of temperature and time of hydrothermal curing on compressive strength development after 1 day of precuring for mix IP3

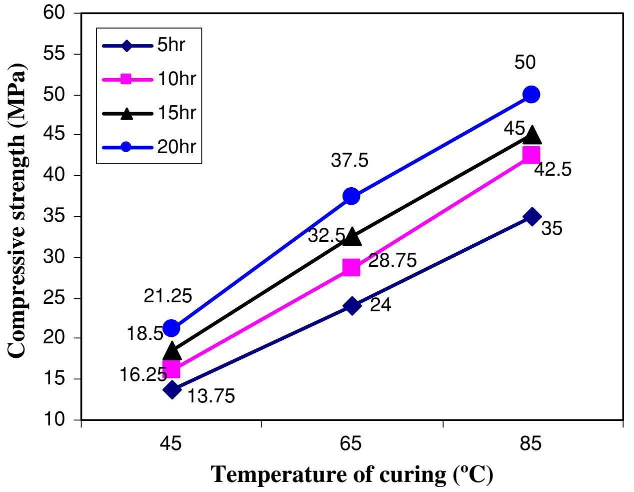

Fig. 9 Effects of temperature and time of hydrothermal curing on compressive strength development after 7 days of precuring for mix IP3

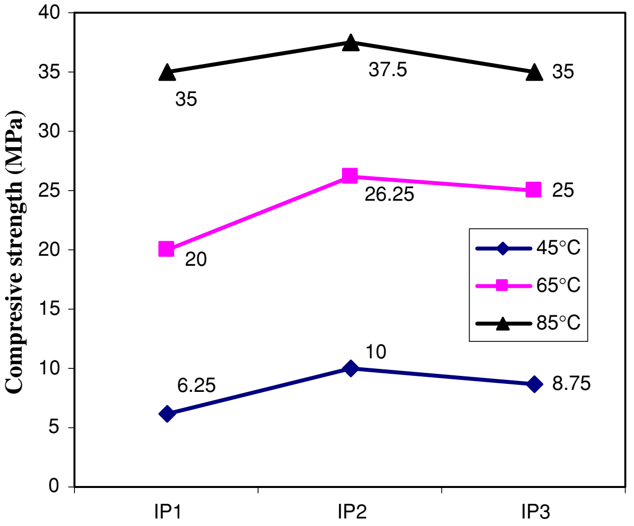

Fig. 10 Effects of different temperatures of hydrothermal curing for a period of 20 h on compressive strength development after 1 day of precuring for different mixes

of hydrothermal curing, i.e., 45, 65, and 85 °C at a time period of 20 h, which give the highest compressive strength after 1 and 7 days of precuring, respectively. As seen, there is a maximum compressive strength at all the curing temperatures. This could be attributed to differences in the chemical compositions of the studied mixes. As mentioned in Table 2, the main difference between these three mixes is in the amount of total Na/Al molar ratio. Maximum compressive strengths were achieved in mix IP2, which had a moderate amount of total Na/Al molar ratio, i.e., 1.08. This means that there could be an optimum in the amount of alkali used for preparation of inorganic polymeric materials. Utilization of too much alkali hydroxide in preparation of alkali-activator is not beneficial and has negative effects on properties of the products and compressive strength developments.

Figure 12 shows the effects of higher times and temperatures of autoclave curing on compressive strength development of mix IP2 after 7 days of precuring. As seen, autoclave curing at temperatures of 125, 150, 180, and 210 °C for different time periods of 20, 30, 40, and 50 h showed an effective increase on strength development. Almost at all temperatures, the compressive strength is increased by increase in the time of curing up to 40 h and then it remains constant. The maximum compressive strength achieved under autoclave curing at 210 °C for 30 h after 7 days of precuring was 108.75 MPa.

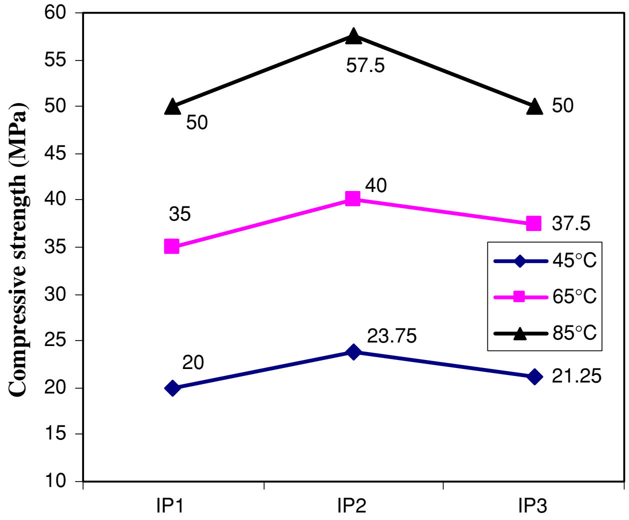

Fig. 11 Effects of different temperatures of hydrothermal curing for a period of 20 h on compressive strength development after 7 days of precuring for different mixes

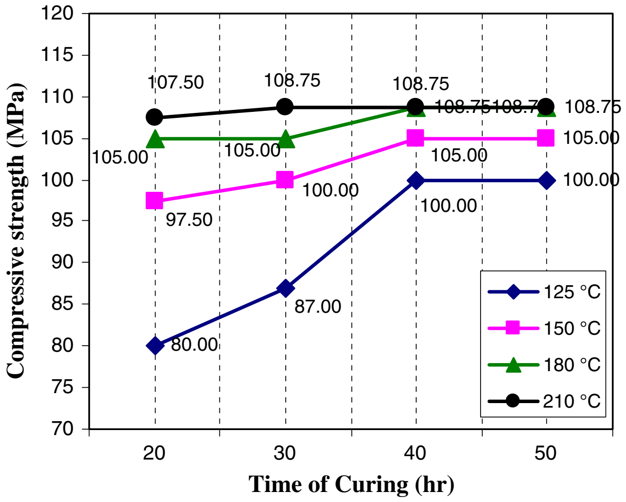

Fig. 12 Effects of higher times and temperatures of autoclave curing on compressive strength development after 7 days of precuring for mix IP2

X-ray diffraction analysis

X-ray diffractometry was used for investigating a number of cured specimens. The obtained patterns however were quite the same showing a mostly amorphous material with few crystalline phases including anorthite and hornblende, which were originally present in the starting raw material. This indicates that the changes responsible for the differences in compressive strength originate and take place within the amorphous part of the structure. Figures 13 and 14 show X-ray diffraction patterns of mix IP2 cured at 85 and 125 °C for 20 h after 7 days of precuring, respectively.

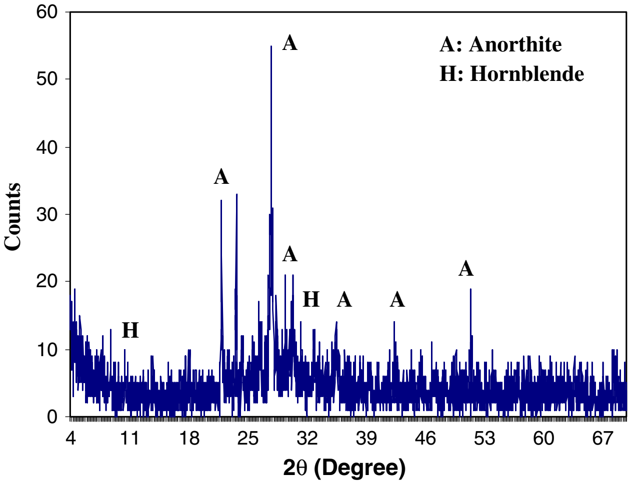

Fig. 13 X-ray diffraction patterns of mix IP2 cured at 85 °C for 20 h after 7 days of precuring

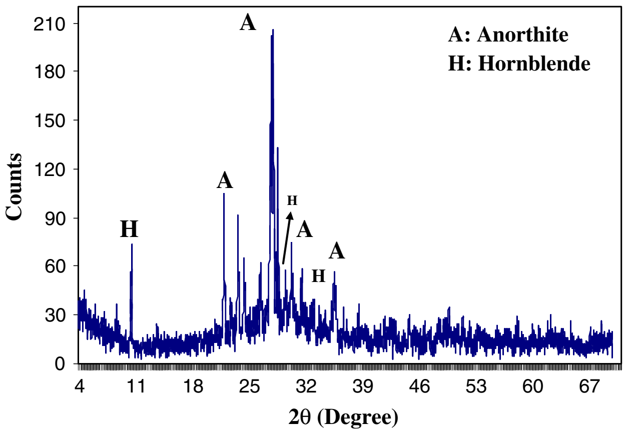

Fig. 14 X-ray diffraction patterns of mix IP2 cured at 125 °C for 20 h after 7 days of precuring

As seen, no crystalline effect appears upon curing at different temperatures.

FTIR analysis

Figure 15 displays infrared spectra of mix IP2 cured at different curing procedures of 28 days at an atmosphere of more than 95% relative humidity at 25 °C (humid curing), 20 h hydrothermal treatment at 45, 65, and 85 °C after 7 days of precuring (steam curing), and autoclave curing at 210 °C for 30 h after 7 days of precuring (autoclave curing). As seen in all the spectra, there exists a main broad and strong absorption peak appearing at about 1000 cm^{-1} and a fairly broad and relatively strong peak at about 460 cm^{-1}. The main broad peak at around 1000 cm^{-1} has been attributed to asymmetric stretching of Al–O and Si–O bonds originating from individual tetrahedra while that at

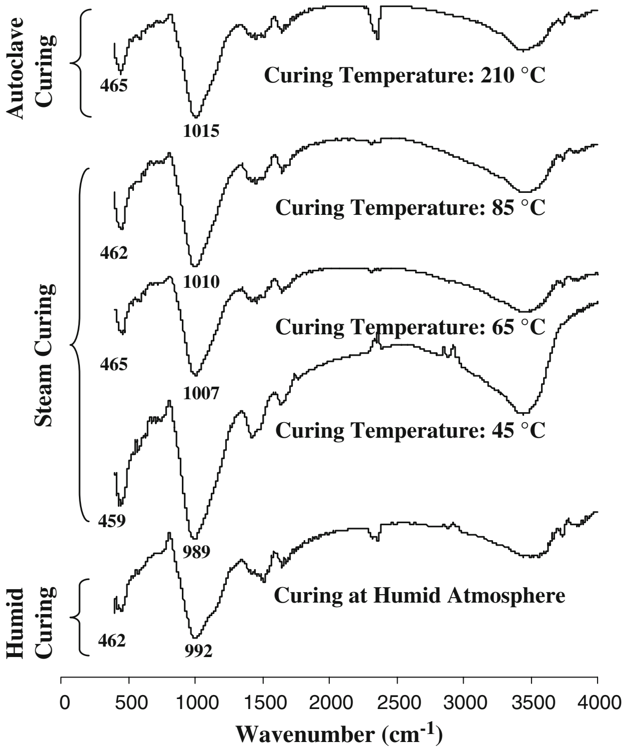

Fig. 15 FTIR spectra of mix IP2 cured under different curing conditions

about 460 cm^{-1} has been assigned to the in-plane bonding of Al–O and Si–O linkages [12, 13]. These two peaks are the main fingerprints of geopolymer materials.

The obtained spectra show some differences when compared to the spectrum of the starting natural pozzolan (see Fig. 2). The broad peak at around 1000 cm^{-1} in natural pozzolan has been concentrated in the cured hardened pastes confirming that geopolymerization reactions have resulted in a more oriented molecular structure. Geopolymerization reactions occurring at relatively higher temperatures will probably result in the formation of more aluminosilicate gel, which in turn produces a more oriented molecular structure upon polycondensation.

A comparison of the spectra also shows that hydrothermal treatment at higher temperatures shifts the main broad peak at around 1000 cm^{-1} to slightly higher wavenumbers. This shows a change in molecular structure caused by a lower degree of silicon substitution by aluminum in the second coordination sphere.

Scanning electron microscopy

Curing conditions usually have significant effects on microstructure and hence mechanical strength development in most cementing mixtures. Microstructures of mix IP2 cured at different curing regimes of 28 days at an atmosphere of more than 95% relative humidity at 25 °C, 20 h hydrothermal treatment at 85 °C after 7 days of precuring, and autoclave curing at 125 °C for 20 h and 210 °C for 30 h after 7 days of precuring were investigated by scanning electron microscopy (SEM). Figures 16, 17, 18, 19 show SEM images taken from the above mentioned specimens, respectively.

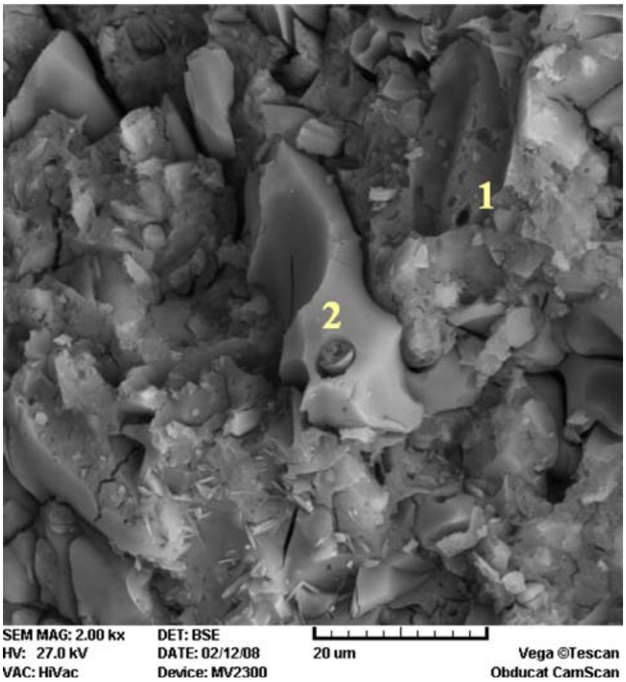

Fig. 16 SEM image of mix IP2 cured for 28 days at more than 95% relative humidity at room temperature (magnification: 2000×)

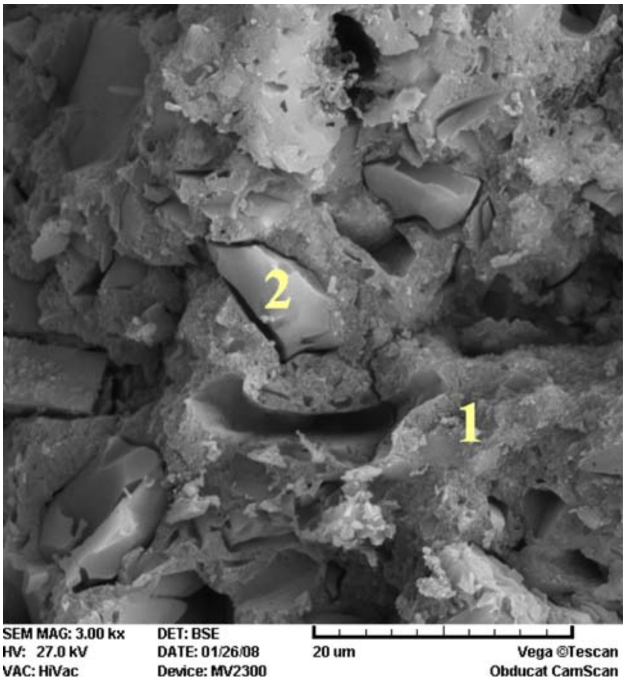

Fig. 17 SEM image of mix IP2 cured at temperature of 85 °C for 20 h after 7 days of precuring (magnification: 3000×)

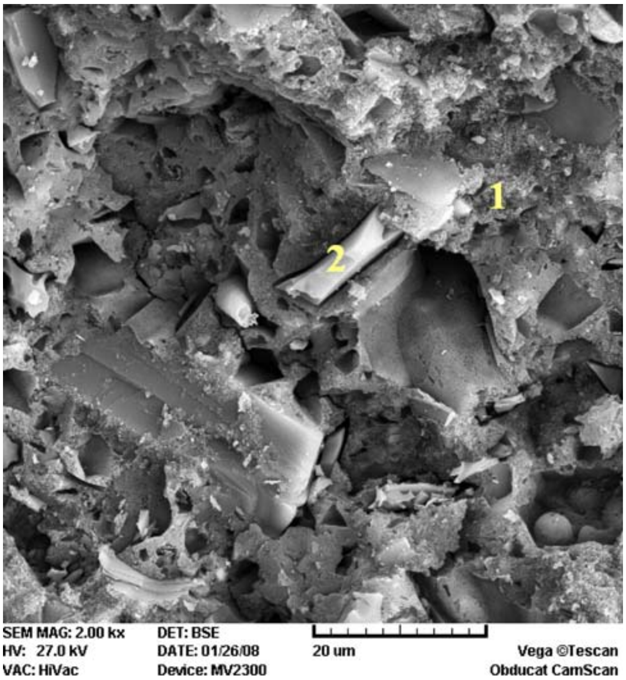

Fig. 18 SEM image of mix IP2 cured at temperature of 125 °C for 20 h after 7 days of precuring (magnification: 2000×)

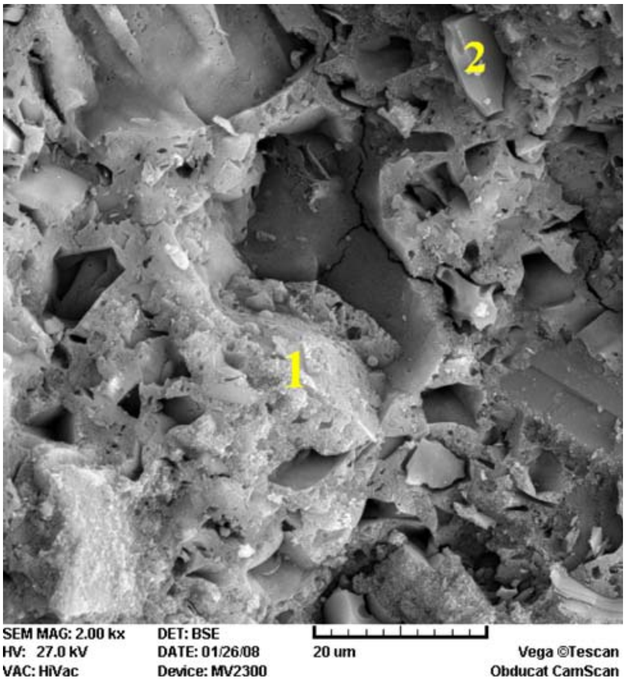

Fig. 19 SEM image of mix IP2 cured at temperature of 210 °C for 30 h after 7 days of precuring (magnification: 2000×)

Table 3 Results of elemental analysis done on regions shown in Fig. 16

Element (wt%)	Region	
	1	2
O	45.69	59.29
Na	4.43	6.26
Mg	–	–
Al	11.43	5.40
Si	28.15	24.52
K	1.25	1.91
Ca	9.06	2.62
Na_2O/Al_2O_3 total molar ratio	0.45	1.36
SiO_2/Al_2O_3 total molar ratio	4.14	7.66

Table 4 Results of elemental analysis done on regions shown in Fig. 17

Element (wt%)	Region	
	1	2
O	49.14	44.27
Na	7.00	3.28
Al	7.48	7.18
Si	27.14	36.24
K	1.04	3.27
Ca	6.99	4.89
Fe	1.20	0.87
Na_2O/Al_2O_3 total molar ratio	1.10	0.54
SiO_2/Al_2O_3 total molar ratio	6.12	8.52

Table 5 Results of elemental analysis done on regions shown in Fig. 18

Element (wt%)	Region	
	1	2
O	46.73	57.69
Na	4.16	3.45
Mg	3.45	–
Al	6.04	5.88
Si	23.07	28.98
K	2.50	1.93
Ca	7.40	2.07
Fe	5.53	–
Na_2O/Al_2O_3 total molar ratio	0.80	0.69
SiO_2/Al_2O_3 total molar ratio	6.44	8.30

All the four resembling microstructures consist of a matrix in which small particles of different sizes and shapes are embedded. Elemental analyses were done by EDX for possibly identifying the microstructures. The results of elemental analyses obtained from regions shown on SEM images are presented in Tables 3, 4, 5, and 6. The SiO_2/Al_2O_3 and Na_2O/Al_2O_3 total molar ratios were also calculated and presented. These molar ratios can be used to identify the geopolymer matrix. Regions shown by No. 1 are the geopolymer matrix. For the embedded particles

Table 6 Results of elemental analysis done on regions shown in Fig. 19

Element (wt%)	Region	
	1	2
O	49.44	45.69
Na	6.28	4.43
Al	6.78	11.43
Si	23.84	28.15
K	2.12	1.25
Ca	9.18	9.06
Fe	2.10	–
Na_2O/Al_2O_3 total molar ratio	1.09	0.45
SiO_2/Al_2O_3 total molar ratio	5.93	4.14

however the values of these molar ratios were quite different from each other.

The interesting conclusion is that for specimens cured hydrothermally or under autoclave condition, the obtained values of SiO_2/Al_2O_3 and Na_2O/Al_2O_3 total molar ratios are more close to the designed composition compared to the corresponding values obtained for specimens cured in humid atmosphere. This confirms the previous conclusion that curing at higher temperatures and for longer times (hydrothermal treatment or autoclave curing) result in the formation of more alkali aluminosilicate gel from the starting material.

Another important microstructural difference observed in SEM studies was microcracks. Figures 20, 21, and 22 show SEM images taken from some of the studied microstructures at a lower magnification. As seen, the microstructure of the specimen cured 28 days in humid atmosphere shows a relatively high number of microcracks

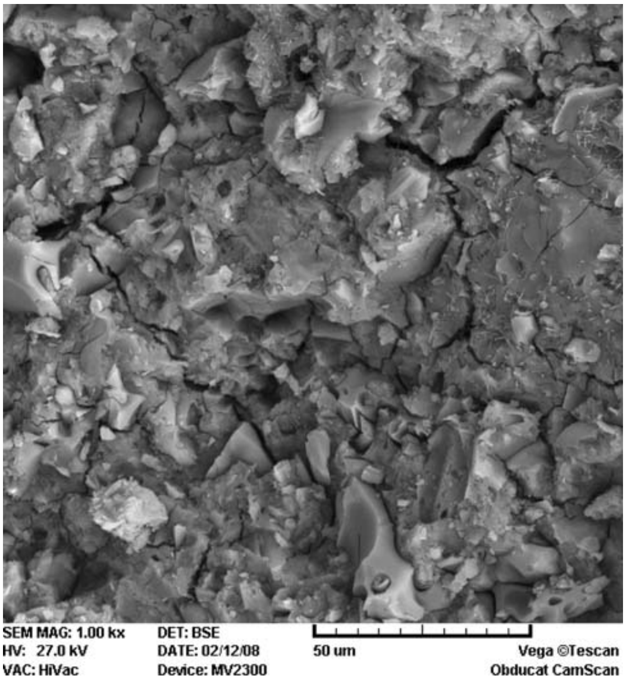

Fig. 20 SEM image of mix IP2 cured for 28 days at more than 95% relative humidity at room temperature (magnification: 1000×)

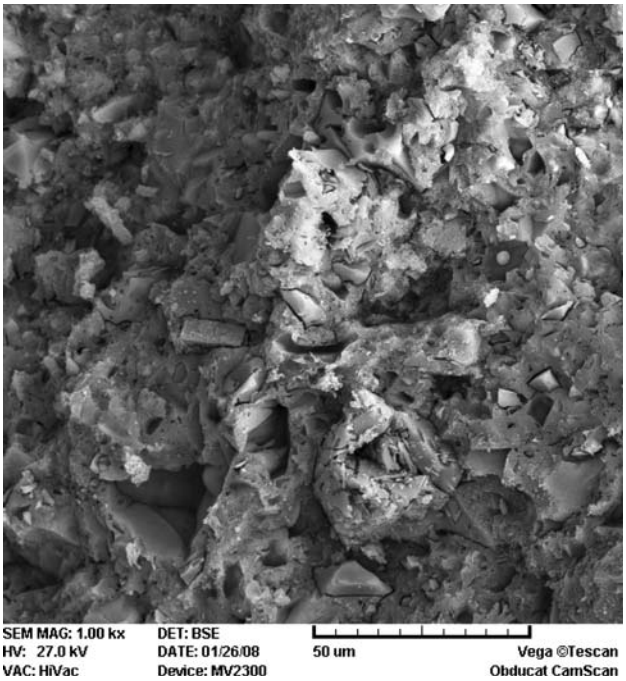

Fig. 21 SEM image of mix IP2 cured at temperature of 85 °C for 20 h after 7 days of precuring (magnification: 1000×)

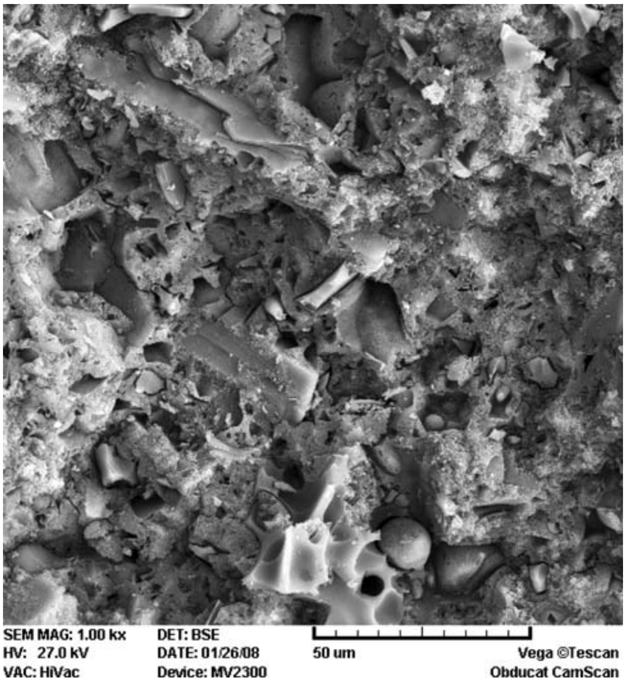

Fig. 22 SEM image of mix IP2 cured at temperature of 125 °C for 20 h after 7 days of precuring (magnification: 1000×)

extending quite nonuniformly, whereas the microstructure of the specimen cured hydrothermally at 85 °C for 20 h after 7 days of precuring and also the microstructure of the specimen cured in autoclave at 125 °C for 20 h after 7 days of precuring are quite sound with no microcrack.

Conclusions

1. Any increase in both time and temperature of curing causes an increase in compressive strength of the studied inorganic polymeric binder based on natural pozzolan.
2. Longer precuring at an ambient of more than 95% relative humidity at room temperature, before the application of heat, is beneficial for higher strength development.
3. Application of heat for curing both under atmospheric pressure (hydrothermal treatment at temperatures up to 100 °C) and higher pressures (autoclave curing, temperatures above 100 °C) could effectively increase the compressive strength of the material by formation of more alkali aluminosilicate gel from the starting material and eliminating the structural microcracks.

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