INVESTIGATING THE POSSIBILITY OF UTILIZING PUMICE-TYPE NATURAL POZZONAL IN PRODUCTION OF GEOPOLYMER CEMENT

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Natural pozzolans are aluminosilicate-type materials which can be activated with solutions of NaOH and Na_2SiO_3. Using a pumice-type natural pozzolan and different alkali-activators based on combinations of Na_2SiO_3 and NaOH, a number of geopolymer cement systems were designed and studied. Water-to-dry binder ratio, silica modulus, and sodium oxide concentration of the systems were adjusted at different levels and setting time, workability, and 28-day compressive strengths of the systems were studied. The results obtained reveal that natural pozzolans of pumice-type can be activated using a proportioned mixture of Na_2SiO_3 and NaOH resulting in the formation of a geopolymer cement system exhibiting suitable workability and acceptable 28-day compressive strengths. All the measured final setting times are acceptable compared to standard values given for Portland cement.

INTRODUCTION

Geopolymer cements are a group of alkali-activated materials exhibiting superior engineering properties compared to Portland cements. The raw materials usually utilized for production of these cements are amorphous and reactive aluminosilicates [1].

The molecular structure of geopolymers consists of an aluminosilicate network that is a product of the chemical reaction between aluminosilicate and alkali-polysialate in a relatively highly alkaline medium [2, 3]. The aluminosilicate network consists of SiO_4 and AlO_4 tetrahedral structural units connected to each other by sharing their oxygen atoms. The presence of positive ions such as Na^+, K^+, Li^+, Ca^{2+}, Ba^{2+}, NH^{4+}, and H_3O^+ is necessary to balance the negative charge of aluminum [3, 4].

The role of alkalis is to activate raw materials such as blast-furnace slag, fly ash, etc, to take part in the geopolymerization reactions [5]. These materials are activated by alkalis so that Si–O bonds in the silicates or aluminosilicates are broken and a number of reactions result in the formation of geopolymer [6]. The exact mechanism of geopolymerization reaction is not yet understood, but all the proposed mechanisms include three stages: (1) dissolution of raw materials in alkaline solution, (2) orientation of the dissolved species, and (3) polycondensation to form networked polymeric oxide structures [7-10]. In general, the presence of alkali-metal salts or their hydroxides is necessary for dissolving aluminosilicates and silicates and for catalyzing the polycondensation reactions.

The resulting products, i.e. geopolymer cements, usually exhibit good engineering properties such as relatively high compressive strengths, short to long setting times, and relatively high resistance against aggressive media compared to Portland cements [11-16].

In recent years, many research works have been carried out to investigate the possibility of utilizing industrials 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 [17-21].

Natural pozzolan which is an almost similar aluminosilicate material, exhibiting cementations behaviour when mixed with calcium hydroxide and water, probably is a suitable raw material for being utilized in the production of geopolymer cements [17]. This work investigates the possibility of utilizing pumice-type natural pozzolan as a raw material in the production of geopolymer cements.

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 firstly characterized for its chemical and mineralogical compositions and also its pozzolanic activity. The results of chemical analysis determined according to ASTM standard C311 [22] and the value of specific surface area determined by Blaine air-permeability apparatus are shown in Table 1. As seen, this natural pozzolan is a relatively highly siliceous and according to ASTM standard C618 [23], chemically it could be considered as a relatively good natural pozzolan. 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; $Na_{0.05}Ca_{0.95}Al_{1.95}Si_{2.05}O_8$,
Hornblende with empirical formula; $Ca_2Mg_4Al_{0.75}Fe^{3+}{}_{0.25}(Si_7AlO_{22})(OH)_2$,
Biotite with empirical formula; $KMg_{2.5}Fe^{2+}{}_{0.5}AlSi_3O_{10}(OH)_{1.75}F_{0.25}$,
Quartz with empirical formula; SiO_2.

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 percent of control respectively for 7 and 28 days, show a relatively good pozzolanic activity in accordance with ASTM standard C618.

Knowing that particle size distribution of pozzolan powder could effectively affect both wet and dry properties of the geopolymer 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 the pozzolan powder was determined by a laser particle size analyzer. The Particle size distribution curve of pozzolan powder prepared by the method of Rosin- Rambler-Sperling-Bennet (RRSB) 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 µm, respectively.

Specimens preparation

Commercial water-glass was used for preparing alkali activators. The silica modulus (Ms = SiO_2/Na_2O) of water glass was 0.86. Enough sodium hydroxide was added to water-glass for preparing three different alkali-activators having silica modules of 0.52, 0.60, and 0.68. The sodium oxide-contents of the designed geopolymer cement systems were adjusted at three different levels of 4, 7, and 10% (by weight of dry binder). The water-to-dry binder ratios (W/DB-ratio) were controlled at three different values of 0.36, 0.40 and 0.44 for investigating its effects on set and strength behaviours of the systems. After adding activators to the dry binders and mixing for about 5 minutes, the pastes were cast into moulds of 2×2×2 cm in size. The moulds were held at an atmosphere of more than 95% relative humidity and ambient temperature, i.e. 25°C. The moulds were opened after 24 hours and the specimens were stored in the humid bath until the testing time.

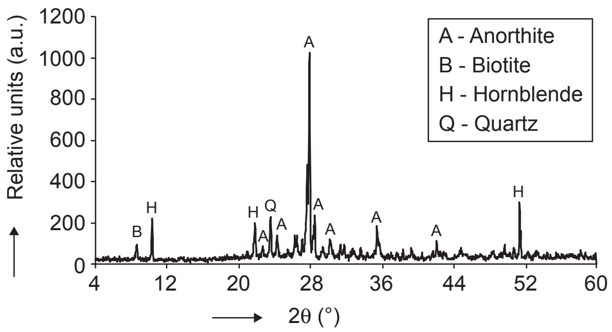

Figure 1. X-ray diffraction pattern of Taftan pozzolan.

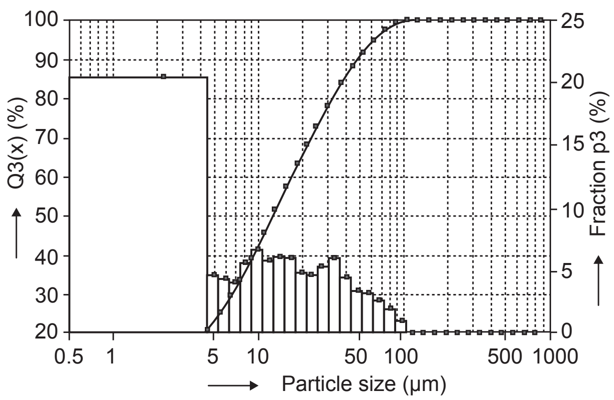

Figure 2. Particle size distribution of ground Taftan pozzolan according to RRSB method.

Table 1. Chemical composition and Blaine fineness of the ground Taftan pumice-type pozzolan.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Cl	LOI	Moisture	Blaine (m^2/kg)
Wt.%	61.57	18.00	4.93	6.69	2.63	0.10	1.95	1.65	0.04	2.15	0.51	309

Test procedure

The pastes prepared were firstly characterized by determining their final setting times and their relative visual workability. Final setting times of all the systems were measured using Vicat needle in accordance with ASTM standard C191-82 [24]. Since all the systems exhibit relatively long setting times, the pastes were stored at an atmosphere of more than 95% relative humidity at 25°C to prevent any setting due to drying and to measure the actual final setting time.
The workability of each paste was determined based on ratings ranging from 4 for a freely flowing paste to 0 for a quite non-workable paste.

At the age of 28 days, the specimens were used to determine their compressive strength for investigating the effects of W/DB-ratio, silica modulus, and Na_2O concentration on 28-day compressive strength of the material and for determining the maximum achievable 28-day compressive strength. The geopolymer cement system exhibiting the highest compressive strength was studied by X-ray diffractometry technique to characterize its crystalline mineral phases. To investigate any possible efflorescence, from each system a 28-day hardened specimen was placed in 50 ml water and kept in an open-air atmosphere at ambient temperature (25°C) until the water was dried completely.

RESULTS AND DISCUSSION

Figures 3 to 5, show the effects of W/DB-ratio and Na_2O concentration on relative visual workability of freshly prepared pastes at different silica modules. As seen in Figures 3 to 5, the rheological properties of the freshly prepared pastes depend on their W/DB-ratio and their sodium oxide content. As the results reveal, in general, an improvement of workability and thus the possibility of reducing the water-to-dry binder ratio could result from increasing the sodium oxide content of the geopolymer cement system. A comparison of the results obtained for different silica modules however show that lower silica modules result in higher paste workabilities. The results obtained for the effects of W/DB-ratio, Na_2O concentration, and silica modulus of the activator on workability of freshly prepared natural pozzolan pastes are quite similar to those reported in a previous work for mixtures of fly ash and blast furnace slag [25].

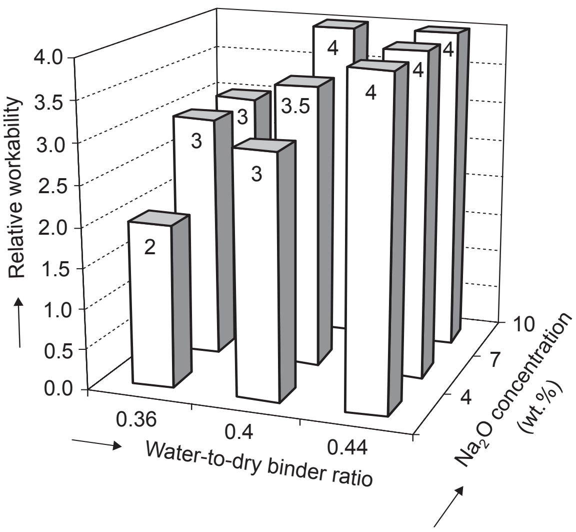

Figure 5. Effects of W/DB-ratio and Na_2O concentration on relative visual workability of freshly prepared pastes at silica modulus of 0.52.

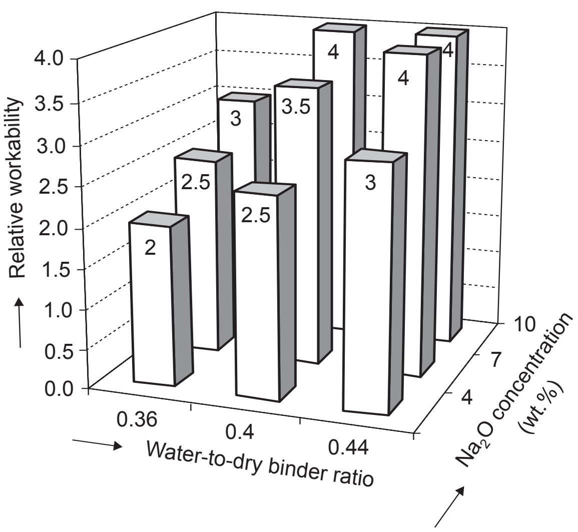

Figure 3. Effects of W/DB-ratio and Na_2O concentration on relative visual workability of freshly prepared pastes at silica modulus of 0.68.

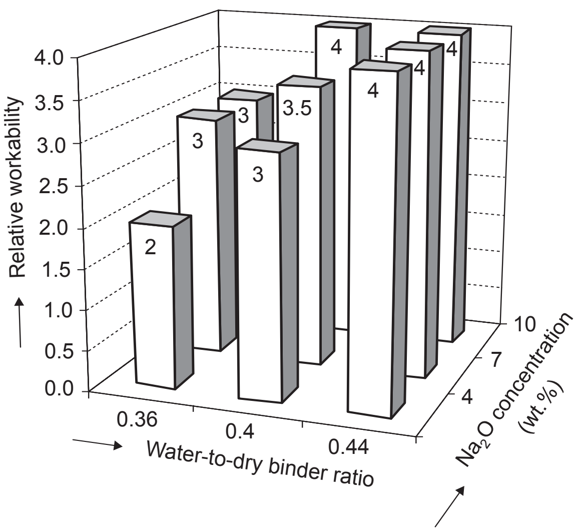

Figure 4. Effects of W/DB-ratio and Na_2O concentration on relative visual workability of freshly prepared pastes at silica modulus of 0.60.

Figures 6 to 8, show the effects of W/DB-ratio and Na_2O concentration on final setting time at different silica modules. As seen, the final setting time reduces when W/DB-ratio is decreased or Na_2O concentration is increased. All the measured final setting times are acceptable compared to standard values given for Portland cement. The time of setting could be considered as an indication for the kinetics of geopolymerization reactions, so that a relatively long setting time shows that the geopolymerization reactions proceed very slowly at ambient temperature. The kinetics of the geopolymerization reactions therefore could be accelerated by curing the material hydrothermally and/or probably changing the chemical and/or mineralogical composition of the dry binder.

Figures 9, 10, and 11, show the effects of water-to-dry binder ratio on 28-day compressive strength at different Na_2O concentrations and different silica modulus respectively. As it is expected, W/DB-ratio could significantly influence the 28-day compressive strength of the material. Usually W/DB-ratio is increased for improving 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/DB-ratio results in an increase in the total pore volume which in turn weakens the strength behaviour of the material. In some cases a relatively high W/DB-ratio could also result in a relatively high drying shrinkage which may itself lead to shrinkage cracks working as macro-defect points. In the case of the material under study however more investigation is necessary to understand the effect of W/DB-ratio on total pore volume and formation of any probable shrinkage-cracks.

Figures 12, 13, and 14 show the effect of silica modulus on the 28-day compressive strength at different Na_2O concentrations and different water-to-dry binder ratios, respectively. The effect of silica modulus on 28-day compressive strength is quite similar for all the three W/DB-ratios tested. As silica modulus increases from 0.52 to 0.68, the 28-day compressive strength increases to a maximum value and then decreases to a relatively small value. For all the three W/DB-ratios tested and all the three Na_2O concentrations, the optimum value for silica modulus is 0.60 giving the maximum 28-day compressive strength. The variations in silica modulus of the activator at a constant Na_2O concentration are brought about by proportioning the amounts of sodium silicate and sodium hydroxide and changing the soluble silica content of the activator. Soluble silica from sodium silicate is very important in formation of monomers and initiation of geopolymerization reactions [10]. Increasing the soluble silica con-

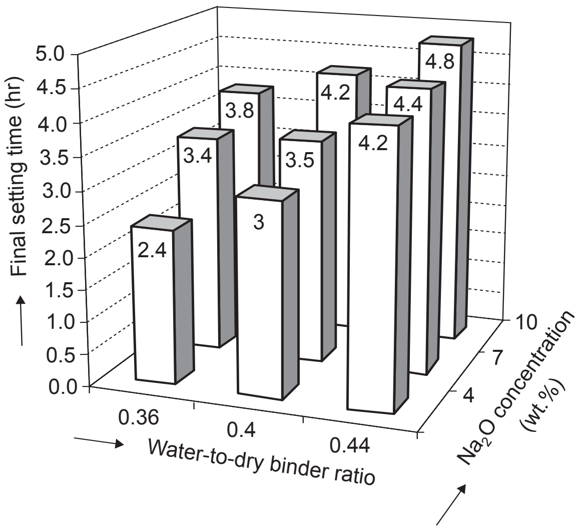

Figure 7. Effects of W/DB-ratio and Na_2O concentration on final setting time at silica modulus of 0.60.

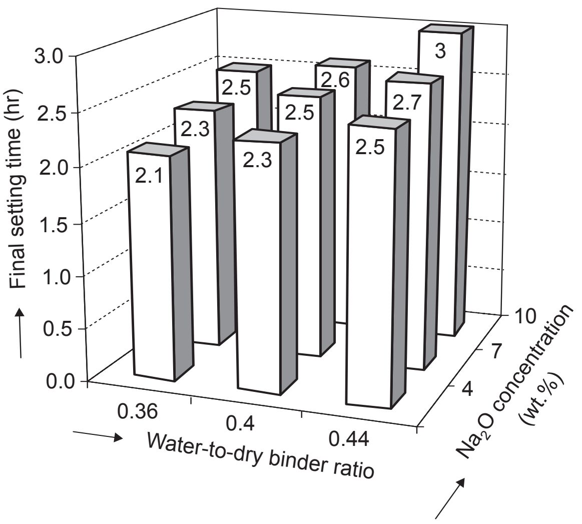

Figure 6. Effects of W/DB-ratio and Na_2O concentration on final setting time at silica modulus of 0.68.

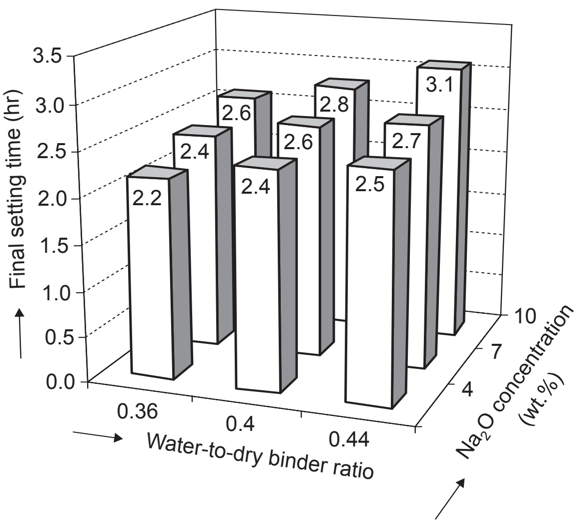

Figure 8. Effects of W/DB-ratio and Na_2O concentration on final setting time at silica modulus of 0.52.

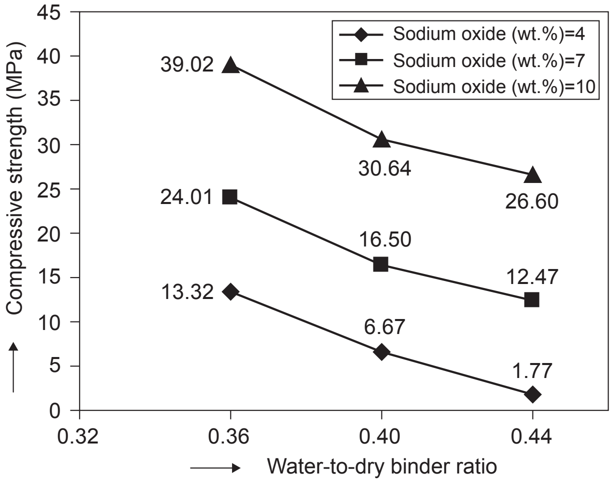

Figure 9. Effect of water-to-dry binder ratio on 28-day compressive strength at different Na_2O concentrations and silica modulus of 0.68.

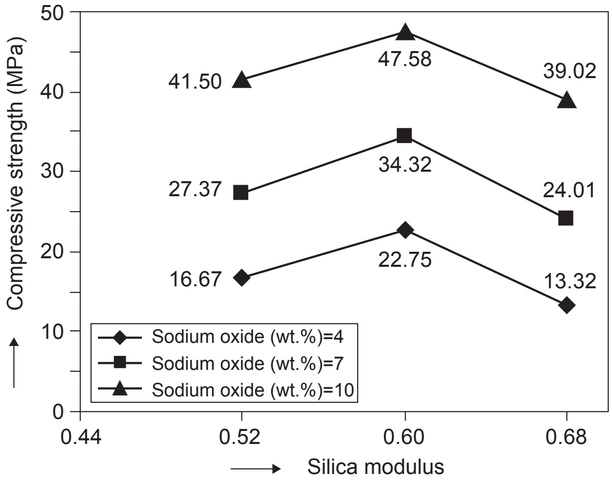

Figure 12. Effects of silica modulus on 28-day compressive strength at different Na_2O concentrations and water-to-dry binder ratio of 0.36.

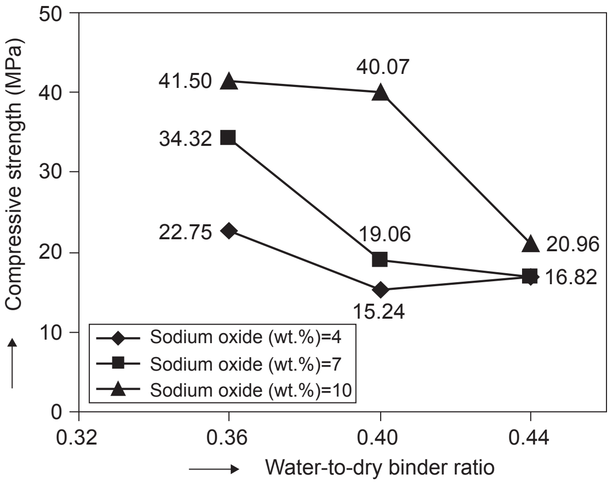

Figure 10. Effect of water-to-dry binder ratio on 28-day compressive strength at different Na_2O concentrations and silica modulus of 0.60.

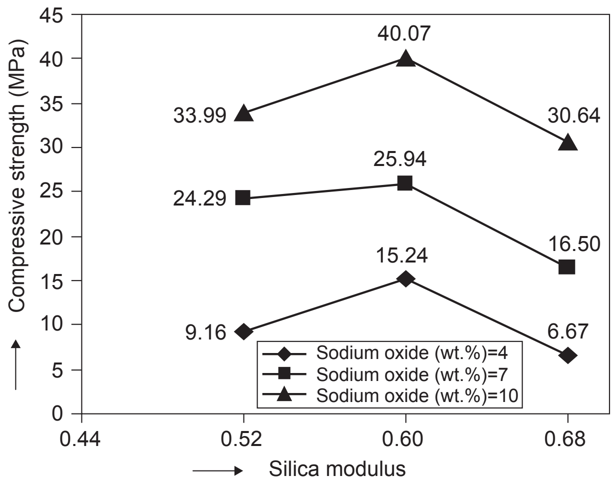

Figure 13. Effects of silica modulus on 28-day compressive strength at different Na_2O concentrations and water-to-dry binder ratio of 0.40.

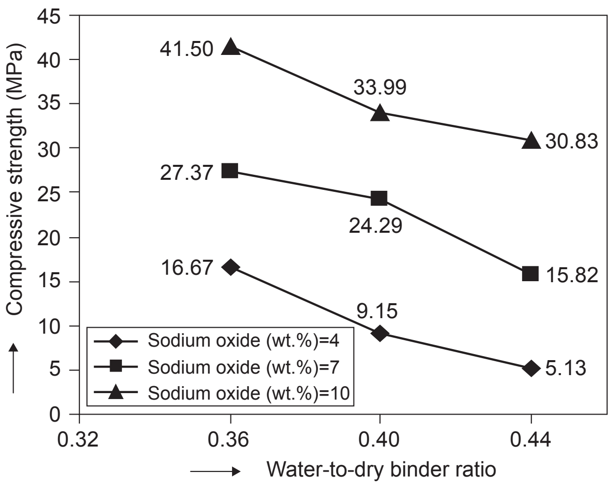

Figure 11. Effect of water-to-dry binder ratio on 28-day compressive strength at different Na_2O concentrations and silica modulus of 0.52.

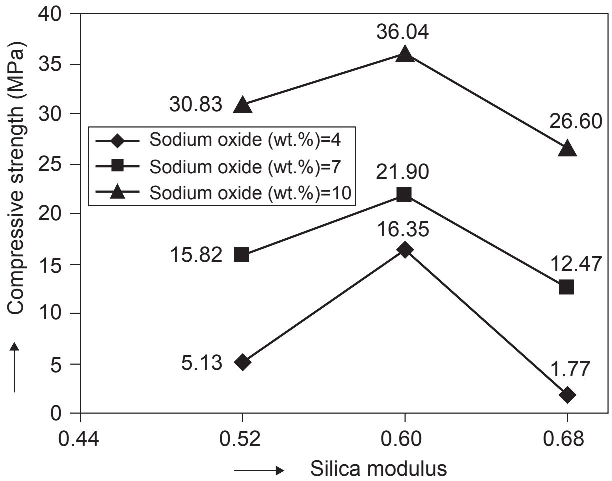

Figure 14. Effects of silica modulus on 28-day compressive strength at different Na_2O concentrations and water-to-dry binder ratio of 0.44.

tent of the activator and its silica modulus to their optimum values, results in an acceleration in the geopolymerization reactions and causes the reactions to proceed to higher extents. These in turn lead to an improvement in the strength behaviour of the geopolymer cement system. Any increase in the soluble silica content of the activator and its silica modulus from their optimum values however, decreases the 28-day compressive strength. The reason for such a decrease in 28-day compressive strength at relatively higher values of silica modulus is not well known. It is probably due to the types of geopolymers formed. More investigations using suitable laboratory techniques such as MAS NMR and FTIR are needed to characterize the molecular structure of the material.

Figures 15, 16, and 17, show the effect of Na_2O concentration on 28-day compressive strength at different water-to-dry binder ratios and different silica modulus, respectively. As seen, any increase in Na_2O concentration in the range between 4 to 10% increases the 28-day compressive strength. The strength increase at relatively lower Na_2O concentrations in the range between 4 to 7% is much steeper and at relatively high concentrations in the range between 7 to 10% becomes gradually. At higher concentrations of Na_2O, the 28-day compressive strength decreases due to excess sodium oxide. The role of sodium oxide in the mechanism of geopolymerization is quite important. Considering the key-role of Na_2O in geopolymerization reactions, dissolution of the aluminosilicates in the very first stage and charge balance of the 3-dimentional network in the last stage, one can simply conclude that increasing the sodium oxide concentration of the system to its optimum value, results in the acceleration of geopolymerization reactions and causes the reactions to proceed to higher extents. The strength behaviour of the geopolymer cement system therefore is improved.

Taftan pozzolan and the hardened paste of Taftan pozzolan-based geopolymer cement exhibiting the highest 28-day compressive strength, i.e. almost 47 MPa, were studied using X-ray diffractometry technique. The corresponding X-ray diffraction patterns are presented in Figures 1 and 18, respectively.

As compared with Figure 1, three of the four crystalline mineral phases observed in Taftan pozzolan including Quartz, Hornblende, Anorthite, and Biotite are present in the hardened paste of Taftan pozzolan-based geopolymer cement exhibiting the highest 28-day compressive strength. The crystalline mineral phases of Taftan pozzolan therefore are not reactive, except Biotite, and do not take part in the geopolymerization reactions. In fact, this is the amorphous part of the Taftan pozzolan which is reactive and takes part in the geopolymerization reactions and results in the formation of geopolymers in the glassy state.

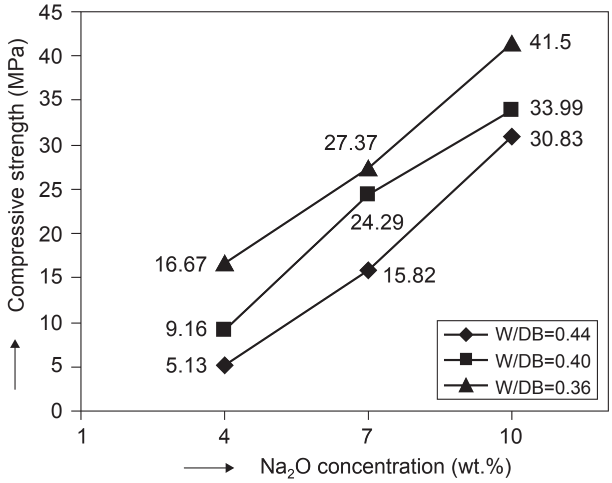

Figure 15. Effect of Na_2O concentration on 28-day compressive strength at different water-to-dry binder ratios and silica modulus of 0.52.

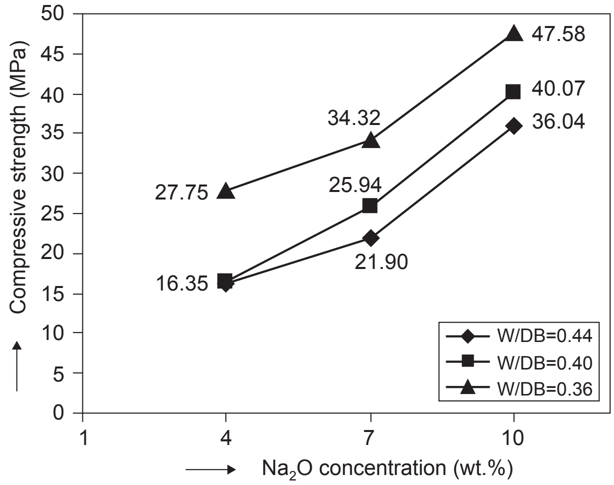

Figure 16. Effect of Na_2O concentration on 28-day compressive strength at different water-to-dry binder ratios and silica modulus of 0.60.

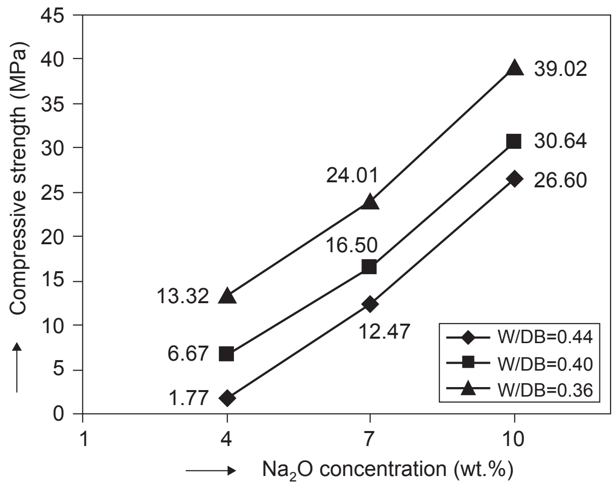

Figure 17. Effect of Na_2O concentration on 28-day compressive strength at different water-to-dry binder ratios and silica modulus of 0.68.

From each system, a 28-day hardened paste specimen was tested to investigate any possible efflorescence. The results of efflorescence test are presented in Table 2 qualitatively by just comparing the specimens visually. The severity of the efflorescence has been differentiated by letters A, B, and C. Systems 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 from left.

As seen in Table 2, most of the systems containing 4 wt.% Na_2O do not show any efflorescence. A 3 wt.% increase in Na_2O concentration however results in appearance of efflorescence. Most of the systems containing 10 wt.% Na_2O exhibit severe efflorescence.

A comparison of the results of 28-day compressive strength and efflorescence reveal that a relatively high compressive strength attainable at higher Na_2O concentrations does not necessarily mean soundness and durability. On the other hand, systems showing no efflorescence do not exhibit acceptable 28-day compressive strength. Measurement of Na_2O concentration in leachates proved that the appearance of efflorescence is due to leaching of non-reacted and free sodium hydroxide which later in a secondary reaction reacts with atmospheric carbon dioxide producing sodium carbonate. An optimum Na_2O concentration along with hydrothermal treatment of paste specimens probably could result in development of a pumice-type natural pozzolan-based geopolymer cement system.

Table 2. Results of efflorescence test.

System No.	Na_2O (wt.%)	Ms	W/DB	Severity of efflorescence
1			0.36	A
2		0.52	0.40	B
3			0.44	A
4			0.36	A
5	4	0.60	0.40	B
6			0.44	A
7			0.36	A
8		0.68	0.40	A
9			0.44	A
10			0.36	C
11		0.52	0.40	B
12			0.44	B
13			0.36	B
14	7	0.60	0.40	C
15			0.44	B
16			0.36	B
17		0.68	0.40	B
18			0.44	B
19			0.36	C
20		0.52	0.40	C
21			0.44	B
22			0.36	C
23	10	0.60	0.40	B
24			0.44	C
25			0.36	C
26		0.68	0.40	B
27			0.44	B

CONCLUSION

1. Based on results obtained for 28-day compressive strength, amorphous aluminosilicates present in the studied pumice-type natural pozzolan are reactive and could take part in the geopolymerizaion reactions.
2. Preliminary results obtained from activating pumice-type natural pozzolan using proportioned mixtures of NaOH and Na_2SiO_3 prove the probable potential of pumice-type natural pozzolan as a suitable raw material in production of geopolymer cement.
3. The quality of natural pozzolan-based geopolymer cement depends on the composition of alkali-activator and water-to-dry binder ratio, in addition to the quality of natural pozzolan, i.e. chemical composition and glass phase content.
4. Using the studied pumice-type natural pozzolan, relatively high 28-day compressive strengths, up to 47 MPa, can be achieved at silica modulus, Na_2O concentration, and water-to-dry binder ratio of 0.60, 10 wt.%, and 0.36, respectively.

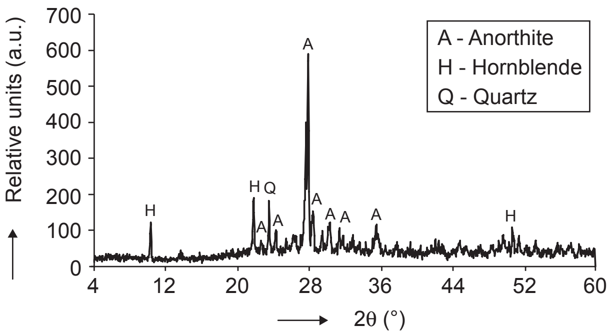

Figure 18. X-ray diffraction pattern of Taftan pozzolan-based geopolymer cement exhibiting the highest 28-day compressive strength.

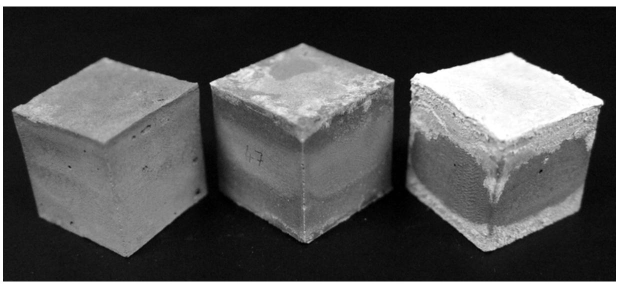

Figure 19. Specimens exhibiting no, slight, and severe efflorescence (from left).

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VÝZKUM MOŽNOSTI VYUŽITÍ PŘÍRODNÍHO PUCOLÁNU PEMZOVÉHO TYPU PŘI VÝROBĚ GEOPOLYMERNÍHO CEMENTU

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Přírodní pucolány jsou hlinitokřemičité materiály, které lze aktivovat roztoky NaOH a Na_2SiO_3. S použitím přírodního pucolánu pemzového typu a různých alkalických aktivátorů na bázi kombinace Na_2SiO_3 a NaOH bylo navrženo a studováno několik geopolymerních cementů. Poměr voda–suché pojivo, modul křemíku a koncentrace oxidu sodného systémů byly upraveny na různé úrovně a u systémů byl studován čas tuhnutí, zpracovatelnost a pevnost v tlaku po 28 dnech. Získané výsledky odhalují, že přírodní pucolány pemzového typu lze aktivovat pomocí úměrné směsi Na_2SiO_3 a NaOH, kdy výsledkem je vytvoření geopolymerního cementového systému, který vykazuje vhodnou zpracovatelnost a přijatelné pevnosti v tlaku po 28 dnech. Konečná doba ztuhnutí materiálu je však příliš dlouhá a prakticky nepřijatelná.