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Effect of type, form, and dosage of activators on strength of alkali-activated natural pozzolans

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It is possible to synthesize environmentally friendly cementitious construction materials from alkali-activated natural pozzolans. The effect of the alkaline medium on the strength of alkali-activated natural pozzolans has been investigated and characterised. This paper highlights the effect of the type and form of the alkaline activator, the dosage of alkali and the SiO_2/Na_2O ratio (silica modulus, Ms) when using water–glass solutions and different curing conditions on the geopolymerisation of natural pozzolans. Activation of natural and calcined pozzolan for production of geopolymeric binder was verified by using Taftan andesite and Shahindej dacite from Iran as a solid precursor. The optimum range for each factor is suggested based on the different effects they have on compressive strength. The concentration of dissolving silicon, aluminium and calcium in alkaline solution, the formation of gel phase and the factors affecting this have been studied by using leaching tests, ICP–AES, and FTIR.

1. Introduction

The use of natural pozzolans in blended cements has the advantages of lower costs and better durability than pure Portland cement (OPC); however, their use leads to longer setting times and lower early strengths compared with pure OPC. Different techniques have been tried to increase the reactivity of natural pozzolans to overcome these disadvantages, including chemical activation, which is the most effective and cheapest one [1,2]. It has been found that geopolymer binders can be synthesized by activating natural pozzolans and condensing them with sodium silicate in a highly alkaline environment [3]. While the main benefit of using a geopolymeric cement produced from natural minerals is the reduction of environmental impact by using lesser amounts of calcium-based raw materials, lower manufacturing temperature and lower use of fuel in comparison with OPC and provides a route towards the concept of sustainable development [4,5].

The term "geopolymer" describes a family of mineral binders that have a polymeric silicon–oxygen–aluminium framework structure. The formation of geopolymers requires reactive precursor materials and a high concentration of the reagents (especially of OH^-) [6,7]. Highly alkaline solutions are used to induce the silicon and aluminium ions in the source materials to dissolve and form the geopolymer paste with three steps in the process including: dissolution of any pozzolanic compound, partial orientation of mobile precursors and re-precipitation of the particles from the initial solid phase [7,8].

The type of activator may also play an important role. Although, the limited research regarding the activation of the natural alumina-silicates has focused on the effect of sodium and/or potassium hydroxide combined (or not) with sodium silicate, it seems that KOH usually shows better reaction products than NaOH [9,10]. Minerals which dissolve more readily in increasing concentrations of alkali particularly in the NaOH rather than KOH solution, demonstrate higher compressive strengths after geopolymerisation in the latter. The larger K^+ ion favours the formation of large silicate oligomers with which $Al(OH)_4^-$ prefers to bind [10]. Therefore in using KOH solutions, more geopolymer is formed which results in more rapid setting and stronger compressive strengths than geopolymers made with NaOH [10].

The optimum dosage differs according to the type of alumina-silicate used and the type of activation solution. Palomo et al. [11] suggested that an excess of OH^- concentration in the system can lead to a strength decrease of the alkali cement. It is possible to say that the molarities of KOH used ranges from 5 M to 10 M for the activation of natural minerals [10]. Increasing the activator

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concentration beyond a certain alkali content (depending on mineral, activator and curing conditions), may not result in further increase in strength, and detrimental effects such as efflorescence and brittleness resulting from the effects of high free alkali in the product have been reported [10].

When compared to the use of alkali hydroxide only, the addition of soluble silicates makes the reaction occur at higher rates and also improves the final binder [7,10]. Addition of extra Na_2SiO_3 to the minerals activated by alkaline hydroxides is essential because the more long-chain silicate oligomers there are; the more geopolymer precursor is formed. The composition of alkali silicate solution can be expressed by two parameters: one is the modulus of solution which is the ratio of SiO_2/Na_2O, and the other is SiO_2 or M_2O content, or the sum of $SiO_2 + M_2O$ [11]. Increasing the SiO_2/Na_2O ratio affects in the positive sense the degree to which, polymerisation occurs significantly [10]. Commercial liquid sodium silicates have a modulus of 1.6–3.85. Sodium silicate liquids outside of the range have limited stability and are not practical. The pH value is the most important characteristic determining stability of high-modulus silicate solution, that is, their inclination to the formation of gel or coagulation [12]. As the formation of a silica gel makes a significant contribution to strength in geopolymerisation, there is an obvious interaction between modulus (SiO_2/Na_2O ratio) and Na_2O. That is, if the Na_2O content is kept constant (i.e. the alkaline activation effect can be considered the same) the higher the modulus the more the contribution from silica gel and the higher the strength within a certain range. However, if the sodium silicate solid content is kept constant, the lower the modulus the higher the Na_2O content and greater the alkaline activation effect but the smaller is the amount of silica gel. These competing effects result in a variable optimum modulus depending on the raw material and curing condition. When alkaline activation is insufficient and thus becomes the main factor slowing down the activation of alumino-silicate, a lower modulus is preferred; otherwise a higher modulus is preferred [13].

The aim of this paper is to study the effect of alkaline activator type, the form on which it is added, the dosage of alkali, and the SiO_2/Na_2O ratio (silica modulus, Ms) when using water–glass solution at different curing conditions on the geopolymerisation of natural pozzolans. The present paper confirms previous findings [4,10,14] and advances knowledge about the effect of type, form of adding and concentration of alkali activators on the mechanical strength of alkali-activated Iranian natural pozzolans, namely Taftan (represents pozzolans with high soluble calcium and higher content of Na_2O relative to K_2O) and Shahindej (represents pozzolans contain sodic zeolites with high soluble silicates) and studies the nature and microstructure of the optimum product under different curing conditions. In the present work it has been already explained that the geopolymer formed will mainly depend on the factors such as nature and concentration of the activator, curing temperature and pressure. The optimum concentration of activator was confirmed by ICP–AES results and extend of the alkali activation of the solid was studied by FTIR analysis; both are explained in Section 3.2.

2. Experimental techniques

2.1. Materials

Two natural pozzolans were used throughout this work to be activated as a geopolymeric cement. The first one was Taftan pozzolan obtained from the SE of Iran which is used to produce a Portland pozzolan cement by the Khash Cement Factory in Iran. It has a particle size of 100% less than 75 μm. Taftan andesite was selected as the most reactive natural pozzolan in Iran due to its chemical composition (Table 1). Its loss on ignition is low at 1.85% and the K_2O content which correlates negatively with strength [13] is lower than Na_2O. It has a comparatively high CaO content at 7.99% which can also affect the properties of geopolymers giving a higher strength. Shahindej pozzolan from the NW of Iran with a particle size of 100% less than 75 μm is also used to produce a Portland pozzolan cement by the Ourmia Cement Factory and was used in both the natural form and after being calcined at 800 °C for 12 h to show how the optimum dosage of alkali and the SiO_2/Na_2O ratio (silica modulus, Ms) when using a water–glass solution changes with the type of pozzolan. Chemical compositions of these pozzolans as detected from X-ray Fluorescence (XRF) analysis, using a Philips PW 1480 instrument, is listed in Table 1. X-ray diffraction (XRD) carried out on a Siemens D500 machine is presented in Figs. 1a–c, which indicates its crystalline and major and minor minerals.

The materials listed below were used as chemical activators to activate the natural pozzolans. Potassium or sodium hydroxide (KOH/NaOH) pellets supplied by MERK International Ltd. were dissolved to produce the alkaline solutions for geopolymeric paste production.

Sodium silicate was also provided by Iran Silicate Industrial Company in the form of granules, powder (with $SiO_2/Na_2O = 2.1$) and solution (water glass) and used to find the best form on which it is added. To study the effect of silica modulus of sodium silicate solution, three different sodium silicate solutions were considered. The chemical composition of the solution provided by the manufacture was:

(a) 12.6per of sodium oxide (Na_2O), 26.5per of silicon oxide (SiO_2) and 60.9per of water; pH = 13.
(b) 11per of sodium oxide (Na_2O), 26.5per of silicon oxide (SiO_2) and 62.5per of water; pH = 12.2.
(c) 8.5per of sodium oxide (Na_2O), 26.5per of silicon oxide (SiO_2) and 65per of water; pH = 11.4.

In a small pilot study on whatever was reported by Palomo et al. [6], this was found that the compressive strengths are higher in geopolymers made by adding alkaline hydroxide solution to natural pozzolan first followed by a sodium silicate solution, instead of adding alkaline and sodium silicate as a mixed solution to natural pozzolan. It seems that by adding alkaline hydroxide solution first, the Al–Si bonds are broken up, thus causing a higher degree of the Al–Si disorder. Then gel formation in hydrated alkaline alumina-silicates is generated by sodium silicate. However, adding alkaline and sodium silicate as a mixed solution creates two opposite reactions. Therefore the paste was prepared by adding the hydroxide solutions (Nos. 1–8 in Table 2) to the natural pozzolans and mixing for 15 min first. The mixing was continued with the addition of sodium silicate solutions (Nos. 9–11).

2.2. Experimental investigations

In order to determine the compressive strengths and follow the effect of different activators on alkali activation of natural pozzolans, the reagent grades of KOH or NaOH were added with stirring to deionised water to provide the alkaline hydroxide solution and cooled. The samples for alkali activation were prepared by adding alkaline hydroxide solution to pozzolan followed by adding sodium silicate solution. The ratio of alkaline hydroxides (ml)/ alkali silicates Na_2SiO_3 (ml) and total dry mix (g)/total solution (ml) were 7.7 and 3.2, respectively based on whatever was reported by Xu and Deventer [13]. At first to study the effect of alkaline activator type and dosage, different molarities of alkaline hydroxide equal to 2.5, 5, 7.5, 10 were considered while the properties of sodium silicate solution used corresponded to type (c) in previous section. In the next stage to find the effect of silica modulus of sodium silicate solution, different types of this solution were used while the

Table 1
Chemical composition (oxide percent) of the materials used in this investigation.

Material	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O
Taftan andesite	1.85	61.67	15.90	4.32	7.99	2.04	0.438	2.12	3.21
Shahindej dacite	10.28	70.13	11.11	1.27	2.52	0.92	0.14	2.25	1.01
Shahindej dacite-800 °C	5.78	73.44	11.88	1.30	2.55	0.98	0.147	2.30	1.10

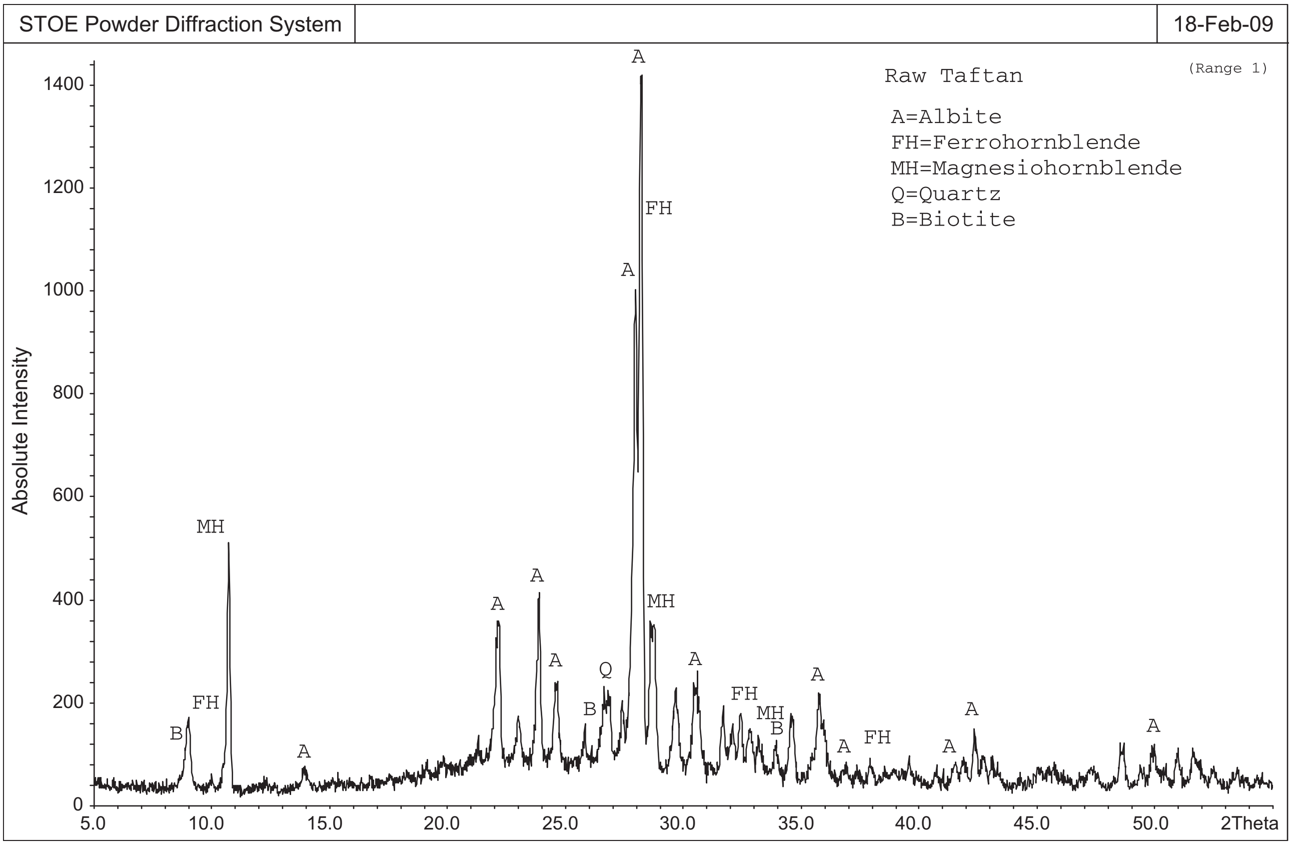

Fig. 1a. Mineralogical composition of Taftan andesite.

molarities of alkaline hydroxide was constant and equal to 7.5 M, found the optimum concentration of alkaline hydroxide for activating natural pozzolans. The mixture was then blended using a Hobart Canada N-50-1425 rpm blender. The resulting paste was transferred to polyvinyl chloride (PVC) cubic moulds of $50 \times 50 \times 50$ mm and left at room temperature for 24 h covered by a plastic sheet. After being removed from the mould, three samples for each formulation were cured in an autoclave at 2 MPa pressure and 150 °C for 3 h. The rest were wrapped and insulated in a special plastic bag (which had been tested and proved adequate to prevent evaporation) and left in the oven for further setting and hardening for 27 days at 40 °C and 60 °C temperatures. At 28 days, the compressive strength according to ASTM C39 of three samples for each formulation was measured.

The optimum concentration of KOH which generated geopolymers with highest compressive strength has been determined in Section 3.2. Simultaneously the composition of components dissolved by each concentration of activator in a leach test, were determined by inductively coupled plasma with atomic emission spectroscopy (ICP–AES). For the leaching tests, a specified mass of natural pozzolan (2.5 g) was mixed with 25 cc of the appropriate KOH (hydroxide pellets 5012 MERK) solution with molarities equal to 2.5, 5, 7.5, 10 in a polypropylene beaker at room temperature for 5 h using a magnetic stirrer. The solution and residue were separated by centrifuging for 25 min at 6000 rpm. After centrifuging, the clear liquid solution was diluted and neutralized to pH < 1 with HCl and analyzed using JY-124 Sequential Jobin–Yvon ICP–AES to determine the concentration of Si, Al, and Ca that had been transferred into the solution so as to generate a gel phase.

In order to investigate the extent of development of alkali activation of the pozzolans as precipitation reactions, the resultant filter cake from leaching was washed with 200 ml distilled water in two stages broken up and scattered on a watch glass and dried for 48 h at 60 °C. Pellets were prepared by the common method (0.5 mg of dried solid residue ground to fine powder and 150 mg of KBr) and put in an oven at 60 °C over night and pressed before scanning. The powder was analyzed by a Bruker Equinox55FTIR spectrometer with an aperture selected at 8 cm^{-1} and a total of 64 scans in each spectrometer.

3. Experimental results

3.1. Type of alkaline activator

From Fig. 2 it can be seen that activation with KOH always achieved higher compressive strength at ambient temperature curing conditions, especially at 60 °C, compared to NaOH activation.

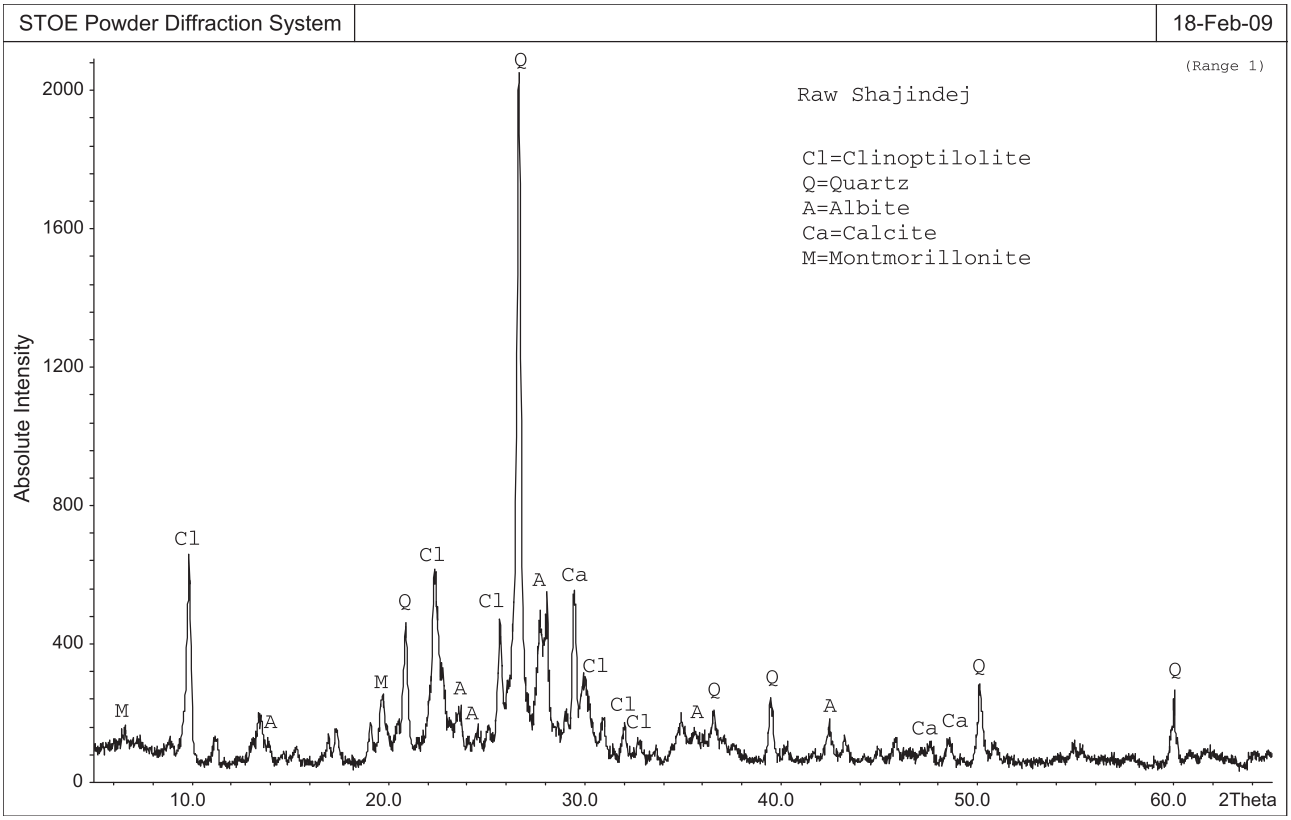

Fig. 1b. Mineralogical composition of Shahindej dacite.

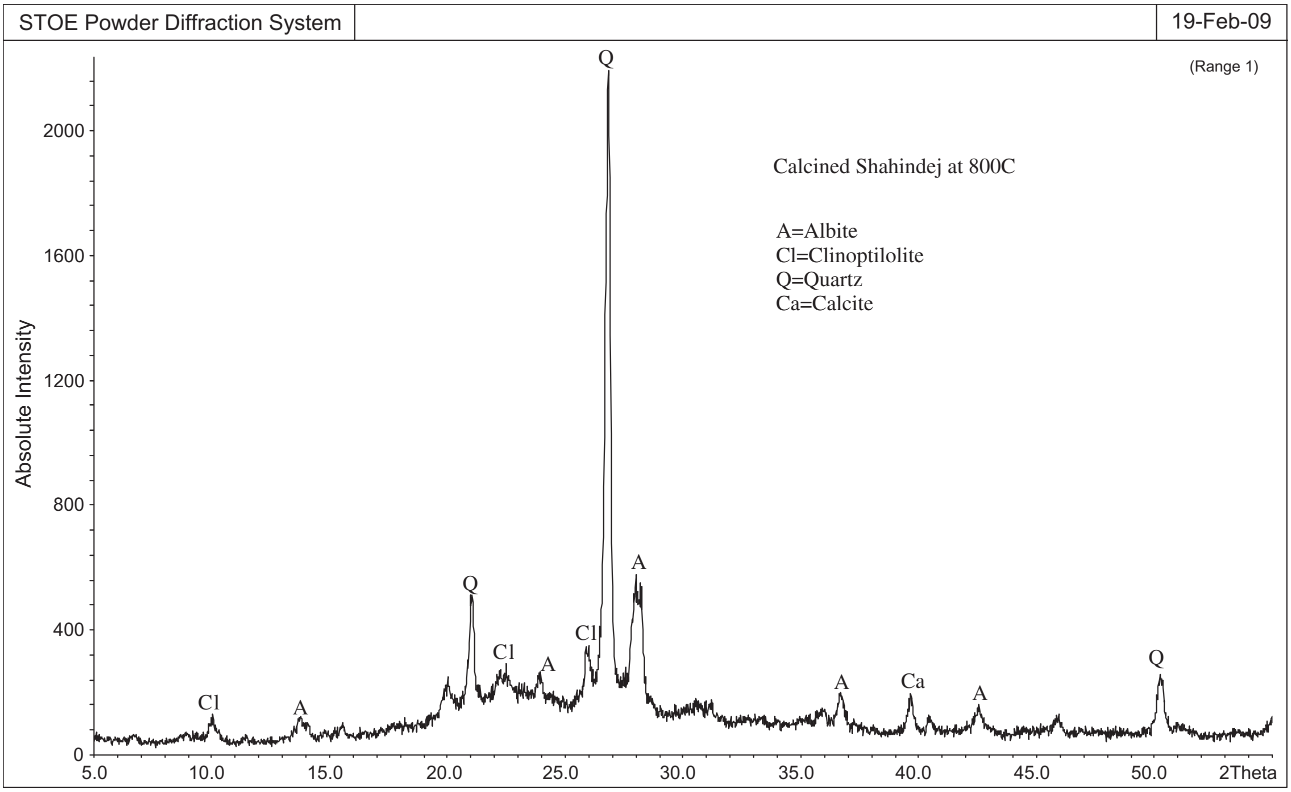

Fig. 1c. Mineralogical composition of calcined Shahindej dacite.

According to Xu and Deventer [9] as Na^+ and K^+ have the same electronic charge; their different effects must be the result of their different ionic sizes. The smaller size cation, Na^+ favours an ion-pair reaction with smaller silicate oligomers. The use of K^+ is expected to result in the formation of large silicate oligomers which is favourable from the strength point of view due to the greater

Table 2
Alkali activation solutions (g/100 ml solution).

Nos.	Notation	K_2O	Na_2O	SiO_2	Total solid
1	2.5 M NaOH	/	7.75	/	10
2	5 M NaOH	/	15.5	/	20
3	7.5 M NaOH	/	23.25	/	30
4	10 M NaOH	/	31.0	/	40
5	2.5 M KOH	11.75	/	/	14
6	5 M KOH	23.5	/	/	28
7	7.5 M KOH	32.25	/	/	42
8	10 M KOH	47	/	/	56
9	WG(SiO_2/Na_2O ratio of 2.1)	/	12.33	26.626	38.959
10	WG(SiO_2/Na_2O ratio of 2.4)	/	10.83	25.992	36.822
11	WG(SiO_2/Na_2O ratio of 3.1)	/	8.54	26.474	35.014

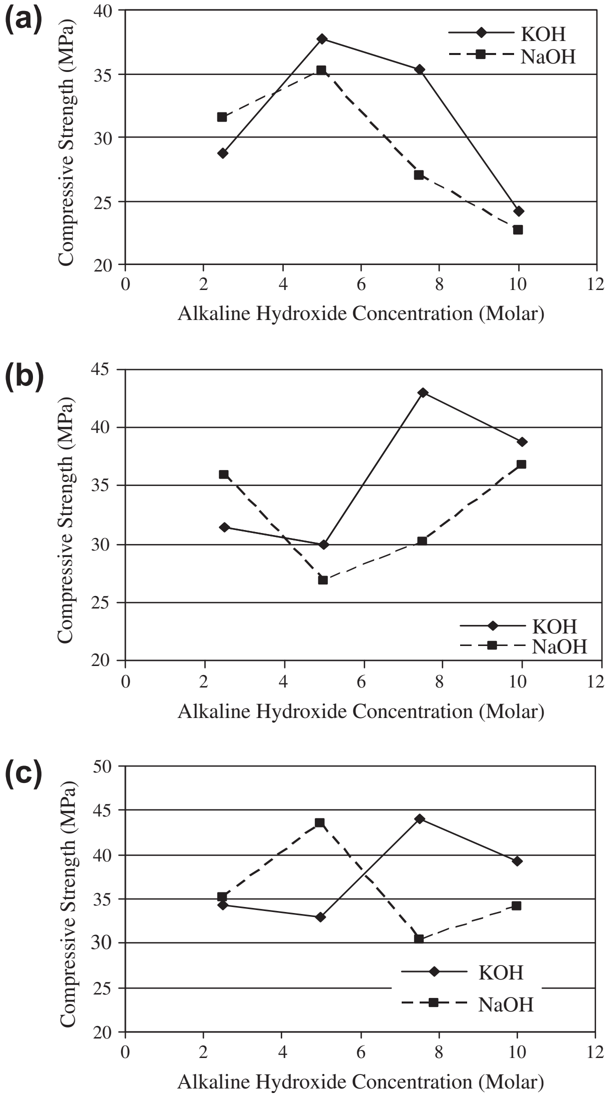

Fig. 2. Effect of type and concentration of activators on Taftan geopolymer compressive strength for different curing conditions: (a) sealed and cured at 40 °C, (b) sealed and cured at 60 °C and (c) autoclave curing.

3.2. Dosage of alkali component

The compressive strength of geopolymer cements made from Taftan pozzolan activated with either KOH or NaOH at concentrations of 2.5, 5, 7.5, 10 M are shown in Fig. 2. KOH concentrations in the range of 5–7.5 M were found to generate the geopolymers with the highest compressive strength. The results of the ICP–AES tests are shown in Table 3. At 7.5 M KOH, the optimum concentration for strength development, 274.4 and 68.22 ppm Si and Al, are dissolved respectively. Increasing the alkali concentration to 10 M did not have a significant effect on the levels of Si and Al leached.

With lower activator concentrations (i.e. less than 5 M KOH) there is significantly lower dissolution of natural pozzolan (see Table 3) resulting in a polymer with lower binding strength. However, the higher viscosity of the alkaline hydroxide solution at concentration greater than 7.5 M means that the resultant geopolymer pastes need a longer time and/or a higher temperature for the excess water to evaporate from the system before forming a monolithic geopolymer, in which full strength is gained due to the development of the 3-D network of aluminosilicate. Thus, the alkali content reaches a certain value (which depends on mineral type, activator type and curing condition), beyond which there is no further significant increase in strength, and according to Xu and Deventer [10] detrimental features such as efflorescence and brittleness may arise due to the increased free alkali content in the product. Therefore, trying to increase the strength by increasing the alkali dosage is not recommended, from both economic and properties points of view.

Some additional tests and elemental analyse were carried out on alkali-activated Taftan pozzolan to understand the gel conformation and its composition. Fig. 3 depicts the FTIR spectra recorded for Taftan powders before and after leaching in 2.5, 5.0, 7.5 M KOH. Before leaching there were two main peaks at 1032 and 1089 cm^{-1} with several smaller peaks. After leaching, the band centred at 1032 cm^{-1} is shifted towards a lower wave number with increasing alkali concentration showing that as the silicate and/or aluminosilicate structures in the natural pozzolan are significantly depolymerised based on electrostatic reactions.

According to Lee and Deventer [15], during alkali activation every bridging oxygen atom (BO) on the surface of the original aluminosilicate is replaced by two negatively charged non-bridging oxygen atoms (NBO), which are charge compensated by alkalis. As a result, the infrared (IR) band attributable to the T–O–Si asymmetric stretching vibration of the TO_4 tetrahedral of an alumino silicate in glass has been found to shift to lower energy with increasing alkali content. The shift observed for Taftan pozzolan in Fig. 3 would suggest that on leaching, all the polymerised alumina-silicate has dissolved leaving layered silicates with a number of siloxyl groups since this corresponds to stretching vibration which is corroborated by the wave number equal to 995 cm^{-1} and its structure is exclusively formed by Si–O–Al bridges.

Generally, the mid IR of these pozzolans contains a number of peaks from 800 to 1200 and the surfaces display a substantially higher degree of the Al–Si disorder with bands becoming broader. This phenomenon suggests that the disordering of the primary structure of aluminosilicate and conforming de-polymers during condensation of the resulting gel phase. Consequently, aluminosilicates demonstrate higher compressive strength after geopolymerisation in KOH than NaOH. However, from the cost view point, the use of NaOH rather than KOH may be more desirable, especially under conditions of accelerated curing. Fig. 2 shows that the same compressive strength (44.0 Mpa) has been achieved while using 5 M NaOH compared to 7.5 M KOH in autoclave curing.

Table 3
ICP–AES results for Taftan pozzolan leaching tests.

(KOH)	(Si) (ppm)	(Al) (ppm)	(Ca) (ppm)
2.5 M	29.75	Not detectable	28
5.0 M	147.99	Not detectable	98.25
7.5 M	274.4	68.22	74.98
10 M	235.2	69.36	51.43

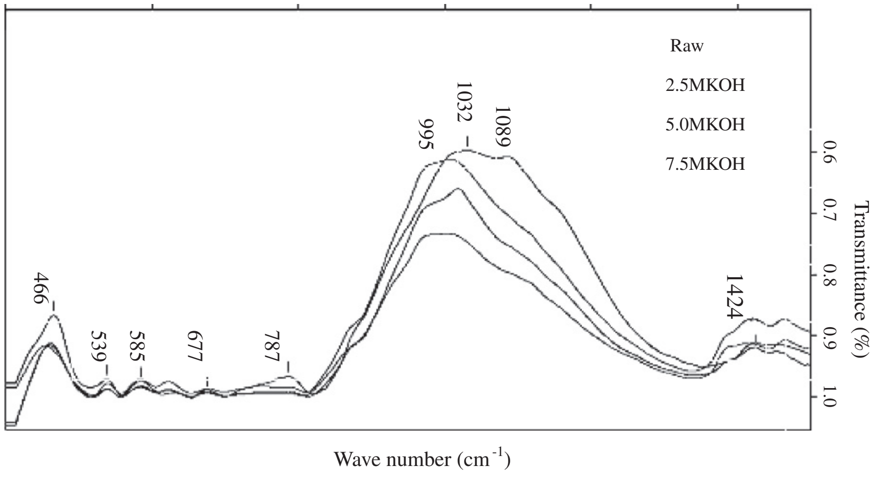

Fig. 3. FTIR results for leached Taftan pozzolan with different concentration of activator.

the treatment could result in some type of Al–Si precipitates forming on the surfaces of un-reactive Taftan pozzolan particles.

All samples display a new absorbance in the region of 1404–1471 cm^{-1} which increases after leaching. (Fig. 3) This absorbance could be due to a vibration of carbonate salts formed on the surface of the residues [15] and with the band around 870 cm^{-1} it might imply that some type of hydrated carbonates and K$^+$ related aluminates are precipitated on the surfaces of the residues produced during leaching.

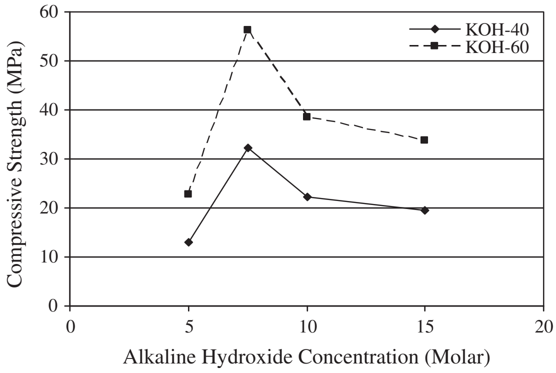

Fig. 4. Effect of concentration of activators on Shahindej geopolymer compressive strength for different curing conditions.

Activation of Shahindej pozzolan with 5, 7.5, 10 and 15 M KOH gives the compressive strengths shown in Fig. 4 at two different curing temperatures with the highest strength of 32.2 MPa at 40 °C and 56.2 MPa at 60 °C .

Fig. 5 depicts the PAS-FT-IR spectra recorded for Shahindej powders before and after leaching in 7.5 M KOH. The spectrum before treatment contained one main peak at 1055 cm^{-1} which display Al–O–Si and Si–O–Si stretching bands. After leaching, the vibration band for untreated Shahindej pozzolan with its maximum at 1055 cm^{-1} is shifted to a lower wave number. Therefore, the original silicate and/or alumina-silicate structures in the natural pozzolan have been significantly depolymerised based on electrostatic reactions.

Therefore potassium hydroxide appears to provide the best activator in the range of 5–7.5 M as it dissolves the greatest amount of material from the precursor and gives the highest values for compressive strength. The larger ion (as the best alkaline hydroxide) first, the Al–Si bonds are broken up. Then the gel formation in hydrated alkaline alumina-silicates is generated by adding sodium silicate.

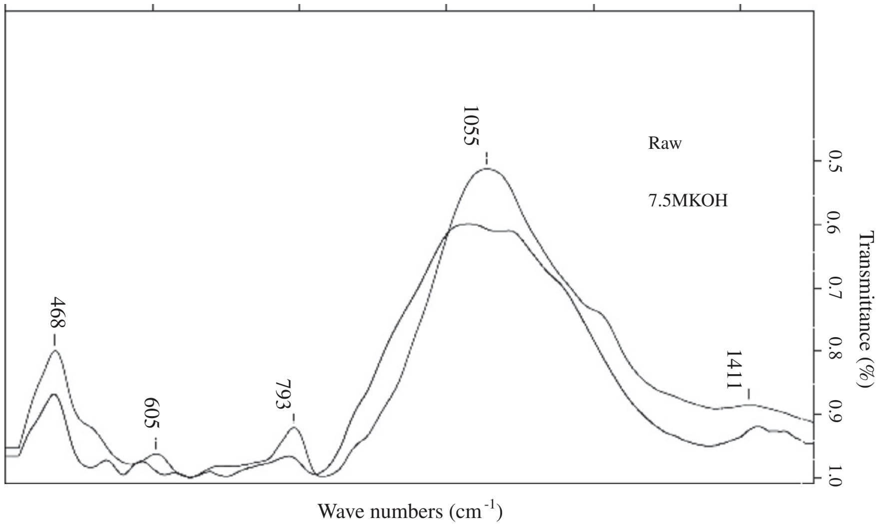

Fig. 5. FTIR results for untreated Shahindej pozzolan and alkali-activated form of it.

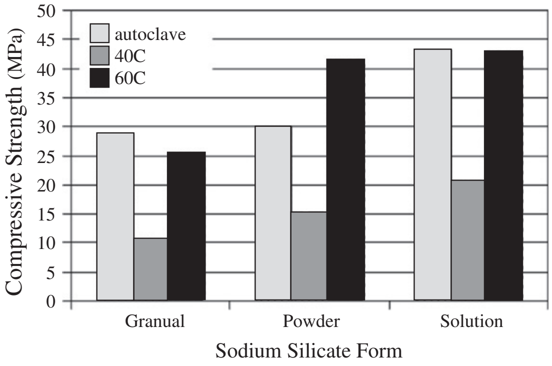

Fig. 6. Effect of sodium silicate form on activation of Taftan pozzolan.

3.3. Form of sodium silicate activator

There are three forms of sodium silicate, granular, powder and solution. The present work confirms that higher strengths are obtained when sodium silicate is added as a solution (strengths of 20.7 and 43.0 MPa corresponding to 40 and 60 °C curing temperature respectively) than when it is added in solid state by powder forms (Strengths of 15.3 and 41.7 MPa corresponding to 40 and 60 °C curing temperature, Fig. 6). The addition of solid alkali silicate not only results in lower strength but also produces much greater strength fluctuation, which can be attributed to lower solubility in the mix and availability of alkali for reaction. The solid alkali silicate might absorb moisture during storage which will inhibit its activating action. Another interesting point is that using hydrous water–glass/sodium meta-silicate containing chemically bound water in the solid form produces low strength equal 11 MPa (Fig. 6) under normal curing conditions.

3.4. Modulus of water–glass solution

The most important property of sodium silicate is the molar ratio of SiO_2 to Na_2O. Silicates are commercially produced in the SiO_2:Na_2O ratio range of 1.5–3.2. In general, high ratio silicates (i.e. 3.2) are most suitable for chemical bonding since it is the siliceous portion of the silicate that reacts with cations. Due to the importance of maintaining a high alkali concentration, it has been recommended that lower ratio silicates, e.g. [2.0], are used for activation of pozzolans [16].

In the present work, three industrial sodium silicates with SiO_2/Na_2O ratios of 2.1, 2.4 and 3.1 were used to form geopolymers with

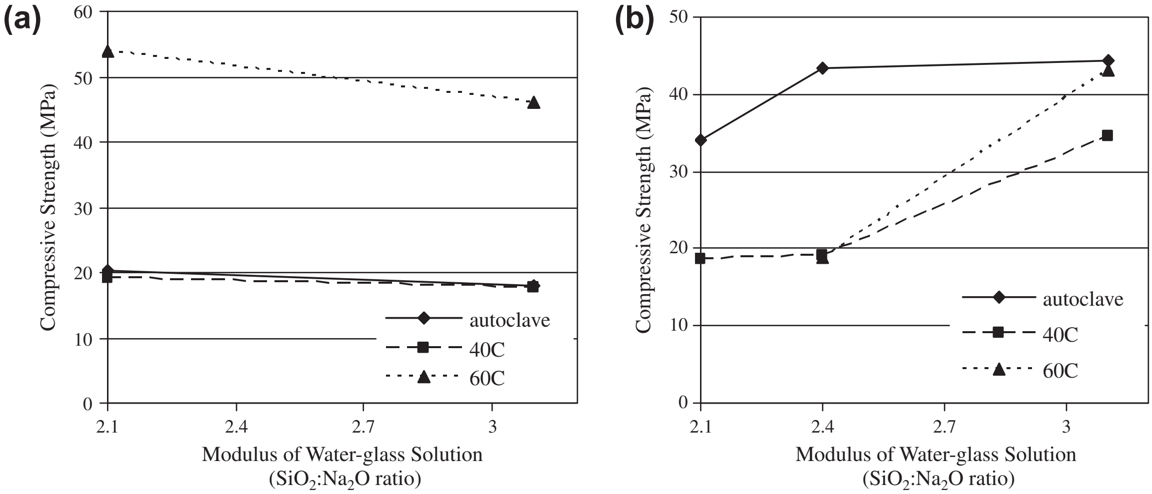

Fig. 7. Effect of sodium silicate ratio on activation of Taftan pozzolan with different CaO contents: (a) low CaO content and (b) high CaO content.

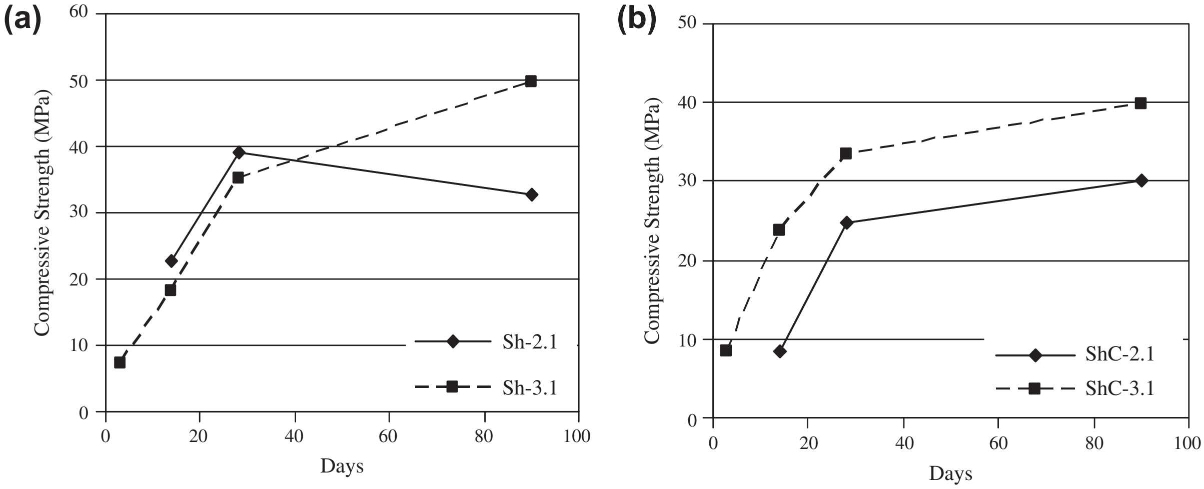

Fig. 8. Effect of sodium silicate ratio on activation of Shahindej pozzolan at different state: (a) natural and (b) calcined.

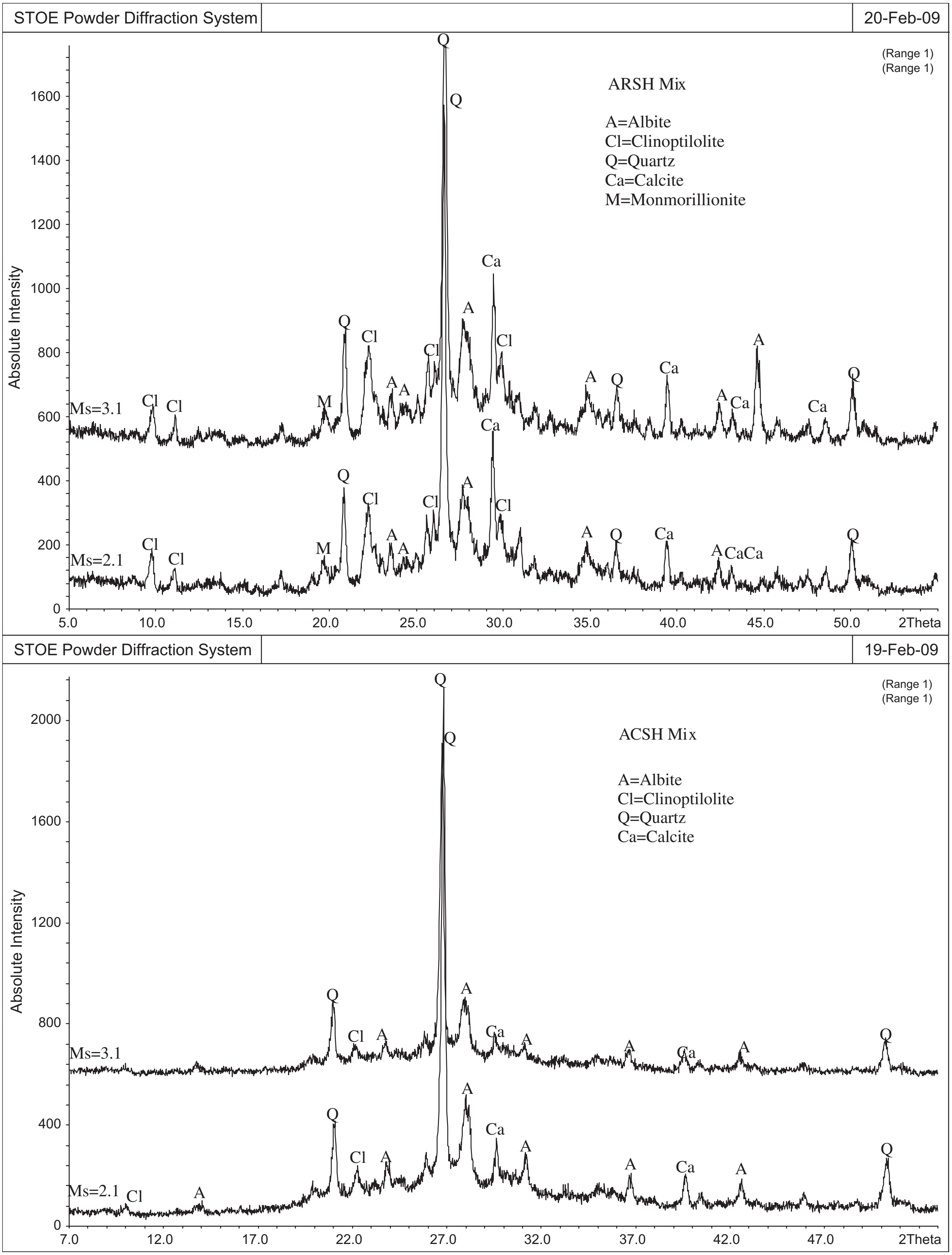

Fig. 9. X-ray diffraction traces of untreated (ARSH) and calcined (ACSH) Shahindej dacite activated with different ratio of sodium silicate.

two Taftan pozzolans which contained 8% and 15% CaO (Taftan pozzolan has variations in chemical composition from batch to batch [3]). It was found that the pozzolan with higher CaO content gives rise to higher strengths (maximum 28 days compressive

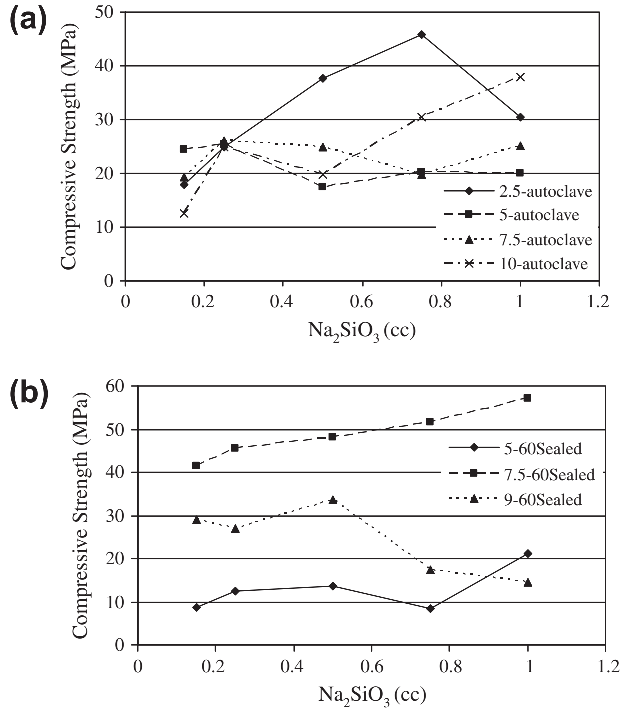

Fig. 10. Influence of amount of sodium silicate on compressive strength of different activated pozzolans (samples dimensions were 20 × 20 × 20 mm in these experiments): (a) Taftan and (b) Shahindej.

strength of 43.0 MPa) with a SiO_2/Na_2O ratio of 3.1. However, for the natural pozzolan with the lower content of CaO it is the amount of alkali that is more important for activation (Fig. 7).

For pozzolans containing sodic zeolites such as Shahindej dacite that are not thermally treated and which exhibit high soluble silicate, lower SiO_2 to Na_2O ratios give higher strengths (at 28 days the compressive strength is 39.0 MPa with SiO_2/Na_2O equal to 2.1) but when calcined the reverse is true (at 28 days, the compressive strength of 33.4 MPa was obtained with the SiO_2/Na_2O ratio of 3.1). However, beyond 40 days the best compressive strengths were obtained with higher amounts of silicate in the system so at 90 days the compressive strengths were 49.7 MPa and 39.8 MPa respectively, both with a SiO_2/Na_2O ratio equal to 3.1(Fig. 8).

The study of geopolymers produced based on untreated and calcined Shahindej pozzolan with different amounts of water–glass ratio using X-ray diffraction and comparing the results, confirms the above results as is presented in Fig. 9. It can be observed that for calcined Shahindej when the water–glass with the SiO_2 to Na_2O ratio of 3.1 is used, the intensity of peaks is less and more activation is occurred while this happens for untreated Shahindej when the water–glass with the SiO_2 to Na_2O ratio of 2.1 is used.

3.5. Various ratios of alkaline hydroxide to water–glass

To study the effect of different contents of sodium silicate on improving the compressive strength, mixes were prepared with different volume range of sodium silicate solution from 0.15 to 1.0 cc while the concentration of potassium hydroxide and water content were keeping constant and the compressive strength was measured. This was repeated for different concentration of alkaline hydroxide (KOH). The effect of Na_2SiO_3 on the development of compressive strength (Fig. 10) shows that the optimum amount of Na_2SiO_3 for achieving strength in a range suited for structural concrete is 0.25 cc to 0.5 cc. The ratios of the alkaline hydroxide (KOH) to sodium silicate in the above mixes were calculated and the strength contours versus different molarities of KOH and various ratio of KOH/Na_2SiO_3 are shown in Figs. 11 and 12. The islands of ideal compositions show that the minimum ratio of KOH to Na_2SiO_3 volume corresponding to the optimum concentration of KOH for achieving high compressive strengths are 7.1 and 7.7 for Taftan and Shahindej pozzolan, respectively. The reason for conforming three islands of ideal compositions in Fig. 12 might be that different molarities of KOH against various ratio of KOH/Na_2SiO_3 provide various circumstances for different relative amounts of SiO_2 and Al_2O_3 of the Shahindej pozzolan to be solved. This phenomena affects on the chemical reaction of alumina-silicate oxides with alkali yielding polymeric Si–O–Al bonds with different dimensional silico-aluminate structures such as Poly(sialite)(–Si–O–AL–O–), Poly(sialate-siloxo)(–Si–O–Al–O–Si–O–), or Poly(sialate-disiloxo)(–Si–O–Al–O–Si–O–Si–O–) with different Al and Si building blocks, which affect the chemical and physical properties of the final product. Considering the price of KOH and Na_2SiO_3, the minimum ratio was found to be the most adequate from the economical point of view.

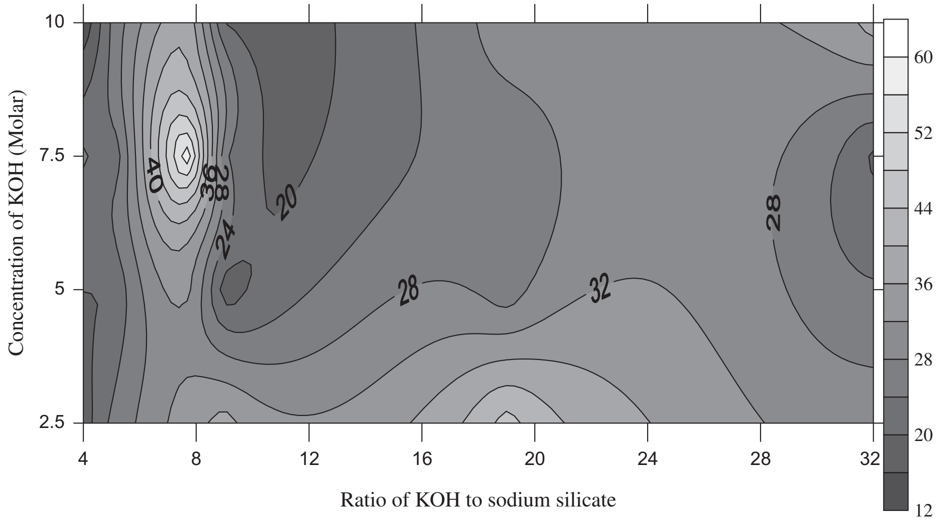

Fig. 11. Strength contour (MPa) for different concentration of KOH and various ratio of KOH/Na_2SiO_3 for Taftan Pozzolan (24 samples were tested).

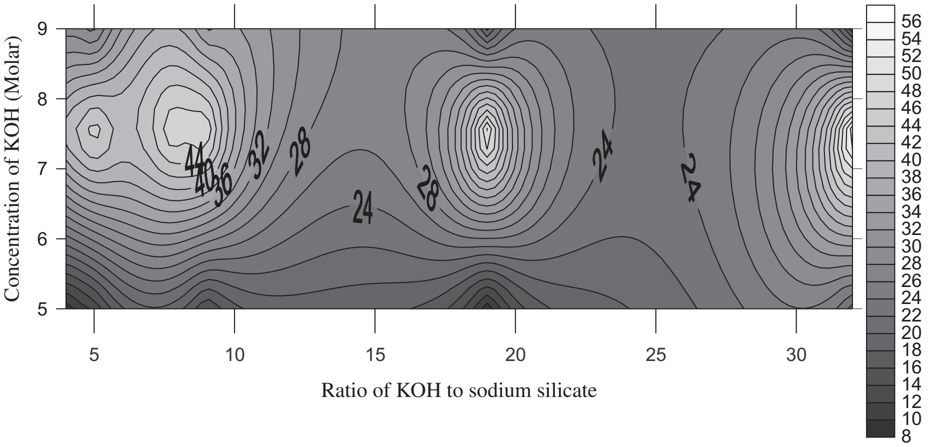

Fig. 12. Strength contour (MPa) for different concentration of KOH and various ratio of KOH/Na_2SiO_3 for Shahindej Pozzolan (16 samples were tested).

4. Conclusions

Two Iranian natural pozzolans, namely Taftan andesite (which represents pozzolans with high soluble calcium and higher content of Na_2O relative to K_2O) and Shahindej dacite (which represents pozzolans contain sodic zeolites with high soluble silicates) were used as a solid precursor to be activated for producing geopolymeric cement throughout this work. With respect to the results obtained in this research, the factors for achieving optimum strength of these alkali-activated natural pozzolan concretes have been determined which are summarized as follows:

(1) A combination of potassium hydroxide with a sodium silicate solution provides the best activator. KOH solutions between 5 and 7.5 M dissolve the greatest amount of material from the precursor and also give the highest values for compressive strength. The alkaline hydroxide first breaks up the Al–Si bonds and dissolves Al ions which catalyses the polymerisation and formation of the gel from hydrated alkaline alumina-silicates created by adding soluble sodium silicate. These follow the pattern reported by Xu and Van Deventer, [10,14].

(2) The most effective alkali activator dosage which gives the highest compressive strength correlates well with that shown by optimum leaching.

(3) For natural pozzolans with low CaO content and for pozzolans containing sodic zeolites that are not thermally treated, such as Shahindej dacite with its high soluble silicate, the optimum water glass modulus (SiO_2/Na_2O ratio) is 2.1 but increases to 3.1 for natural pozzolans with high CaO or which have been calcined.

(4) The optimum dosage of activator and the optimum ratios of alkaline hydroxide to sodium silicate were determined by examining the islands of ideal compositions determined from a new method which draws the strength contours versus different molarities of alkaline hydroxide and various ratio of alkaline hydroxide to alkaline silicate.

(5) The optimum curing temperature to achieve the highest strength for alkali-activated Taftan pozzolan was 60 °C. However, 40 °C was found to be adequate for achieving strength in a range suited for structural concrete (Fig. 2).

(6) Comparable strengths to those obtained at 60 °C curing can be obtained by autoclaving alkali-activated Taftan pozzolan at 2.5 MPa and 150 °C for 3 h (Fig. 2).

(7) Natural Shahindej pozzolan must be cured at 60 °C to produce structural concrete (Fig. 4) but the form calcined at 800 °C can be cured at 20 °C [3].

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