Coventry University and
The University of Wisconsin Milwaukee Centre for By-products Utilization,
Second International Conference on Sustainable Construction Materials and Technologies
June 28 - June 30, 2010, Università Politecnica delle Marche, Ancona, Italy.
Special Technical Proceedings ed. P Claisse, E Ganjian, F Canpolat and T Naik
ISBN 978-1-4507-1488-4 http://www.claisse.info/Proceedings.htm

Geopolymer Cement from Alkali-Activated Natural Pozzolans: Effect of Addition of Minerals

D Bondar[(a)], C. J. Lynsdale[(b)], N. B. Milestone[(c)], N. Hassani[(d)]
A. A. Ramezanianpour[(e)]

(a) Ph.D. candidate of University of Sheffield and P.W.U.T. Research Associate. (b) Dept. of Civil and Structural Engineering, University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK. (c) Dept. of Engineering Materials University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK. (d) Research Centre of Natural Disasters in Industry, P.W.U.T., Tehran, Iran (e) Dept. of Civil Engineering, Amir Kabir University, Tehran, Iran <dlbondar@gmail.com>, <c.lynsdale@sheffield.ac.uk>, <neil.milestone@gmail.com>, <nemathassani@yahoo.com>, <aaramce@aut.ac.ir>

ABSTRACT

Natural pozzolans are raw materials from geological deposits with a range of chemical compositions that when combined with suitable alkali activators can be converted to geopolymer cement for concrete production. In this paper the concept of adding mineral additives to enhance the properties of geopolymer cement is introduced. Taftan andesite, a natural Iranian pozzolan, was used to study the effect of adding mineral additives such as kaolinite, lime and other calcined pozzolans on the compressive strength of geopolymer cement under both normal and autoclave curing. Scanning electron microscopy (SEM) / energy dispersive X-ray (EDX) was used to determine the composition of the gel phase in both alkali-activated Taftan pozzolan with and without mineral additions. The work has shown that deficiencies in SiO_2, Al_2O_3 and CaO content in the raw natural pozzolan can be compensated for by adding mineral additives for enhanced properties.

INTRODUCTION

Geopolymers form by the co-polymerization of dissolved silicon and aluminium species in the presence of high pH alkali silicate solutions and can be synthesized from a wide range of aluminosilicate powders including natural pozzolans [Davidovits, 1991, 1994]. Recent work [Bondar, 2009] has shown that natural pozzolans from Iran show good potential as a source of aluminosilicate. Previous work has shown that factors such as increasing molar Si-Al ratio and %CaO have positive effects on the final compressive strength of geopolymer cement [Xu and Deventer, 2000].

The aluminosilicate used for the production of a geopolymer cement must contain Al which is readily soluble with an overall molar ratio of Al_2O_3:SiO_2 lying between 1:3.3 and 1:6.5 [Jaarsveld et al., 1997, Rahier et al., 1996, 1997, Hos et al., 2002]. However, these ratios are not critical and are for the most part only an indicator of approximate composition. The reason for this is that while these compositional ratios are based on chemical analysis, it is highly unlikely that all of the silica or alumina actually take part in the synthesis reaction [Jaarsveld and Deventer, 1996]. Often the rate of dissolution of Al from natural aluminosilicates is insufficient to produce a gel of desired composition [Xu and Deventer, 2000]. Kaolinite is a relatively inexpensive aluminosilicate which might be suitable as a secondary source of soluble Si and Al when added to natural pozzolans to synthesize geopolymers. Consequently, when an optimum amount of kaolinite is added to natural aluminosilicates activated by alkaline solutions, a desired gel composition may be produced with a longer setting time. However, if kaolinite on its own is used without the presence of other natural minerals, a weak structure is formed [Xu and Deventer, 2000].

Additionally, the calcium content is also an important factor affecting the setting time and final strength in concrete, and there are indications that it may also affect the properties of geopolymers [Xu and Deventer, 2000]. Therefore the addition of an optimum amount of CaO content to a natural aluminosilicate may also increase the strength of an alkali-activated natural pozzolan.

Natural pozzolans are geological deposits with a wide range of chemical compositions which vary from batch to batch but they are usually high in available SiO_2. Deficiencies in the SiO_2, Al_2O_3 and CaO content in a natural pozzolan might be compensated for by adding mineral additives, such as kaolinite or lime enabling them to be used as a geopolymer cement. This paper studies the effect of addition of active mineral additives containing readily available Al, Si, and Ca to compensate for the lack of ready availability of these species in the initial raw material. To this end, Kaolinite, calcined Shahindej pozzolan from Iran, and slaked lime, were chosen as the mineral additives to be added to Iranian Taftan pozzolan to enhance its composition, before activation, and the effects of this treatment on compressive strength, and the composition of the gel phase and its structure observed.

EXPERIMENTAL TECHNIQUES

Materials

The natural pozzolan used throughout this work was Taftan pozzolan obtained from SE of Iran which is used to produce a Portland pozzolan cement by the Khash Cement Factory in Iran. It has variations in chemical composition from batch to batch. Different batches were used in this work [Bondar, 2009]. It has a particle size of 100% less than 75µm. For this study, three additives, kaolin, calcined Shahindej pozzolan and burnt lime were chosen as mineral additives; Kaolin SL-KAD has a particle size of 66% less than 2µm and 0.1% greater than 45µm, Shahindej pozzolan from NW of Iran (particle size of 100% less than 75µm) used to produce Portland pozzolan cement by Ourmia Cement Factory was calcined at 800°C for 12hr; and burnt lime with the same particle size were used. Chemical compositions of Taftan pozzolan and the mineral additives were analysed by X-ray Fluorescence (XRF) analysis at the Kansaran Binaloud X-ray laboratory in Tehran, Iran using a Philips PW 1480 instrument and are shown in Table1.

Table 1 Typical chemical composition of mineral additives

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
Kaolin	13.84	52.2	30.90	0.45	0.26	0.24	0.125	0.90	0.45
Calcined Shahindej	5.78	73.44	11.88	1.3	2.55	0.98	0.147	2.3	1.1
Burnt lime	10	-	-	-	90	-	-	-	-

Potassium hydroxide (KOH) pellets, supplied by MERK International Ltd, were dissolved to produce the alkaline solutions for geopolymeric paste production. Sodium silicate was provided by Iran Silicate Industrial Company in the form of a solution (water glass). The chemical composition of the solution provided by the manufacture was: 8.5% of sodium oxide (Na_2O), 26.5% of silicon oxide (SiO_2) and 65% of water; pH=11.4

Sample preparation and methods

In order to determine the compressive strengths and follow the effect of adding different minerals to natural pozzolans a different approach of mixing the activators than normally used was taken. KOH was added with stirring to deionised water to provide a 7.5 M potassium hydroxide solution and cooled. This was found to be the optimum concentration of alkaline hydroxide for activating natural pozzolans in previous work [Bondar et al., 2007]. The samples for alkali activation were prepared by mixing Taftan natural pozzolan with or without the mineral additives above at different ratios (the mineral additives were dry mixed with Taftan pozzolan at specified mass ratios for 5 minutes) before the addition of the potassium hydroxide solution to the pozzolan followed by the sodium silicate solution. The ratio of KOH (ml)/ Na_2SiO_3 (ml) and total dry mix (g)/total solution (ml) were 7.7 and 3.2, respectively. The mixture was then blended using a Hobart Canada N-50-1425rpm blender. The resulting paste was transferred to polyvinyl chloride (PVC) cubic moulds of 50x50x50mm and left at room temperature for 24 hr covered by a plastic sheet. After being removed from the mould, three samples for each formulation were cured in an autoclave at 2MPa pressure and 150°C for 3hr. The rest were wrapped and insulated in a special plastic bag (which had been tested and shown adequate to prevent evaporation) and left at room temperature to further set and harden for 27 days at 25°C. At 28 days, three samples for each formulation were measured for compressive strength according to ASTM C39.

To investigate the microstructure of pastes, samples were cut by a diamond wheel saw from the cubes, epoxy-impregnated, polished and carbon-coated for examination by scanning electron microscopy and microanalysis (SEM and EDX) using a Cambridge 2000EX scanning electron microscope equipped with EDX analysis system at the Material and Energy Research Centre laboratory, Tehran, Iran.

RESULTS AND DISCUSSION

To determine the effect of active mineral additives on compressive strength in geopolymer cements and to describe the behaviour of their reaction, the method of specific strength determination (SS) devised by Pu (1999) was carried out. Specific compressive strength can be defined as the contribution 1 wt% of a natural pozzolan makes to the strength of a geopolymer cement at 28 days. It equals the real 28 days compressive strength divided by the percentage of the natural pozzolan, namely Taftan, in this research. The results are given in

Table 2 and Figures 1 to 3 for the different mineral additives. At 28 days of age, the specific strength increased when mineral additives were used compared to activation of pure natural pozzolan as a geopolymer cement at room temperature. It can be seen that for each mineral additive there is an optimum addition although it does depend on temperature. Specific strength is also increased with an increase of aluminium or calcium containing additives up to that optimum amount after which increasing the amount of mineral additive has no significant effect on the increase of the specific strength.

Table 2 Mix proportion, strength, specific strength (SS) and SS of mineral effect

Mix Proportion (%)		**Mix 1**	**Mix 2**	**Mix 3**	**Mix 4**	**Mix 5**	**Mix 6**	**Curing**
Taftan Pozzolan		100	85.7	83.3	80	73.33	60	
Kaolinite		0	14.3	16.7	20	26.67	40	
W/B		0.31	0.31	0.31	0.31	0.31	0.31	
compressive strength(MPa)		44.03	23.85	24.21	45.61	22.9	22.36	Autoclave
	28 days	19.48	18.61	19.04	19.26	16.81	10.49	25°C
SS of pozzolan in the cement (MPa)		0.44	0.27	0.29	0.57	0.31	0.37	Autoclave
		0.195	0.22	0.23	0.24	0.23	0.17	25°C
SS of mineral effect (MPa) (SSME)		0	-0.17	-0.15	0.13	-0.13	0	Autoclave
		0	0.025	0.035	0.045	0.035	0	25°C
Mix Proportion (%)		**Mix 7**	**Mix 8**	**Mix 9**	**Mix 10**			
Taftan Pozzolan		100	85.7	83.3	0			
Calcined Shahindej		0	14.3	16.7	100			
W/B		0.31	0.31	0.31	0.31			
compressive strength(MPa)		44.03	37.22	45.56	0			Autoclave
	28 days	19.48	15.53	25.28	16.07			25°C
SS of pozzolan in the cement (MPa)		0.44	0.43	0.55	-			Autoclave
		0.195	0.18	0.3	-			25°C
SS of mineral effect (MPa) (SSME)		0	-0.01	0.11	-			Autoclave
		0	-0.015	0.105	-			25°C
Mix Proportion (%)		**Mix 11**	**Mix 12**	**Mix 13**	**Mix 14**			
Taftan Pozzolan		100	98.3	96.66	93			
Burnt lime		0	1.7	3.4	7			
W/B		0.31	0.31	0.31	0.31			
compressive strength(MPa)		44.03	16.33	27.8	14.98			Autoclave
	28 days	19.48	10.84	19.6	17.19			25°C
SS of pozzolan in the cement (MPa)		0.44	0.17	0.29	0.16			Autoclave
		0.195	0.11	0.2	0.18			25°C
SS of mineral effect (MPa) (SSME)		0	-0.27	-0.15	-0.28			Autoclave
		0	-0.085	0.005	-0.015			25°C

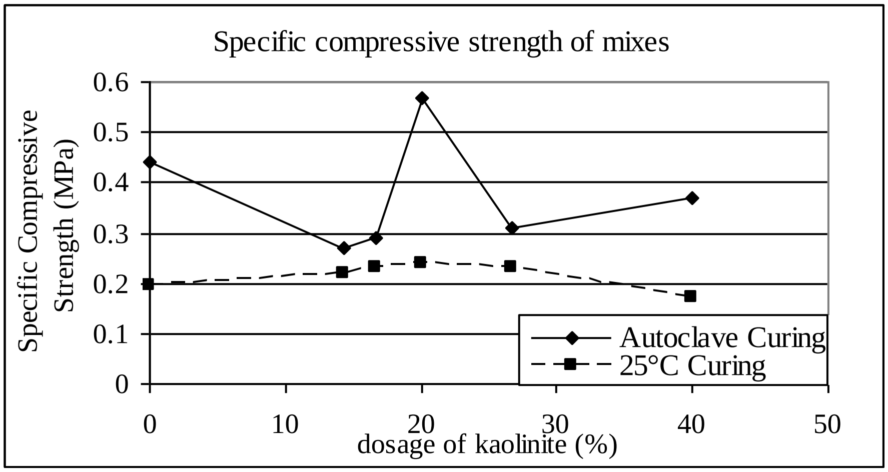

Fig. 1 Specific compressive strength of mixes containing kaolinite (The pronounced optimum is real and occurs in a number of samples at other ages.)

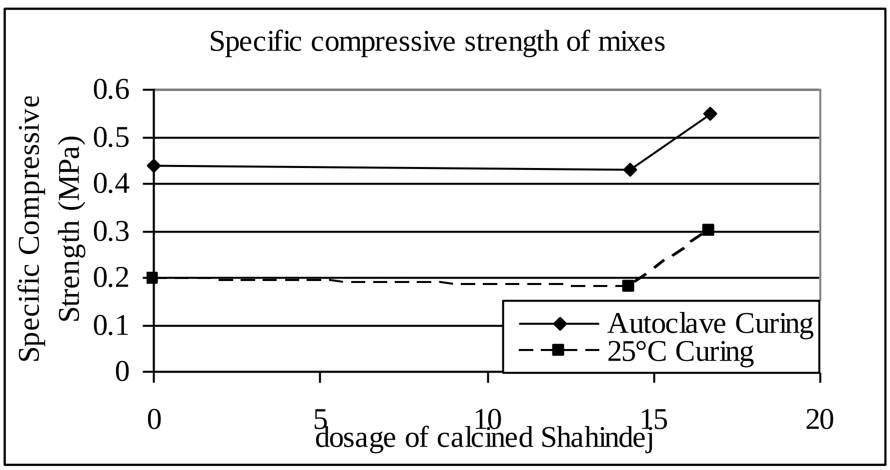

Fig. 2 Specific compressive strength of mixes containing calcined Shahindej

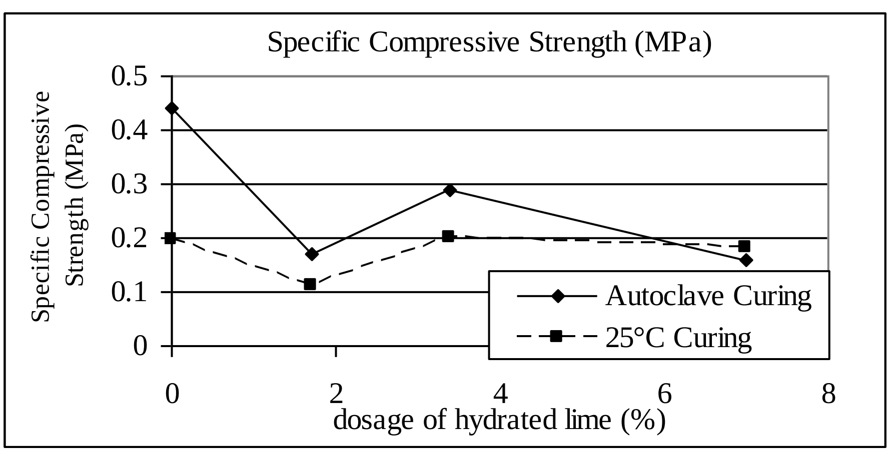

Fig. 3 Specific compressive strength of mixes containing burnt lime

The strength of a geopolymer cement containing active mineral additives can be considered to consist of two parts. The main contributor to strength for this type of cement is the polymerised Al and Si network obtained from the reaction between active silica and alumina in the main pozzolan. Addition of the active mineral additives provides additional aluminium or silicon to enhance the three dimensional amorphous and/or semi-crystalline polymer structures with alkali metals cations compensating the negative charges caused by Al substitution. The secondary part of strength is contributed by formation of semi-crystalline tobermorites (C-S-H) or calcium aluminosilicate hydrates (Pu, 1999). In this research, kaolinite and calcined Shahindej pozzolan have been used as mineral additives to provide additional aluminium and silicon sources. The maximum strength resulted when 20% kaolinite was used giving 45.6 and 19.3MPa for autoclave and sealed curing at 25°C, respectively. Similar results were obtained by adding 16.7% calcined Shahindej pozzolan as an additive where 45.6 and 25.3MPa were obtained for autoclave and sealed curing at 25°C respectively. Using burnt lime the maximum strength resulted when 3.4% lime was used giving 27.8 and 19.6MPa for autoclave and sealed curing at 25°C, respectively (Table 2).

Figures 4 to 7 show some of the microstructural characteristics as seen by SEM of the binder obtained by alkaline activation of a natural pozzolan with and without addition of different minerals cured at both 25ºC and autoclave conditions. The samples studied have quite different microstructures. Autoclaving samples have made the structure microcrystalline, dense and provide higher strength. Table 3 shows that in all of the samples, the standard composition criteria have been met for geopolymerization to occur. The standard molar oxide ratio of SiO_2/Al_2O_3 in geopolymer composition was suggested by Davidovits et al. to be between 3.3 and 6.5 for finished product (in Jaarsveld et al., 1997, Rahier et al., 1996, 1997, Hos et al., 2002). In Table 3, the increase of the SiO_2 content in the autoclaved samples can be explained by an increased dissolution of the pozzolan upon autoclaving. The percentage of reacted pozzolans can be found by dividing the weight percentage of silicon concentration observed in the binders (Table 3) by the total amount of the silicon content in the Taftan pozzolan and the mineral additives, considering the optimum percent of mixture, in each case (Table 1 and 2). It should be mentioned that the reacted pozzolan in different formulation gives rise to the geopolymer gel, zeolites and calcium silicate hydrate in the different cases.

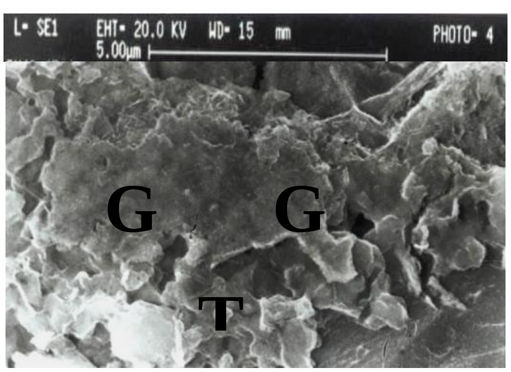

Fig. 4-a SEM of activated Taftan cured at 25ºC
(G) Geopolymer Gel, (T) Non reacted Taftan

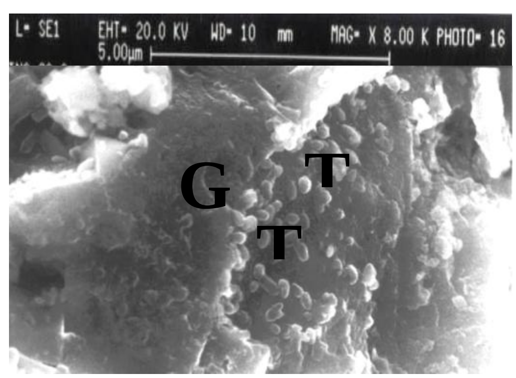

Fig. 4-b SEM of activated Taftan autoclave cured
(G) Geopolymer Gel, (T) Non reacted Taftan

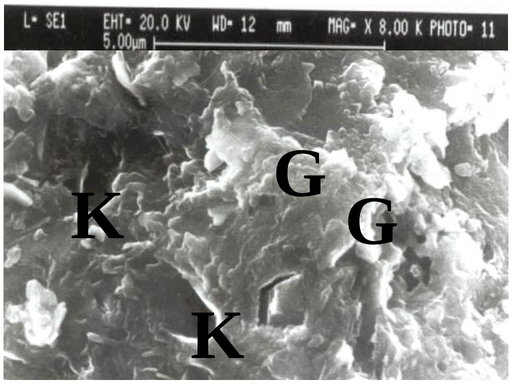

Fig. 5-a SEM of activated Taftan mixed with Kaolinite cured at 25ºC (G) Geopolymer Gel, (K) Non reacted Kaolinite

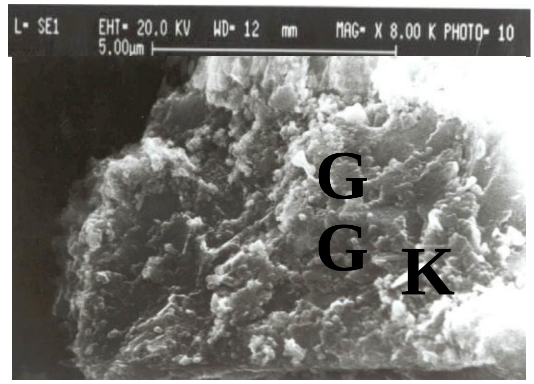

Fig. 5-b SEM of activated Taftan mixed with Kaolinite autoclave cured (G) Geopolymer Gel, (K) Non reacted Kaolinite

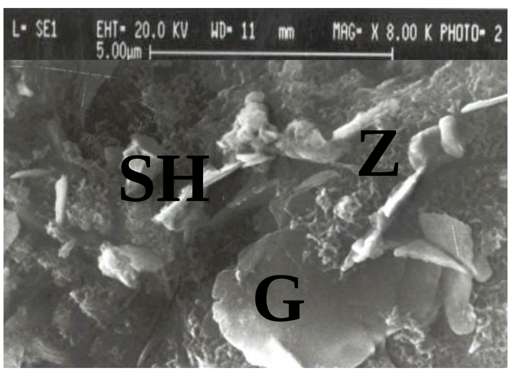

Fig. 6-a SEM of activated Taftan mixed with calcined Shahindej cured at 25ºC (G) Geopolymer Gel, (Z) zeolite (SH) Non reacted Shahindej

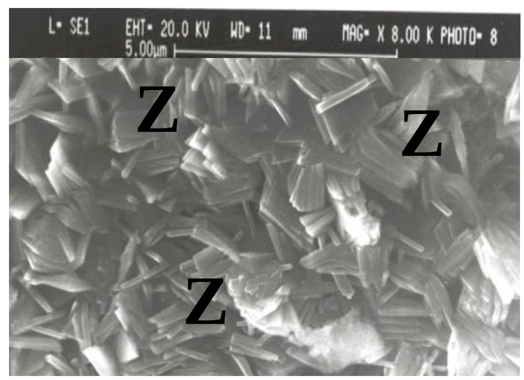

Fig. 6-b SEM of activated Taftan mixed with calcined Shahindej autoclave cured (Z) Zeolite

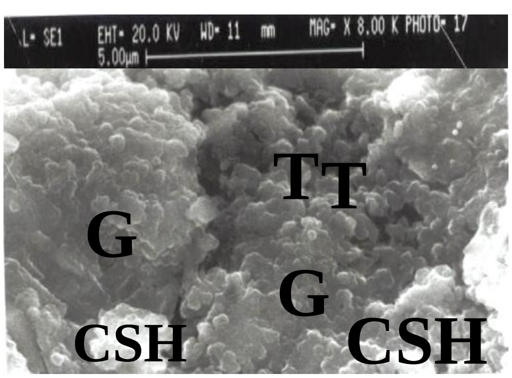

Fig. 7-a SEM of activated Taftan mixed with burnt lime at 25ºC (G) Geopolymer Gel, (CSH) Calcium Silicate Hydrate (T), Non reacted Taftan

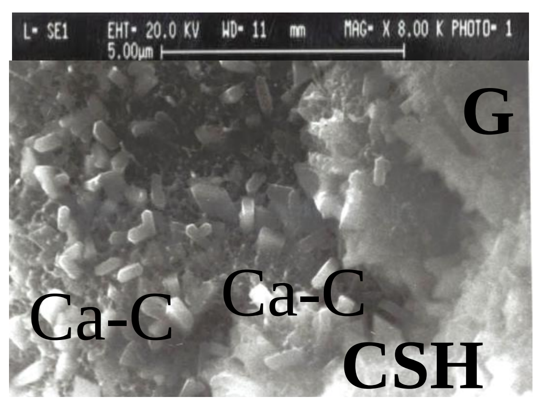

Fig. 7-b SEM of activated Taftan mixed with burnt lime autoclave cured (G) Geopolymer Gel, (CSH) Calcium Silicate Hydrate (Ca-C) Calcium Carbonate

Table 3 Weight percentage concentration observed in EDX (TN=Taftan, TNK=Taftan added Kaolinite, TNSH=Taftan added Calcined Shahindej, TNL=Taftan added burnt Lime)

Compositions	TN	TN-Au	TNK	TNK-Au	TNSH	TNSH-Au	TNL	TNL-Au
SiO_2	48.8	55.81	44.81	52.27	52.09	56.83	55.88	58.2
Al_2O_3	12.41	15.3	14.26	16.88	11.36	11.45	14.81	13.44
CaO	7.23	8.74	19.33	14.23	15.04	12.25	10.05	10.65
Fe_2O_3	4.11	3.88	2.98	3.47	3.11	3.22	3.38	3.59
MgO	1.06	0.79	0.82	0.84	0.92	0.97	0.899	0.78
Na_2O	2.52	2.68	2.08	1.83	2.27	2.06	2.45	1.9
K_2O	13.36	12.21	15.46	10.01	14.88	12.75	12.1	10.97
TiO_2	0.5	0.57	0.25	0.48	0.32	0.47	0.42	0.48
Density (gr/cm^3)	1.88	1.91	1.92	1.76	1.96	1.66	2.18	1.75
Pozzolan reacted%	79.1	90.5	75	87.5	82.5	90	93.7	97.6

EDX results were measured for three points within the gel and the average is shown in Table 3.

When Taftan pozzolan was activated after mixing with kaolinite as an aluminum source, kaolinite activated in the reaction with Taftan and the resulting material was an impermeable sticky gel. Autoclave curing at 2MPa pressure and 150ºC for 3hrs resulted in a more uniform microstructure for the gel produced (Figure 5-b). The average molar ratios for the reaction product when the sample was cured at 25ºC, were SiO_2/Al_2O_3=3.1 and K_2O/Al_2O_3=1.1 while for autoclave curing, the K_2O/Al_2O_3 ratio decreased to 0.59. The aluminium oxide content was increased in the finished product compared to that of Taftan pozzolan activated without adding kaolinite(Table 3).

The binder obtained from the activation of Taftan pozzolan and calcined Shahindej is more porous than that mixed with kaolinite but it still has a uniform texture (Figures 5a and 6a). Using the Taftan and calcined Shahindej mix to produce geopolymers seems to show the best gel. When autoclave cured this shows a uniform micro crystalline texture. Thus autoclave curing seems to produce a zeolitic form which consists of a potassium aluminosilicate (Figure 6b). The average molar ratios found in this reaction product when the sample was cured at 25ºC, were SiO_2/Al_2O_3=4.58 and K_2O/Al_2O_3=1.31 while for autoclave curing, the SiO_2/Al_2O_3 ratio increased to 4.96. The silica content was increased in the finished product compared to when Taftan pozzolan was activated without adding calcined Shahindej (Table 3).

The type of additive mineral used affects the development of reactions. When $Ca(OH)_2$ was used as an additive, the materials obtained following activation showed the co-existence of a geopolymer formed from natural pozzolan particles which had reacted with the alkali forming a potassium aluminosilicate gel together with a calcium silicate hydrate and particles of calcium carbonate likely to form from the carbonation process when calcium hydroxide reacts with carbon dioxide, CO_2, from atmosphere. This has increased the compressive strength of the product immediately (Figure 7). The average molar ratios for this product cured at 25ºC were SiO_2/Al_2O_3=3.77 and K_2O/Al_2O_3=0.82 while for autoclave curing, the SiO_2/Al_2O_3 ratio increased to 4.33. The calcium oxide content in finished product had increased compared to when Taftan pozzolan was activated without adding burnt lime (Table

3). Compared to the above materials, the morphology of the gel obtained from the activation of natural pozzolan without a mineral additive is expected to lead to higher gel porosity (Figures 4 to 7). This formation at lower curing temperature produces more uniform gel although when the product was cured at a higher curing temperature the compressive strength was increased (Figure 4).

CONCLUSIONS

- ⇒ Mineral additives including kaolinite, calcined Shahindej pozzolan and slaked lime when added to Taftan pozzolan as a solid precursor give comparable compressive strength to when the pozzolan is activated without mineral additives, although the gel porosity seems to decrease.
- ⇒ Autoclave curing provides an increase in strength which can be explained by an increased dissolution of the pozzolan upon autoclaving and it has made the structure microcrystalline and dense.
- ⇒ The deficiency of oxides such as SiO_2, Al_2O_3 and CaO in a natural pozzolan such as Taftan can be compensated for by adding mineral additives to increase the level of oxides in the final product before activation.

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