

TAFTAN POZZOLAN-BASED GEOPOLYMER CEMENT

Ali Allahverdi, Kamyar Mehrpour & Ebrahim Najafi Kani

Abstract: In recent years, many research works have been done to investigate the possibility of utilizing a broad range of materials as raw materials in the production of geopolymer cements. The use of artificial pozzolans or aluminosilicate-type industrial waste materials such as granulated blast-furnace slag and fly ash has been reported in many research works. Natural pozzolans are also aluminosilicate-type materials which can be activated with solutions of NaOH and Na_2SiO_3 . Using a pumice-type natural pozzolan from Taftan Mountain located at the south east of Iran and different alkali-activators based on combinations of Na_2SiO_3 and NaOH, a number of natural-pozzolan-based geopolymer cement systems were designed and prepared. Final setting time, workability, and 28-day compressive strength of the systems were studied. The results obtained reveal that Taftan pozzolan 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 relatively high 28-day compressive strengths up to 63 MPa.

Keywords: Geopolymer cement, Natural pozzolan, Alkali-activator, Compressive strength, Final setting time

1. Introduction

Geopolymer cements are a group of alkali-activated materials exhibiting superior engineering properties compared to Portland cements [1-10].

The molecular structure of geopolymer consists of an aluminosilicate network. The simplest aluminosilicate network of this type is called poly-sialate which is the abbreviation of silicon-oxo-aluminate [2,3]. In fact, geopolymers are a product of the chemical reaction between aluminosilicate and alkali-polysialate in a relatively highly alkaline medium [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].

Geopolymer cements exhibit a number of good engineering properties including relatively high compressive strength, short to long setting times, and relatively low pore volume. The role of alkalis is to activate raw materials such as blast-furnace slag and fly ash 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 resulting products, i.e. geopolymer cements, usually exhibit better engineering properties such as compressive strength and resistance against aggressive media, compared to Portland cements [6]. According to Davidovits theory, geopolymer cements are synthetic analogues of natural zeolites [7]. The geopolymerization reaction time however is shorter than that of zeolite formation reaction because geopolymers are mostly amorphous whereas zeolites have highly crystalline structures [7]. The exact mechanism of geopolymerization reaction is not yet understood, but all the proposed mechanisms include three stages of dissolution, orientation, and polycondensation [8]. In general, the presence of alkali-metal salts or their hydroxides is necessary for dissolving aluminosilicates and silicates and for catalyzing the polycondensation reactions. In the molecular structure of aluminosilicates, silicon atoms are usually present in tetrahedral form whereas aluminum atoms can be present both in tetrahedral and hexagonal form. The tetrahedral or hexagonal configurations of aluminum atom can influence its orientation in the final aluminosilicate network [8-10]. In recent years, many research works have been carried out to investigate the possibility of utilizing industrial waste materials as raw material in the production of geopolymer cements. The use of granulated blast-furnace slag and fly ash has been reported in many research works [11-13]. Natural pozzolan which is an almost similar aluminosilicate material, exhibiting cementation behavior when mixed with calcium hydroxide and water [11], probably is a suitable raw

Paper first received June. 06, 2006, and in revised form June.06, 2008.

Ali Allahverdi, is with the School of Chemical Engineering, Iran University of Science & Technology, Ali.allahverdi@iust.ac.ir.

Kamyar Mehrpour, is a M.Sc. Student at the same School. Kamyar2662@yahoo.com

Ebrahim Najafi Kani, is a Ph.D. Student at the same School. najafi@iust.ac.ir

material for being utilized in the production of geopolymer cements. This work investigates the possibility of utilizing natural pozzolan as a raw material in the production of geopolymer cements. Using Taftan natural pozzolan and different alkali-activators based on combinations of Na_2SiO_3 and NaOH , a number of natural-pozzolan-based geopolymer cements were designed and prepared and tested for their set and strength behaviors.

2. Experimental

2.1. Raw Materials

A sample of pumice-type natural pozzolan was prepared from Taftan Mountain located at the south east of Iran. The obtained pozzolan was firstly characterized for its chemical composition and also its pozzolanic activity. The results of chemical analysis determined according to ASTM standards C311 [14] are shown in table 1.

Tab. 1. Chemical composition of Taftan natural pozzolan

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	LOI
61.57	18.00	4.93	6.69	2.63	1.95	1.65	2.15

As seen, this natural pozzolan is a relatively highly siliceous one and according to ASTM standard C618 [15], chemically it could be considered as a relatively good natural pozzolan. The pozzolanic activity of Taftan pozzolan was also evaluated by determining its strength activity index with Portland cement at 7 and 28 days (ASTM C311). According to ASTM standard C618, 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. The prepared natural pozzolan was ground in an industrial closed mill. Knowing that particle size distribution of pozzolan powder can significantly influence the wet and dry properties of geopolymer cement, an analysis of particle size distribution was carried out using a laser particle size analyzer. Figure 1 shows the results obtained for the particle size distribution of ground Taftan pozzolan.

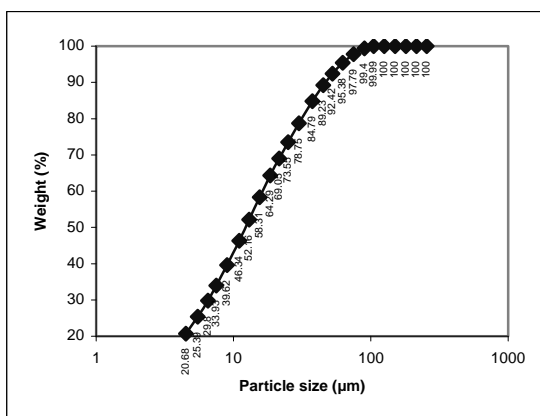


Fig 1. RRSB-Curve of particle size distribution of ground Taftan pozzolan

The slope of the curve shows the broadness of the range of particle size distribution. Ground Taftan pozzolan with an average particle size of $18.75 \mu\text{m}$ has a uniformity factor of 0.95. Such a particle size distribution, compared to that of Portland cements usually with an average particle size between 30 to 35 μm and a uniformity factor in the range 0.95 to 1, shows a suitably fined powder of relatively good size distribution. It should be noted that a relatively broad range of size distribution could adversely affect the wet and dry properties of the material, e.g. workability and compressive strength respectively.

2.2. Specimen Preparation

Commercial water-glass was used for preparing alkali-activators. The silica modulus ($M_s = \text{SiO}_2/\text{Na}_2\text{O}$) of water-glass was 0.86. Enough sodium hydroxide was added to water-glass for preparing three different alkali-activators having silica moduli 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-cement ratios were adjusted at three different values of 0.36, 0.40, and 0.44. After adding activators to the dry binders and enough mixing, the pastes were cast into molds of $2 \times 2 \times 2 \text{ cm}$ in size. The molds were held at ambient conditions until the specimens were enough hardened to be removed. The specimens were then stored at ambient condition without any curing.

2.3. Test Procedure

The workability of the pastes was determined using mini slump test and measuring spread diameter. The final setting times of the systems were measured using the method of Vicat needle [16]. Since all the systems exhibit relatively long setting times, the pastes were stored at an atmosphere of nearly 100% relative humidity to prevent any setting due to drying and to measure the actual final setting time.

At the age of 28 days, the specimens were used to determine their compressive strength. X-ray diffractometry technique was used to determine the crystalline mineral phases in Taftan pozzolan and in the geopolymer cement system exhibiting the highest compressive strength.

3. Results and Discussion

Results obtained for final setting time and workability of the systems are presented in table 2. As seen, the rheological properties of the systems strongly depend on their silica modulus and their sodium oxide contents. As the results reveal, in general it is possible to improve the workability of the pastes and to lower the water-to-cement ratio by increasing the sodium oxide content of the geopolymer cement system. The final setting times of all the systems are relatively long. Such long final setting times could negatively influence the properties of the material, because before

completion of actual setting due to geopolymerization reactions, the material will lose water and dry unless being kept in an atmosphere of 100% relative humidity. The relatively long setting times observed in the geopolymer cement systems actually show that the geopolymerization reactions including dissolution of amorphous aluminosilicates, formation and orientation of intermediate compounds, and finally polycondensation reactions, are quite slow. However, it should be noted that the geopolymerization reactions could be probably accelerated by changing the chemical composition of dry binder and/or alkali-activator. More research works are therefore necessary for possibly improving the set behavior of the material.

Tab. 2. Workability and final setting time of Taftan pozzolan-based geopolymer cement systems

Sample No.	Ms	Na ₂ O (wt%)	water-to-cement ratios	Spread diameter (mm)	Final Setting Time (h)
1	0.52	4	0.36	109	38
2	0.52	7	0.40	125	36
3	0.52	10	0.44	132	42
4	0.60	7	0.36	120	34
5	0.60	10	0.40	131	30
6	0.60	4	0.44	132	48
7	0.68	10	0.36	121	24
8	0.68	4	0.40	120	42
9	0.68	7	0.44	130	44

Figures 2 and 3 show the effect of silica modulus and sodium oxide-content on 28-day compressive strength of geopolymer cement systems tested. Knowing that silica modulus is inversely proportional to the sodium oxide-content of the alkali-activator, it should be noted that a decrease in the value of silica modulus is equal to an increase in the concentration of sodium ion. Now considering the key-role of sodium ion in the mechanism of geopolymerization reaction, i.e. dissolution of the aluminosilicates in the very first stage and charge balance of the 3-dimensional network in the last stage, one can simply conclude that increasing the sodium oxide-content of the system to its optimum value results in the acceleration of geopolymerization reactions and causes the reactions to proceed to a higher extent. These in turn lead to an improvement in the strength behavior of the geopolymer cement system. On the other hand, increasing the sodium oxide-content of the systems to values higher than optimum values results in a decrease in 28-day compressive strength. One of the important factors significantly influencing the 28-day compressive strength of the systems is water-to-cement (W/C) ratio.

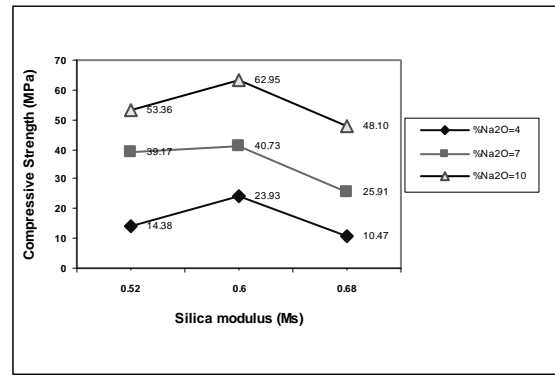


Fig 2. Effect of silica modulus on 28-day compressive strength of geopolymer cement systems based on Taftan pozzolan (W/C = 0.40)

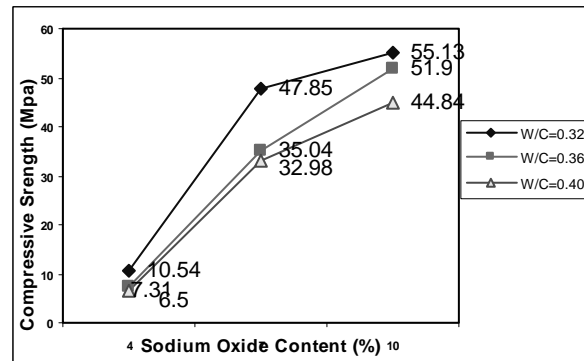


Fig 3. Effect of sodium oxide content on 28-day compressive strength of geopolymer cement systems based on Taftan pozzolan (Ms = 0.60)

Usually W/C-ratio is increased for increasing the workability of the material. However it should be noted that increasing W/C-ratio will result in an increase in the total pore volume and this could significantly weaken the strength behavior of the system. On the other hand, a relatively high W/C-ratio could also result in a relatively high drying shrinkage which may itself lead to macro-defects, i.e. shrinkage cracks. Figure 4 shows the effect of W/C-ratio on 28-day compressive strength of a number of geopolymer cement systems based on Taftan pozzolan.

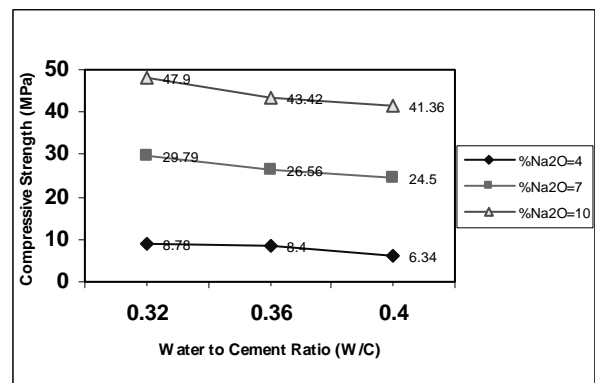


Fig 4. Effect of water-to-cement ratio on 28-day compressive strength of geopolymer cement systems based on Taftan pozzolan (Ms = 0.68)

Taftan pozzolan and the hardened paste of Taftan pozzolan-based geopolymer cement exhibiting the highest 28-day compressive strength, i.e. almost 63 MPa, were studied using X-ray diffractometry technique. The corresponding X-ray diffraction patterns are presented in figures 5 and 6 respectively.

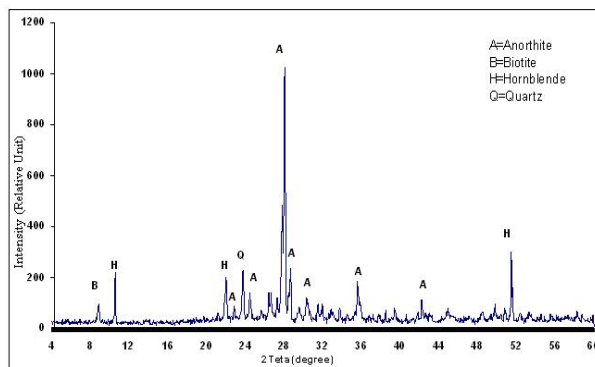


Fig 5. X-ray diffraction pattern of Taftan pozzolan

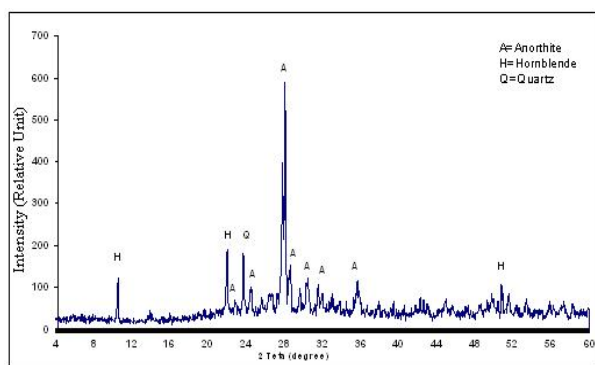


Fig 6. X-ray diffraction pattern of Taftan pozzolan-based geopolymer cement exhibiting the highest 28-day compressive strength

As seen, three of the four crystalline mineral phases (Quartz, Hornblende, Anorthite, and Biotite) observed in Taftan pozzolan are present in the hardened paste of Taftan pozzolan-based geopolymer cement exhibiting the highest 28-day compressive strength. The crystalline mineral phases of the 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 Taftan pozzolan which is reactive and takes part in the geopolymerization reactions and results in the formation of geopolymers in the glassy sate.

4. Conclusions

1. It is possible to activate natural-pozzolan and to produce geopolymer cement using a proportioned mixture of sodium hydroxide and sodium silicate as an alkali-activator.
2. The quality of natural pozzolan-based geopolymer cement depends on the composition of alkali-activator, and W/C-ratio, in addition to the quality of natural pozzolan (its chemical composition and glass phase content).

3. Relatively high 28-day compressive strengths, up to 63 MPa, can be achieved by controlling the factors influencing strength behavior.

References

- [1] Lyon, R.E., Balaguru, P.N., Foden, A., Sorathia, U., Davidovits, J., & Davidovits, M., "Fire Resistant Alumina-silicate Composites", Journal of Fire and Materials, Vol. 21, 1997, PP. 67-73.
- [2] Davidovits, J., "Man-Made Rock Geosynthesis and the Resulting Development of Very Early High Strength Cement", Journal of Materials Education, Vol.16 (2&3), 1994, PP. 91-139.
- [3] Davidovits, J., "Chemistry of Geopolymeric Systems, Terminology" Proc. Geopolymer Int. Conf. 2nd, Saint-Quentin, France, 1999.
- [4] Fletcher, R.A., Kenneth, J., MacKenzie, D., Nicholson, C.L., & Shimada, S., "The Composition Range of Aluminosilicate Geopolymers", J. Euro. Ceramic Society, Vol. 25, No. 9, 2005, PP. 1471-1477.
- [5] Davidovits, J., "Synthesis of Mineral Polymer Compound of the Silico-aluminates Family and Preparation Process", US Patent, No. 4472199, September 18, 1984.
- [6] Davidovits, J., "Mineral Polymers and Method of Making Them", US Patent, No. 4349386, September 14, 1982.
- [7] Davidovits, J., "Process for Obtaining a Geopolymeric Alumino-silicate and Products thus Obtained", US Patent, No. 5342595, August 30, 1994.
- [8] Davidovits, J., & Davidovits, C.F., "The Pyramids an Enigma Solved", Dorset Press, New York, 2nd Edition, 2001.
- [9] Van Jaarsveld, J.G.S., Van Deventer, J.S.J., & Lorenzen, L., "The Potential Use of Geopolymeric Materials to Immobilizes Toxic Metals", Part I, Theory and Applications, Minerals Engineering, Vol. 10, No. 7, 1997, PP. 659-669.
- [10] Hua, Xu., & Van Deventer, J.S.J., "The Geopolymerisation of Alumino-silicate Minerals", Int. J. Miner. Process. 59, 2004, PP. 247-266.
- [11] ACI Manual of Concrete Practice, American Concrete Institute (ACI), Part 1,116R, P. 49, 2004.
- [12] Swanepoel, J.C., & Strydom, C.A., "Utilization of Fly Ash in a Geopolymeric Material", Applied Geochemistry, Vol. 17, No. 8, 2002, PP. 1143-1148.

- [13] Hardjito, D., Wallah, S.E., Sumajouw, D.M.J., & Rangan, B.V., "*Brief Review of Development of Geopolymer Concrete*", Invited Paper, George Hoff Symposium, American Concrete Institute, Los Vegas, USA, 25th May, 2004.
- [14] ASTM C 311-92, "*Standard Methods of Sampling and Testing Fly ash or Natural Pozzolans for use as a Mineral Admixture in Portland Cement Concrete*", American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 04.02, West Conshohocken, Pennsylvania, 2005.
- [15] ASTM C 618-92a, "*Standard Specification for Fly Ash or Raw or Calcined Natural Pozzolan for use as a Mineral Admixture in Portland Cement Concrete*", American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 04.02, West Conshohocken, Pennsylvania, 2005.
- [16] ASTM C 191-82, "*Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle*", American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 04.02, West Conshohocken, Pennsylvania, 2004