Geopolymer Cement from Sirjan Pozzolan

Ali Allahverdi[i], Kamyar Mehrpour[ii], Ebrahim Najafi Kani [iii]

ABSTRACT

The use of alkali-activated cementitious materials, especially over the past decades, has significantly been increased not only due to their potential in reducing CO_2 emission from manufacture of Portland cements, but also due to their superior long-term engineering properties. Alkali-activation process, which was originally limited to slag cements, recently has been extended for several industrial mineral by-products and waste materials. Geopolymer cements are a group of alkali-activated material exhibiting superior engineering properties compared to Portland cement. This work investigates the possibility of utilizing natural pozzolan as a raw material in the production of geopolymer cements. Using Sirjan 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. Setting time, workability, and 28-day compressive strength of the systems were studied. The results obtained reveal that Sirjan 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 strength up to 56 MPa.

KEYWORDS

Geopolymer Cement, Natural Pozzolan, Alkali - activator, Workability, Compressive Strength

1. INTRODUCTION

The production of Portland cement consumes a lot of resources and energy and involves the emission to the atmosphere of CO_2, SO_2 and NO_x. It is, therefore, very important to look for new resources, (especially industrial by-products) and new environmental friendly technologies [1, 2]. Alkaline cements such as alkali-activated slag cement [3, 4], gypsum-free Portland cement [5], and geopolymer binders are interesting materials [7,8,9] whose common feature is alkaline activation of clinker or substances with latent hydraulic properties, such as slag or fly ash. The effect of solutions of alkaline compounds (such as NaOH, Na_2CO_3 or Na_2SiO_3) on hydraulically active substances consists of disrupting the Si-O-Si bonds and producing hydrates of alkali-lime aluminosilicates similar to zeolites, and hydrates of the type C-S-H phase, gehlenite hydrate and hydrogarnates. Alkali-activated binders provide the possibility of utilizing waste materials, because the properties of materials based on alkali-activated binders are often superior to those of concrete and mortar prepared from standard Portland cement. The presence of zeolite-type substances is responsible for modifying the properties of the alkali-activated binders, for instance, by increasing their resistance to acids [10] or improving their ability to immobilise heavy metals [11,12].

The exact mechanism of geopolymerization reaction is not yet understood, but all the proposed mechanisms include three stages of dissolution, orientation, and polycondensation [13]. 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 where as aluminum atoms can be present both in tetrahedral or hexagonal form. The tetrahedral or hexagonal configurations of aluminum atom can influence its orientation in the final aluminosilicate network [13-15].

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 [16-18].

Natural pozzolan, which is an almost similar aluminosilicate material, exhibiting cementations behavior when mixed with calcium hydroxide and water [16],

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probably is a suitable raw material for being utilized in the production of geopolymer cements.

Utilization of natural pozzolans in synthesis and production of geopolymeric materials has not been reported in the literature. These materials, which are almost similar aluminosilicate minerals, exhibiting cementitious behavior when mixed with calcium hydroxide and water [16], probably are suitable source materials for being utilized in the production of geopolymeric products.

The present study is concerned with the effect of alkaline activators of the type NaOH and Na_2SiO_3 on aqueous suspensions of Sirjan natural pozzolan and its probable potential for production of geopolymeric cement.

2. EXPRIMENTAL

A. Raw Materials

Natural pozzolan of pumice-type was prepared from a location at the south east of Iran called Sirjan. The chemical composition of Sirjan pozzolan is presented in Table 1.

TABLE 1
CHEMICAL COMPOSITION OF SIRJAN NATURAL POZZOLAN (WT %)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
62.95	19.55	4.16	3.52	0.20	3.05	3.10	3.50

The prepared natural pozzolan was ground in a laboratory ball mill. Knowing that particles 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 Sirjan pozzolan.

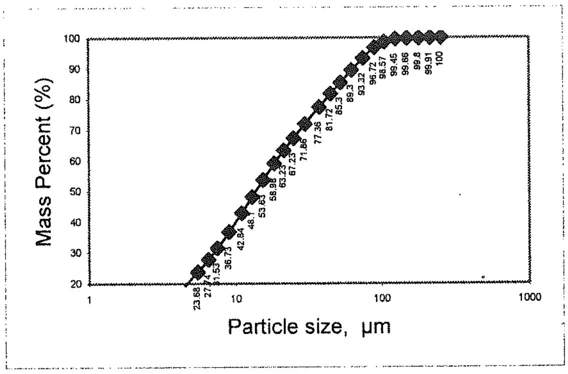

Figure 1: RRSB-Curve of particle size distribution of ground Sirjan pozzolan.

The slope of the curve shows the broadness of the range of particle size distribution. Ground Sirjan pozzolan with an average particle size of 22.63 μm has a uniformity factor of 0.85. Such a particle size distribution compared to that of Portland cements shows a suitably fined powder of relatively broad size distribution. It should be noted that the relatively broadness range of size distribution could adversely affect the wet and dry properties of the material, e.g., workability and compressive strength, respectively.

The pozzolanic activity of Sirjan 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., 78.6 and 84.3 percent of control respectively for 7 and 28 days, show a relatively good pozzolanic activity in accordance with ASTM standard C618.

B. Specimens Preparation

Commercial sodium silicate was used for preparing alkali activators. The silica modulus ($Ms=SiO_2/Na_2O$) of sodium silicate 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 ratio was adjusted at three different values of 0.36, 0.40, and 0.44 for investigating the effect of which on strength behavior of the systems. After adding activators to the dry binders and enough mixing, the pastes were formed into specimens of 2×2×2 cm in size. The moulds were held at ambient conditions for 6 days until the specimens were enough hardened to be removed. After demoulding, the specimens were stored at ambient conditions.

C. 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. Since all the systems exhibit relatively long setting times, the pastes were stored at an atmosphere of nearly 100% relative humidity at 25 °C to prevent any setting due to drying and to measure the actual final setting time.

The workabilities of the pastes were determined and compared visually using relative units. For this reason, four different levels of workability were defined and assigned by relative units between zero to four, such that the workability of a quite non-workable paste was assigned zero and that of a freely flowing one was assigned four.

At the age of 28 days, the specimens were used to measure their compressive strength and to determine the maximum achievable 28-day compressive strength.

3. RESULTS AND DISCUSSION

Results obtained for workability and setting time of the systems are presented in Table 2. A review of the relative workabilities shows that the rheological properties of the systems strongly depend on their silica modulus and their sodium oxide contents in addition to water-to-cement ratio. 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.

As the results obtained for final setting time show at a constant water-to-cement ratio, any increase in silica modulus results in a reduction in the final setting time. Such a behavior could be attributed to the increase in the concentration of soluble silica of the systems. Probably an increase in the concentration of soluble silica could accelerate the geoplymerization reactions and hence resulting in a decrease in setting time. It is also seen that at a constant silica modulus an increase in water-to-cement ratio causes an elongation in setting time. This behavior, however, is the same as what is usually observed in systems based on Portland cement.

The final setting times of all the systems are quite long. Such long final setting times could strongly restricts the applications of the material, because before any actual setting due to geopolymerization reactions the material will lose water and dry unless being kept in an atmosphere of 100% relative humidity.

The long setting times observed in the geopolymer cement systems actually shows that the geopolymerization reactions including dissolution of amorphous aluminosilicates, formation and orientation of intermediate compounds, and finally polycondensation reactions, are very 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.

Before measuring the 28-day compressive strength, the specimens were observed visually for any possible crack. The specimens were quite sound and no crack was observed visually.

TABLE 2
WORKABILITY AND FINAL SETTING TIME OF SIRJAN POZZOLAN-BASED GEOPOLYMER CEMENT SYSTEMS.

Sample No.	Ms	Na_2O (wt %)	water-to-cement (W/C)	Workability	Final Setting Time (hr)
1	0.52	4	0.36	1	84
2	0.52	7	0.40	3	90
3	0.52	10	0.44	slurry	120
4	0.60	4	0.36	3	78
5	0.60	7	0.40	3	86
6	0.60	10	0.44	4	144
7	0.68	4	0.36	2	72
8	0.68	7	0.40	3	96
9	0.68	10	0.44	3	132

Figures 2 to 7 show the effect of silica modulus and sodium oxide-contents on the 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 decreases in 28-days compressive strengths.

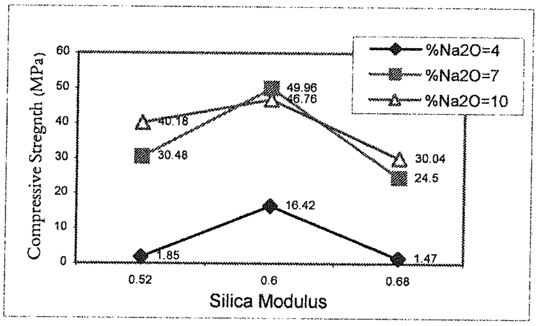

Figure 2: Effect of silica modulus on 28-day compressive strength of geopolymer cement systems based on Sirjan pozzolan (W/C = 0.44).

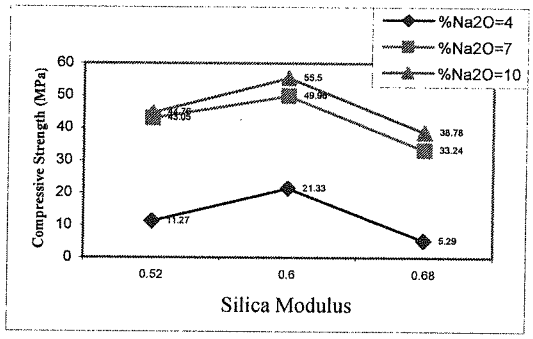

Figure 3: Effect of silica modulus on 28-day compressive strength of geopolymer cement systems based on Sirjan pozzolan (W/C = 0.40).

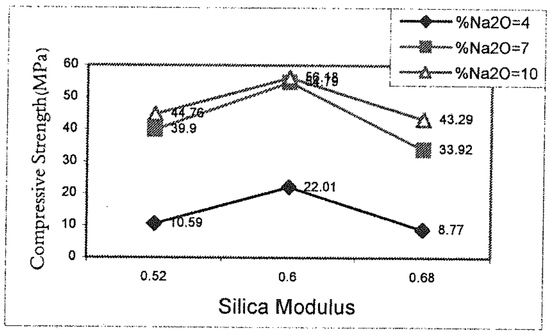

Figure 4: Effect of silica modulus on 28-day compressive strength of geopolymer cement systems based on Sirjan pozzolan (W/C = 0.36).

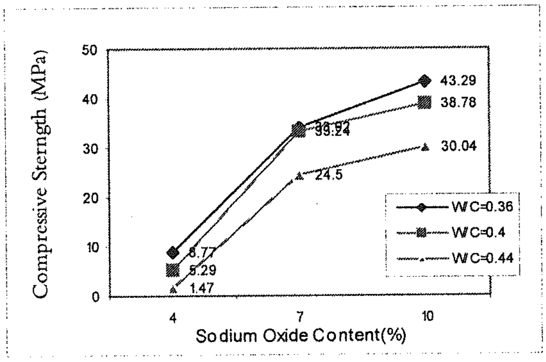

Figure 5: Effect of sodium oxide content on 28-day compressive strength of geopolymer cement systems based on Sirjan pozzolan (Ms = 0.68).

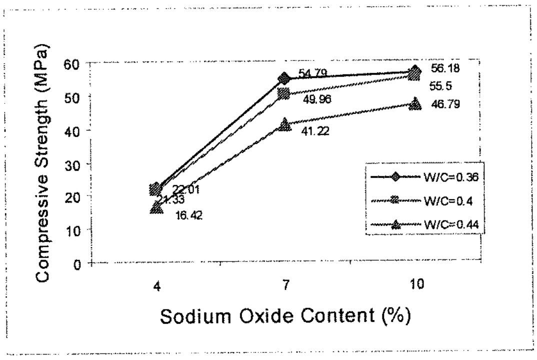

Figure 6: Effect of sodium oxide content on 28-day compressive strength of geopolymer cement systems based on Sirjan pozzolan (Ms = 0.60).

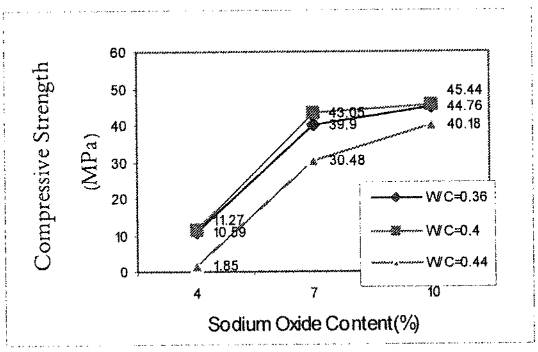

Figure 7: Effect of sodium oxide content on 28-day compressive strength of geopolymer cement systems based on Sirjan pozzolan (Ms = 0.52).

One of the important factors significantly influencing the 28-day compressive strength of the systems is the water-to-cement (dry binder) ratio. Usually, water-to-cement 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 water-to-cement ratio results in an increase in the total pore volume, which in turn, weakens the strength behavior of the material. In some cases, a relatively high water-to-cement 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 water-to-cement ratio on total pore volume and formation of any probable shrinkage-cracks.

Figures 8 to 10 show the effect of water-to-cement ratios on 28-day compressive strength of the studied systems. As seen, in most cases, the 28-day compressive strength reduces with increasing water-to-cement ratio. This could be attributed to the corresponding increase in total pore volume in the hardened cement paste, the same behavior observed in systems based on Portland cement. However, as seen in a few cases, contrary to the usual observations, increasing water-to-cement ratio at first results in a limited increase in 28-day compressive strength and then decreases the strength. Such an unexpected limited increase in 28-day compressive strength probably could be attributed to the time and method of mixing the cement paste before casting which could significantly affects the extent of distribution of chemical reacting compounds, e.g., sodium hydroxide, at different water-to-cement ratios and hence the kinetics of geopolymerization reactions.

In addition, experimental results showed that compressive strength of the similar hardened paste specimens of the studied geopolymeric cement varies in a relatively broad range. The reason for such a variable compressive strength is probably due to the possibility for the presence of relatively large air voids that are visually observable. The freshly prepared paste of this material is so sticky with thixotropic rheological properties that normal vibration cannot effectively remove air bubbles. The presence of these air voids therefore could produce errors in the results and hence unexpected variations in the strength behavior.

Future research works therefore can be focused on possibilities for eliminating air voids and not only reducing total pore content, but also eliminating the corresponding errors.

As mentioned before, different materials have been used in producing geopolymeric cements and nowadays, there is increasing interests in utilizing fly ash as raw material. Many researchers reported [10, 12, 17] that 28-day compressive strengths up to 90 MPa can be achieved by utilizing suitable raw materials. Results obtained in this research work confirm that acceptable compressive strengths can be achieved in geopolymeric cements based on Sirjan pozzolan. Detailed research and more experimental work, however, is necessary to characterize the material and to improve its setting time possibly.

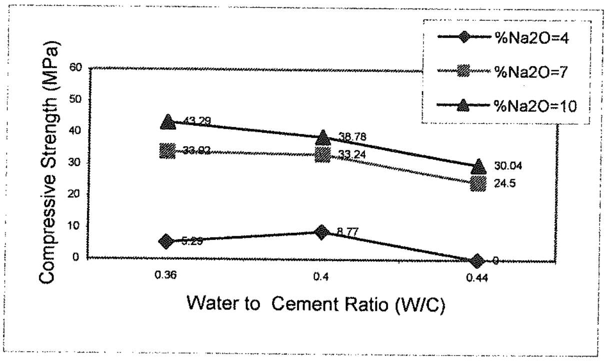

Figure 8: Effect of water-to-cement ratio on 28-day compressive strength of geopolymer cement systems based on Sirjan pozzolan (Ms = 0.68).

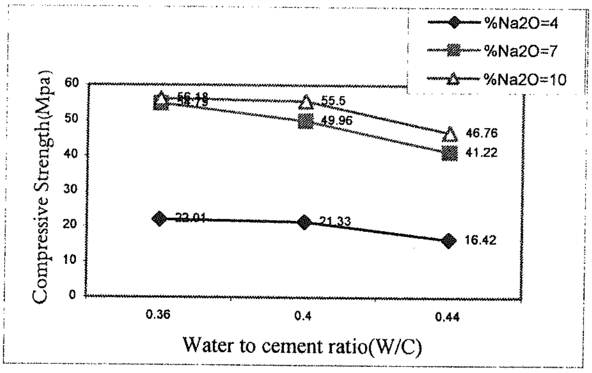

Figure 9: Effect of water-to-cement ratio on 28-day compressive strength of geopolymer cement systems based on Sirjan pozzolan (Ms = 0.60).

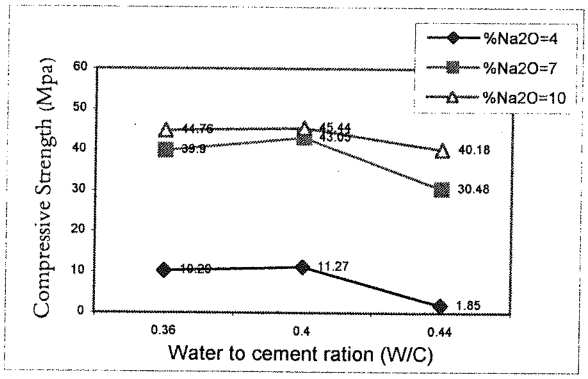

Figure 10: Effect of water-to-cement ratio on 28-day compressive strength of geopolymer cement systems based on Sirjan pozzolan (Ms = 0.52).

4. CONCLUSIONS

1. Amorphous aluminosilicates present in natural pozzolan are reactive and could take part in the geopolymerizaion reactions resulting in the formation of geopolymer products.
2. Results obtained from activating natural Sirjan pozzolan using a proportioned mixture of NaOH and Na_2SiO_3 prove the possible utilization of natural pozzolan in the production of geopolymer cement.
3. 28-day compressive strengths up to 56 MPa can be achieved by controlling parameters influencing the strength behavior of the material, e.g., water-to-cement ratio, silica modulus and sodium oxide content of the material.

5. ACKNOWLEDGMENT

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