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Mechanical and Durability Properties of Alkali Activated Slag for Sustainable Concrete

Mohsen Jafari Nadoushan *[1], Ali A. Ramezanianpour [2], and Seyed Mohsen Kheirandish[3]

[1]PhD Student, Dept. of Civil Engineering, Amirkabir University of Technology, Tehran, Iran. E-mail: <m_jafarin@yahoo.com>.

[2]Department of Civil Engineering, Amirkabir University of Technology, Head of Concrete Technology and Durability Research Center, Tehran, Iran, E-mail: <aaramce@aut.ac.ir>.

[3]BSc Student, Dept. of Civil Engineering, Amirkabir University of Technology, Tehran, Iran. E-mail: <kheyrandish@aut.ac.ir>.

ABSTRACT

Geopolymers are cementitious binder with three dimensional structures that are formed by alkali activation of Si and Al containing raw materials such as natural and artificial pozzolans. It has been found that slag- based geopolymer binders can be synthesized by alkali activation of ground granulated blast furnace slag in presence of sodium silicate. Slag-based geopolymer binders can contribute to the reduction of environmental impact by using lesser amounts of calcium-based natural materials, lower manufacturing temperature, lower use of fuel and cost and lower greenhouse gas emissions in comparison with ordinary Portland cement binder and provides a route towards the concept of sustainable development.

Materials resulting from alkali activation of slag show a wide range of workability, compressive strength and permeability. The main objectives of this work is to determine effects of alkaline solution type and concentration, modulus of sodium silicate, sodium silicate to alkaline solution ratio and natural pozzolan replacement on the mechanical properties of alkali activated slag. Results reveal that the geopolymer paste specimens containing KOH solution had higher compressive strength when compared with the concrete specimens containing NaOH solution. The optimum range for each factor is suggested based on the different effects they have on compressive strength.

INTRODUCTION

The concrete industry is one of the major consumers of natural resources. Natural resources which must be remained for next generations are used in Portland cement production process. On the other hand Portland cement clinker production is an energy-intensive process. This energy is mostly supplied by fossil fuels which is cost- intensive in addition to producing a large amount of greenhouse gas emissions, mostly CO_2. One possible way to reduce energy consumption and greenhouse gas emissions in concrete industry is the replacement of clinker with supplementary cementitious materials (SCMs) that has been used considerably over past five decades. Nowadays, SCMs such as slag and fly ash are used up to 70% replacement with Portland cement in concrete, while it is possible to produce geopolymer concrete with 100% Si and Al rich materials replacement with cement.

Disposal of industrial wastes in nature rather than being cost intensive causes environmental issues. Some industrial wastes contain heavy metals which their disposal increases the possibility of leaching to ground water. Geopolymerization process can reduce industrial wastes disposal and their environmental impact besides producing durable masonries with good mechanical properties. Geopolymers produced from solid waste as starting material have benefits such as reducing environmental impacts by using lesser amounts of calcium-based minerals, lower manufacturing temperature, lower fuel consumption and lower greenhouse gas emissions in comparison with ordinary Portland cement and provides a route towards the concept of sustainable development. Blast furnace slag is a byproduct that is formed during the production of hot metal in blast furnace. If the molten slag is cooled and solidified by rapid water quenching, ground granulated blast furnace slag is formed. When crushed or milled to very fine cement-sized particles, ground granulated blast furnace slag (GGBFS) has cementitious properties, which is a suitable replacement with Portland cement. It has been found that slag- based geopolymer binders can be synthesized by alkali activation of ground granulated blast furnace slag in presence of sodium silicate. The use of slags as geopolymer binding materials requires their preparation involving granulation, alkali activation and hydration [Mozgawa and Deja 2009].

The recent studies that have been completed on geopolymer concretes indicate that there is a potential for 25-45% [Stengel et al. 2009] or 70% [Weil et al. 2009] reduction in greenhouse gas emissions. Benjamin et al. indicate that there is great potential for fly ash based geopolymers to reduce the climate change impacts of cement production. For the proposed "typical" Australian geopolymer product, there is an estimated 44- 64% improvement in greenhouse gas emissions over OPC, while the cost of these geopolymers can be higher than OPC [Benjamin et al. 2011]. Louise et al. indicate that the CO_2 footprint of fly ash based geopolymer concrete was only 9% less than comparable concrete containing 100% OPC binder: much less than predictions by earlier studies [Stengel et al. 2009; Weil et al. 2009]. The key factors that have led to the differences in reported results include: (i) Transportation emissions were considered by Louise et al. (ii) Expenditure of significant energy during sourcing of raw materials and manufacturing of the sodium silicate and sodium hydroxide alkali activators for the geopolymer concrete was not included in previous estimates. (iii) Elevated temperature curing contributed 12.4% CO_2 for the geopolymer concrete in [Louise et al. 2013], compared with negligible emissions for OPC concrete that was cured at ambient temperature.

Habert et al. used the Life Cycle Assessment methodology to carry out a detailed environmental evaluation of the production of geopolymer concrete. Their results show that the production of most standard types of geopolymer concrete has a slightly lower impact on global warming than standard Ordinary Portland Cement (OPC) concrete. However they also reveal that the production of geopolymer concrete has a higher environmental impact regarding other impact categories than global warming. This is due to the heavy effects of the production of the sodium silicate solution. Geopolymer concrete made from fly ashes or granulated blast furnace slags based require less of the sodium silicate solution in order to be activated. They therefore have a lower environmental impact than geopolymer concrete made from pure metakaolin. This study highlights that future research and development in the field of geopolymer concrete technology should focus on two potential solutions. First of all the use of industrial waste that is not recyclable within other industries and secondly on the production of geopolymer concrete using a mix of blast furnace slag and activated clays [Habert 2011].Therefore in this study we describe the effects of different alkaline solution types and concentrations, modulus of sodium silicate, sodium silicate to alkaline solution ratio and natural pozzolan on the flowability and mechanical properties of alkali activated slag. Properties of fresh and hardened geopolymer specimens such as workability and compressive strength were measured.

EXPERIMENTAL INVESTIGATION

Materials. Two raw materials containing ground granulated blast furnace (GGBF) slag and natural Pozzolan used throughout this work to be activated as geopolymer cement. The first one GGBF slag with a specific surface area of 3383 cm^2/g and an average particle size of 25.97 μm was obtained from a local Company.

The second, Taftan pumice pozzolan with a specific surface area of 5074 cm^2/g and an average particle size of 22.24 µm was obtained inside the country which is used to produce Portland pozzolan cement by the Khash cement factory. Specific surface of pumice is greater than specific surface of slag. The raw materials have been analyzed by X-ray Fluorescence (XRF) analysis using a Philips PW 1480 instrument. Chemical and physical characteristics of GGBF slag and Taftan pumice are shown in Tables 1 and 2. X-ray diffraction (XRD) carried out on GGBF slag and pumice by an EQuniox 3000 machine is presented in Fig. 1. The XRD patterns of the raw materials show that all of them are a mixture of minerals with various degrees of crystallization. Crystalline particles were observed in the pumice sample. Two weak peaks in X-ray diffraction studies of slag powder reveal some crystalline components.

Table 1. Chemical characteristics of raw materials

Chemical Components	GGBF slag	Pumice
Calcium Oxide (CaO) (%)	36.75	7.4
Silicon Dioxide (SiO_2) (%)	37.21	64.9
Magnesium Oxide (MgO) (%)	8.52	1.98
Aluminum Oxide (Al_2O_3) (%)	11.56	12.1
Ferric Oxide (Fe_2O_3) (%)	1.01	5.2
Sulphate Oxide (SO_3) (%)	0.97	0.22
Sodium Oxide (Na_2O) (%)	0.61	2.49
Potassium Oxide (K_2O) (%)	0.70	1.88
Titanium Oxide (TiO2) (%)	1.23	0.79
Manganese Oxide (MnO) (%)	0.99	.123
Phosphorus Oxide (P_2O_5) (%)	0.03	0.2
LOI (%)	0.02	2.5

Table 2. Physical characteristics of cementitious materials

Physical properties	GGBF slag	Pumice
Blaine (cm^2/g)	3383	5047
Specific gravity (g/cm^3)	2.79	2.54

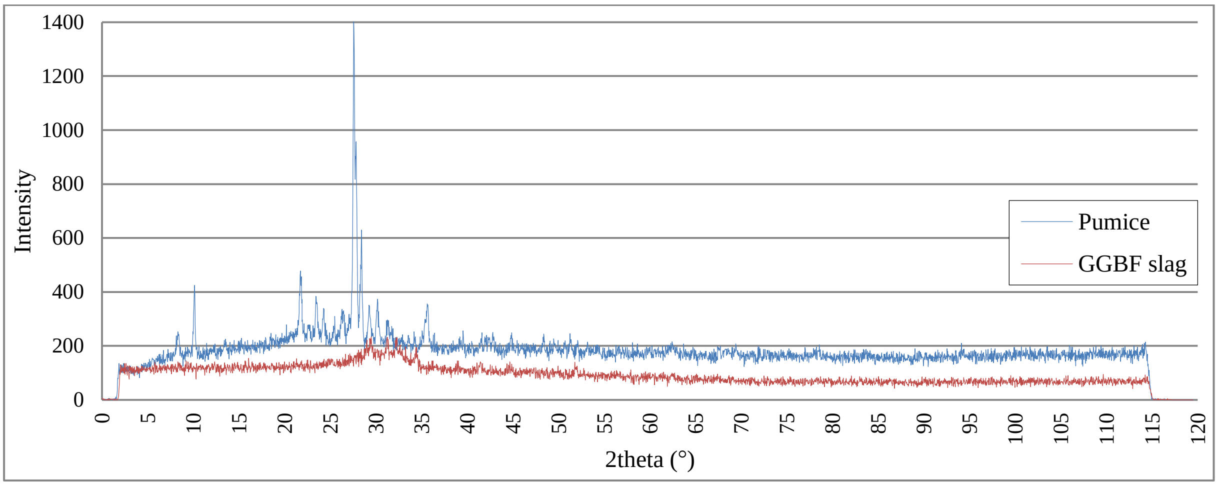

Figure 1. XRD patterns of GGBF slag and pumice

Potassium hydroxide (KOH) and sodium hydroxide (NaOH) pellets have dissolved to produce the 6, 8 and 10 molar alkaline solutions for geopolymer paste production. Sodium silicate (water glass) provided by Iran Silicate Industrial Company in the form of solution with modulus of 2.1, 2.33 and 3.13. The modulus of water glass is the ratio of SiO_2/Na_2O. Deionized water was used to produce all alkaline solutions.

Mixture proportions. At first, four factors related to strength of slag- based geopolymer cement paste such as alkaline solution type, alkaline solution concentration (mole), modulus of sodium silicate (weight ratio) and sodium silicate to alkaline solution (weight ratio) have been investigated. The level of each factor and the values of the tested factors chosen based on the previous researches are presented in table 3. A total of 90 geopolymer paste mixtures were made in this step. The geopolymer cement paste mixtures were prepared with a constant total binder (GGBF slag) content of 1547 kg/m^3 and the activator (alkaline solution+ sodium silicate) to binder ratio in the mixes was 0.4. In the next step to find the effect of natural pozzolans on properties of slag- based geopolymer cement paste, 9 different replacement levels were considered. The factors and their levels are presented in Table 4. In this step the geopolymer cement paste mixtures were prepared with optimum modulus of sodium silicate and optimum ratio of sodium silicate to alkaline solution (2.33 and 0.4 respectively). The activator (alkaline solution+ sodium silicate) to binder ratio in the mixes was 0.4.

Geopolymer and OPC mortar mixture proportions are presented in tables 5 and 6 respectively. According to previous step the optimum values of sodium silicate to alkaline solution ratio, modulus of sodium silicate and alkaline solution concentration were used for mortar mixtures (0.4, 2.33 and 6 respectively).

KOH or NaOH pellets were added to deionized water to provide a 6, 8 and 10 M potassium and sodium hydroxide solution and cooled. Geopolymer cement pastes were prepared by adding potassium and sodium hydroxide solution to raw materials and blending for 2 minutes. Then, the sodium silicate was added and mixed for 2 more minutes to form geopolymer paste. The resulting geopolymer paste was transferred to plexiglass moulds of 20×20×20 mm dimension. Geopolymer cement pastes specimens were compacted by external vibration to reduce entrapped air and kept protected after casting to avoid water evaporation. After 24 hours specimens were removed from the mould and cured in a special plastic bag at 23 ± 2˚C. Rapid drying should be avoided to eliminate shrinkage cracking.

Table 3. The introduced levels for each factor in phase 1

Factor	Unit	Level 1	Level 2	Level 3	Level 4	Level 5
Alkaline Solution Type	-	NaOH	KOH	-	-	-
Alkaline Solution Concentration	Mole	6	8	10	-	-
Modulus of Sodium Silicate	Weight Ratio	2.1	2.33	3.13	-	-
Sodium Silicate to Alkaline Solution	Weight Ratio	0	0.1	0.2	0.3	0.4

Table 4. The introduced levels for each factor in phase 2

Factor	Unit	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8	Level 9
Alkaline Solution Type	-	NaOH	KOH	-	-	-	-	-	-	-
Alkaline Solution Concentration	Mole	6	8	-	-	-	-	-	-	-
Slag Replacement with Natural Pozzolan	Weight %	0	5	10	15	20	25	50	75	100

Table 5. The geopolymer mortar mixture proportion

Mix	Alkali Solution	Based Material (Kg/m^2)	Slag Replacement with Natural Pozzolan (%)	Activator to Based Material (Weight Ratio)	Aggregate to Based Material (Weight Ratio)	Water to Solid (Weight Ratio)
Na6-Pu0	NaOH	463.8	0	0.9	2.75	0.487
Na6-Pu10	NaOH	463.8	10	0.9	2.75	0.487
K6-Pu0	KOH	463.8	0	0.9	2.75	0.418
K6-Pu10	KOH	463.8	10	0.9	2.75	0.418

Table 6. The OPC mortar mixture proportion

Mix	Based Material (Kg/m^2)	Water to Cement (Weight Ratio)	Aggregate to Cement (Weight Ratio)	Superplasticizer Dosage (Cement Weight Percent)
OPC	592.60	0.487	2.75	0.3

Flowability of fresh geopolymer mortars was determined by ASTM C 1437 which consists of measuring the increase in average base diameter of the paste mass, expressed as a percentage of the original base diameter. Geopolymer paste cubes of 20×20×20 mm and mortar cube of 50×50×50 mm dimension were cast for compressive strength. Geopolymer paste specimens were tested for compressive strength after 3, 7, 14, 21, 28 and 91 days maintained in the sealed curing. The specimens were wrapped and insulated in a special plastic bag to prevent evaporation and left at room temperature till the age of test. Three samples for each formulation were measured for compressive strength according to ASTM C39.

RESULTS AND DISCUSSIONS

Compressive strength of geopolymer pastes. Alkaline solution causes the dissolution of the raw materials. Alkaline solution must be carefully selected because their composition has different impacts on the properties of fresh geopolymer paste and development of the mechanical properties in the hardened geopolymer. Two mostly used alkaline solutions in geopolymer formation are NaOH and KOH. The type of alkaline solution plays an important role on the dissolution rate. As been demonstrated in Fig. 2 for example, the slag- based geopolymer paste specimens containing potassium hydroxide had higher compressive strength at various ages up to 91 days when compared with the specimens containing sodium hydroxide. For example at 91 days of curing, the mean compressive strength of slag- based geopolymer specimens containing potassium hydroxide is 16.1% higher than that for specimens containing sodium hydroxide. The ionic size of Na^+ is 116 pm while ionic size of K^+ is 152 pm. The larger K^+ favours the formation of larger silicate oligomers with which Al $(OH)^{-4}$ prefers to bind. Therefore, in KOH solutions more geopolymer precursors exist which result in better setting and stronger compressive strength of the geopolymers than in the case of NaOH [Xu and Deventer 2000].

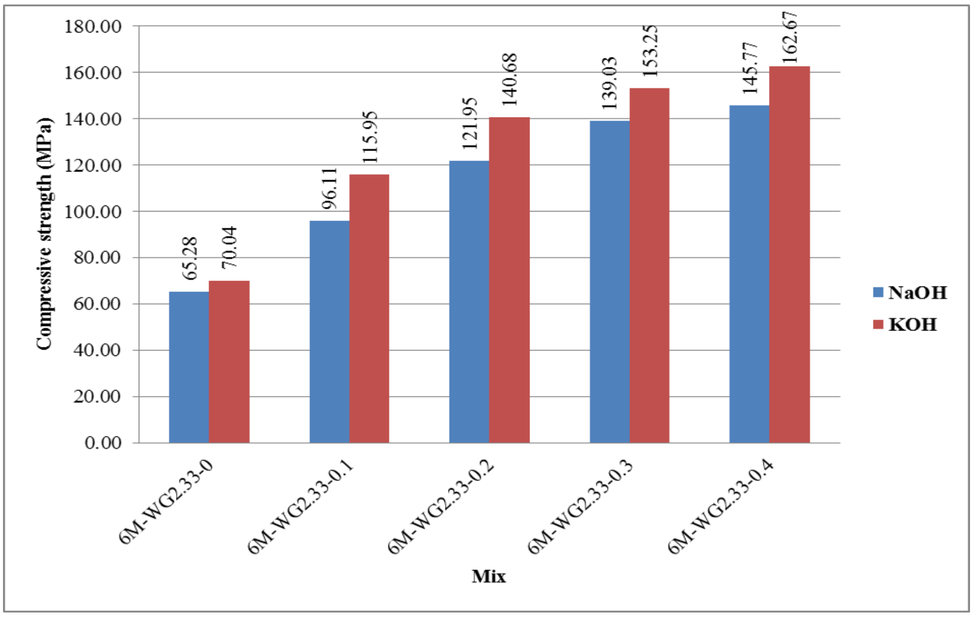

Figure 2. Compressive strength of slag- based geopolymer pastes containing NaOH and KOH

The activating solution can contain a supplementary source of silica such as sodium silicate, to promote geopolymerization phases. It has been demonstrated in Fig. 3 that the presence of sodium silicate in the slag- based geopolymer paste results in increasing the compressive strength.

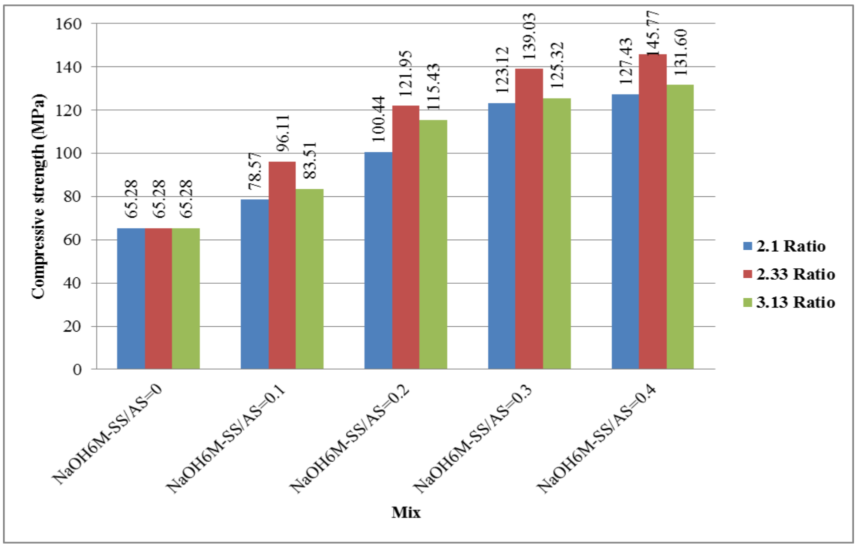

Figure 3. Compressive strength of slag- based geopolymer pastes containing NaOH 6M in the presence of different types of sodium silicate and sodium silicate contents

It is clear that increasing the sodium silicate to alkaline solution ratio from 0 to 0.3 causes the increase in compressive strength about 100 % whereas increasing from 0.3 to 0.4 has a slight effect on enhancement of compressive strength. Sodium silicate promotes the compressive strength of slag- based geopolymer paste in two ways: (1) the sodium silicate solution improves the dissolution rate of Si and Al; (2) because the bonds of Al in the raw material are weaker than the bonds of Si, it dissolves rapidly in alkali solution. Therefore if Si ion is provided prior to being available through dissolution of raw material, it can increases the degree of geopolymerization and improves the mechanical properties. The two most important properties of sodium silicate solution in geopolymer paste production are its modulus (SiO2:Na2O) and amounts. It has been demonstrated in Fig. 3 that the optimum value of modulus of sodium silicate for compressive strength is 2.33.

The effect of slag replacement with pumice after 91 days of curing on the compressive strength of geopolymer paste is shown in Fig. 4. It can be concluded that in presence of 6M and 8M alkaline solution, the maximum strength could be reached with 5% and 10% replacement respectively. Fig. 5 demonstrates the relationship between Si/Al and compressive strength of geopolymer pastes containing slag and pumice. The optimum value of Si/Al molar ratio for compressive strength is about 3.1 to 3.2.

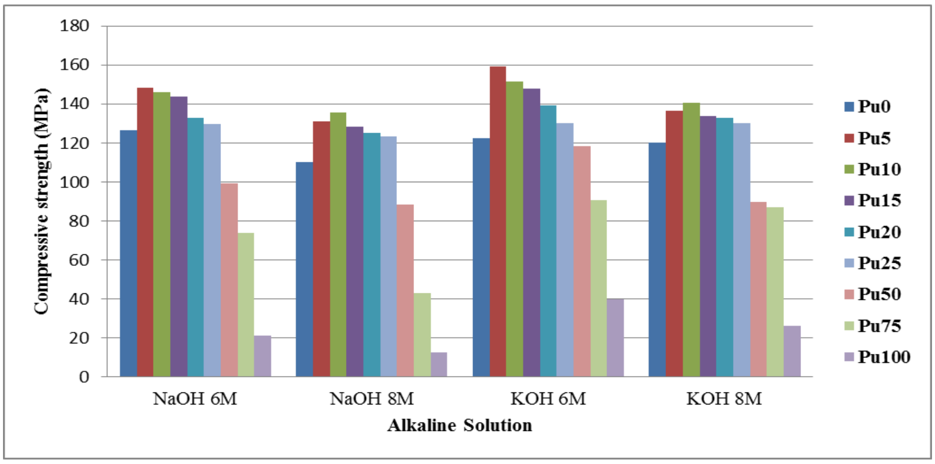

Figure 4. The effect of slag replacement with pumice on compressive strength after 91 days of curing

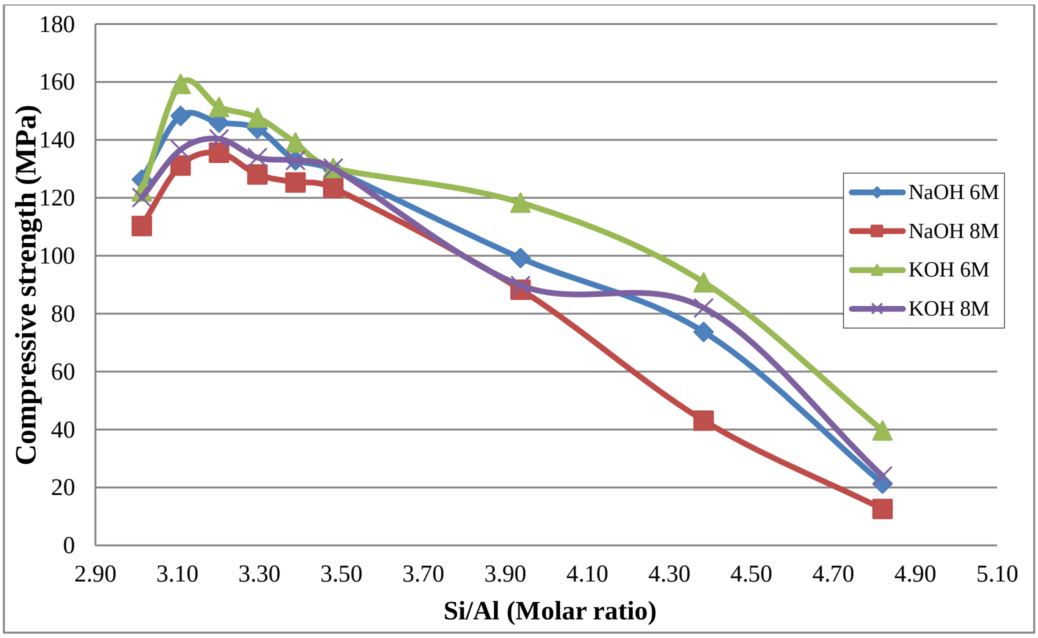

Figure 5. The effect of Si/Al molar ratio on compressive strength of geopolymer paste after 91 days of curing

Flowability and Compressive strength of geopolymer mortar. The flow of slag- based geopolymer fresh mortars are presented in Fig. 6. The flowability of slag- based geopolymer mortars containing KOH is higher than identical NaOH. The flow of the geopolymer mortar reduces by 10% slag replacement with pumice. This is because of the higher amount of specific surface area of pumice than slag (5074 cm^2/g vs 3383 cm^2/g) which causes more water demand to reach constant flowability. It was considered that 50% flow (equilibrium 150 mm flow diameter) is the minimum value suitable for geopolymer mortars that can easily be worked and placed in the mould. The flowability of slag- based geopolymer mortars is higher than OPC.

The compressive strength of slag- based geopolymer mortars are presented in Fig. 7. It can be observed from Fig. 7 that the compressive strength of geopolymer mortars is almost twice the compressive strength OPC mortar at 28 days of curing.

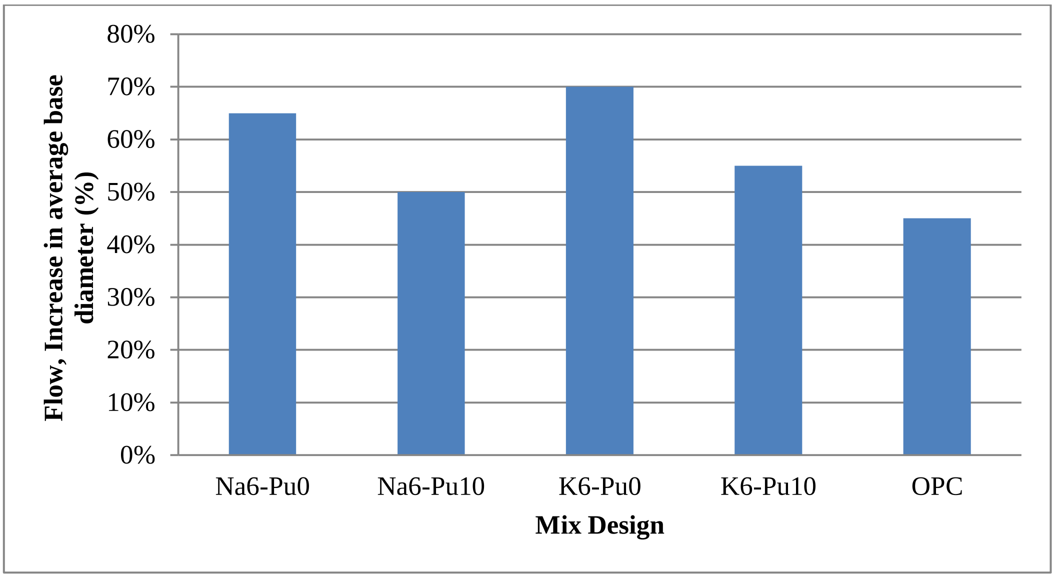

Figure 6. The flow of slag- based geopolymer and OPC fresh mortars

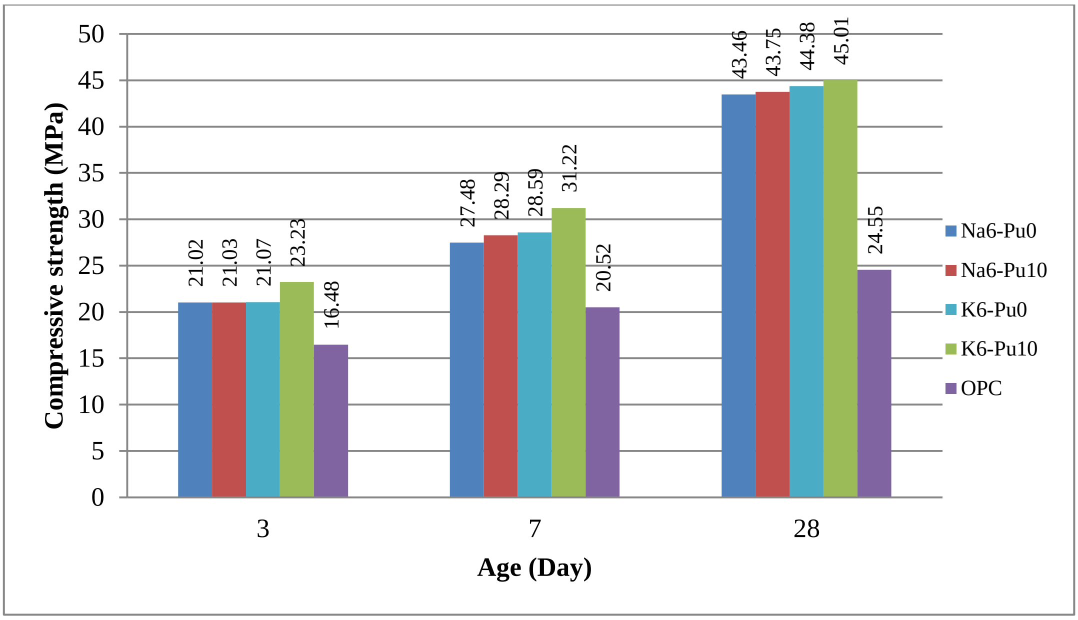

Figure 7. The compressive strength of slag- based geopolymer and OPC mortars at different ages of curing

CONCLUSION

The following general conclusions can be drawn from the study provided in the paper:

- The presence of sodium silicate in the slag- based geopolymer paste largely enhances the workability and results in increasing the compressive strength. The optimum modulus of sodium silicate and optimum ratio of sodium silicate to alkaline solution is 2.33 and 0.4 respectively.
- The slag- based geopolymer paste specimens containing potassium hydroxide had higher compressive strength at various ages up to 91 days when compared with the specimens containing sodium hydroxide.
- It can be concluded that in presence of 6M and 8M alkaline solution the maximum strength could be reached with 5% and 10% replacement respectively.
- The flowability of slag- based geopolymer mortars containing KOH is higher than identical NaOH.
- The compressive strength of geopolymer mortars is almost twice the compressive strength OPC mortar at 28 days of curing.
- The optimum value of Si/Al molar ratio for compressive strength is about 3.1 to 3.2.

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