

# INFLUENCE OF SLAG ON MECHANICAL PROPERTIES AND DURABILITY OF SHIRASU GEOPOLYMER

Dhruva N. KATPADY<sup>\*1</sup>, Koji TAKEWAKA<sup>\*2</sup>, Toshinobu YAMAGUCHI<sup>\*3</sup>, Yoshikazu AKIRA<sup>\*4</sup>

## ABSTRACT

Shirasu, a pyroclastic flow deposit, is used as aluminosilicate in producing geopolymer. Ground granulated blast furnace slag is used as an admixture for development of higher initial strength of Shirasu geopolymer. Sodium hydroxide and sodium silicate solution are used as alkaline activators. Mortars are atmospheric cured or oven dry heat cured for 24 hours. Compressive strength and sulfuric acid immersion tests are carried out. Based on the experimental study, it was observed that the initial and long term strength development of Slag-Shirasu geopolymer improved and acid resistance increased.

**Keywords:** shirasu, geopolymer, GGBS, alkali activators, compressive strength, acid resistance

## 1. INTRODUCTION

### 1.1 Research background

Geopolymer concrete has gained considerable attention as a sustainable construction technology of the future. Geopolymer concrete with industrial wastes or byproducts like fly ash, blast furnace slag, metakaolin and silica fumes as aluminosilicates are being studied extensively. These geopolymer concretes show potential characteristics and beneficial applications. Among these pozzolanic materials, fly ash geopolymer has been vastly studied and fly ash geopolymer has been regarded as more strong and durable in general [1]. Combination of alkali activators and heat curing triggers the polymerization reaction of an aluminosilicate source to form a chain of three dimensional polymer structure high in strength and durability. Other parameters like concentration of alkali activators and their amounts, type of aluminosilicate source, curing techniques and ratios of geopolymer materials have profound effect on the performance of geopolymer concrete [2]. Lower temperatures leads to increased amount of unreacted fly ash before final hardened structure is formed [3,4]. Effective polymerization can be achieved only at elevated temperatures due to its lower reactivity if aluminosilicate is used as a sole binder. In fact, fly ash geopolymer shows higher compressive strength when heat cured than ambient cured [5-7] and that addition of slag is required to obtain better strength under ambient curing conditions.

Requirements of elevated temperatures for heat curing contributes to high cost in production of geopolymer concrete. Further, low reactivity of fly ash

resulting in delayed strength development is considered to be a limiting factor. Hence, as a countermeasure to these limitations, addition of slag is considered. One of the ways to achieve polymerization at room temperature or reduced temperature is by partial addition of slag. To overcome the problem of low reactivity of fly ash, Kumar et al. also considered addition of slag [8]. Their study on combination of fly ash and slag proved that at room temperatures slag dominated the reaction forming C-S-H gel contributing to higher initial strengths and at higher temperatures, polymerization is dominated by combination of fly ash and slag justified by the coexistence of C-S-H and A-S-H. Coexistence of C-A-S-H and N-A-S-H gel forms are also confirmed in fly ash slag based geopolymers [9,10] and these influence densification and improvement in strength. Geopolymer concrete cured at ambient temperature further reduces the cost incurred on heat curing. Strength development of the slag blended fly ash geopolymer concrete cured at ambient temperature was similar to that of water-cured OPC concrete although the workability reduced with increase in slag content [11,12]. Temuujin et al. stated that the calcium compounds are a factor for improved strengths for concretes cured at ambient temperatures [13].

### 1.2 Shirasu as a potential source for geopolymer

Shirasu is a pyroclastic flow deposit abundantly available in the southern part of Kyushu Island of Japan. It was deposited in the region few hundred thousand years ago and is one of the unused natural resources. There are different types of Shirasu deposits available in Kagoshima Prefecture of Japan at different locations

\*1 Researcher, Dept. of Ocean Civil Engineering, Kagoshima University, PhD, JCI member

\*2 Prof., Dept. of Ocean Civil Engineering, Kagoshima University, JCI member

\*3 Prof., Dept. of Ocean Civil Engineering, Kagoshima University, JCI member

\*4 Associate Prof., Dept. of Ocean Civil Engineering, Kagoshima University, JCI member

based on density current and origin. The density of Shirasu available ranges from 2.1 to 2.7 g/cm<sup>3</sup>. Shirasu is sandy but porous material with large amount of very fine particles. It has about 80% density of that of sea sand and three times higher water absorption capacity when compared to sea sand. It also has high quantity of volcanic glasses in its mineral composition and has been confirmed by Takewaka (2004) to show pozzolanic reaction [14]. Shirasu concrete (Shirasu as fine aggregate) is successfully applied to the concrete foundation for piers constructed in hot spring environment and investigations have proved that Shirasu concrete behaves performs well in hot conditions and is resistant to sulfate attacks [15]. Laboratory tests on Shirasu concrete by Katpady et al. proved that Shirasu concrete is highly resistant to chemical attacks and possess higher capabilities in corrosion protection of reinforcement [16]. As Shirasu is rich in silica and alumina, it can be potentially used as aluminosilicate source in geopolymer.

Studies on Shirasu as aluminosilicate has been tried with various mix proportions in the past. It was observed that Shirasu geopolymer showed lower reactivity and delayed strength development compared to that of fly ash. Shirasu geopolymer exhibited no strength gain at the first 24hrs to 48hrs of oven dry heat curing at 90°C even at higher amounts and concentration of alkali activator [17]. Many factors influence the strength gain of geopolymer concrete. In this case, fineness of Shirasu particles and its mineral composition is found to have immense effect on the performance of Shirasu geopolymer. Although Shirasu is comprised of high volcanic glass, silica to alumina ratio is found to be too high. This is because the alumina content is around 12-14% by mass against 22-25% in fly ashes generally used worldwide. Alumina is one of the prime ingredients that effects strength development of geopolymer. Moreover, physical nature of Shirasu particle is thought to have an effect on the strength. Therefore, to improve the initial strength development of Shirasu geopolymer, investigation on strength properties with addition of slag is considered. The present investigation is an attempt to study the performance of Shirasu geopolymer with addition of slag.

## 2. TEST PROGRAMS

### 2.1 Materials

Two component binder mixes are adopted in the study. Shirasu as primary binder with partial addition of slag. Milled Shirasu with Blaine specific surface area of 4486cm<sup>2</sup>/g and specific gravity of 2.48 is used. Slag with a Blaine specific surface area of 4189cm<sup>2</sup>/g is used as an additive. Table 1 shows the physical and chemical properties of materials used and Fig.1 shows particle size distribution of slag, Shirasu and slag used in the study by Laser Diffraction Particle Size Analyzer. River sand is used as fine aggregate having a specific gravity of 2.64. Alkaline activator solution is a combination of sodium hydroxide solution of 14M and sodium silicate (55% assay, SiO<sub>2</sub>/Na<sub>2</sub>O=2.2). One is the

alkali activator solution to binder ratio (here-in-after referred as “AA/B”) set at 0.4. Sodium silicate (NS) to sodium hydroxide solution (NH) ratio (“NS/NH”) is kept at 2. Extra water is added to the mixture to adjust the water to binder ratio of the system to 40%.

Table 1 Physical and chemical characteristics of binder materials used

	Shirasu	Slag
Specific gravity	2.48	2.90
Blaine specific surface area (cm <sup>2</sup> /g)	4486	4189
Mass %		
SiO <sub>2</sub>	70.2	30.7
CaO	4.55	44.1
Al <sub>2</sub> O <sub>3</sub>	13.9	14.1
SO <sub>3</sub>	0.07	1.68
Fe <sub>2</sub> O <sub>3</sub>	3.92	0.40
MgO	0.40	7.39

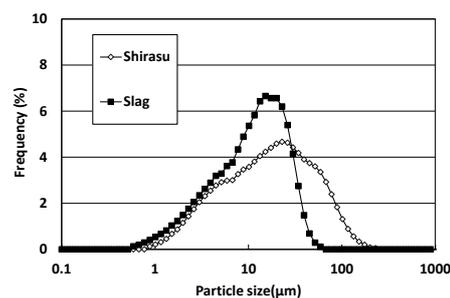


Fig.1 Particle size distribution of Shirasu and slag

Table 2 Mix Proportion

Mix No.	G0	G10	G20	G30	G50
AA/B			0.4		
NS/NH			2		
Slag/Total binder (%)	0	10	20	30	50
Extra water (kg/m <sup>3</sup> )	116	117	118	118	120
NaOH solution (NH) (kg/m <sup>3</sup> )	77	78	78	79	80
Water glass (NS) (kg/m <sup>3</sup> )	155	156	157	158	160
Shirasu (kg/m <sup>3</sup> )	580	526	471	415	300
Slag (kg/m <sup>3</sup> )	0	58	118	178	300
Sand (kg/m <sup>3</sup> )			1315		

Partial addition of slag (represented as “G”) in the place of total binder content is set at 0%, 10%, 20%, 30% and 50% and named as G0, G10, G20, G30 and G50 respectively. Mix proportions employed in the study is shown in Table 2.

## 2.2 Casting and curing method

Initially dry mixture of binders and aggregate is mixed for up to 1 minute. After dry mix, mixture of alkaline activators are introduced and mixed for another 3 minutes. Fresh mortars are the cast on to molds of 5cm in diameter and 10cm in length and then vibrated for 30 seconds on a table vibrator. Cast molds are wrapped with polyvinylidene chloride film over which aluminum tapes are wrapped to ensure water tight wrapping on the exposed part of the mold to prevent water loss during heat curing. Two types of curing conditions are employed. One is atmospheric condition where the above prepared molds are kept at  $20^{\circ}\text{C}\pm 1^{\circ}\text{C}$ , relative humidity of around 70% up to 28 days. The other is, after the preparation, cast molds are kept in the room temperature condition for 2 hours prior to heat curing. Specimens are then initially oven dry heat cured at  $90^{\circ}\text{C}$  for 24 hours (1 day) and then subjected to ambient curing until 28 days.

## 2.3 Experimental tests

### (1) Compressive strength test

Compressive strength test is carried out for all specimens cured under different conditions at predetermined curing periods of 1 day, 7 days and 28 days.

### (2) Sulfuric acid immersion test

After 28 days of curing, specimens are epoxy coated on the top and bottom surfaces. The specimens are then immersed in 5% (w/w) sulfuric acid solution for a target period of 12 weeks. The sulfuric acid solution is changed at a frequency of once in a week to maintain stability of concentration. Change in size and weight is determined at a frequency of once in 4 weeks. After 12 weeks of immersion, specimens are cut open at the mid portion to obtain two phases. 1% phenolphthalein is sprayed on the surface to study the depth of degradation. Mortar with ordinary Portland cement (OPC) is also made for comparative study with water cement ratio of 40%, paste volume of 50%. OPC mortar is cured under 2 conditions; water curing and atmosphere curing.

## 3. RESULTS AND DISCUSSION

### 3.1 Compressive strength variation with age

The compressive strength development with age for specimens subjected to atmospheric curing and heat curing are shown in Fig.2 and Fig.3 respectively. The compressive strength increases with increase in curing period for both the curing conditions. Especially when atmosphere cured, the initial strength is slightly lesser compared to heat curing. This difference would have been much higher without slag addition. It helps in improving initial compressive strength of Shirasu geopolymer. Hence atmosphere curing is sufficient if

slag is used. The 28 day strength is somewhat similar between atmosphere and heat curing. Hence, the rate of strength development is higher for atmosphere curing. During heat curing, the polymerization reaction is faster, but the ultimate strength is similar to atmosphere curing. From this it can be understood that heat curing only accelerates the strength development. Heat curing shows slightly higher initial strength, but the long term strength is similar to atmospheric cured specimens. In the case of heat curing, G30 and G50 show large variation in test results. Otherwise, in general, variation is less.

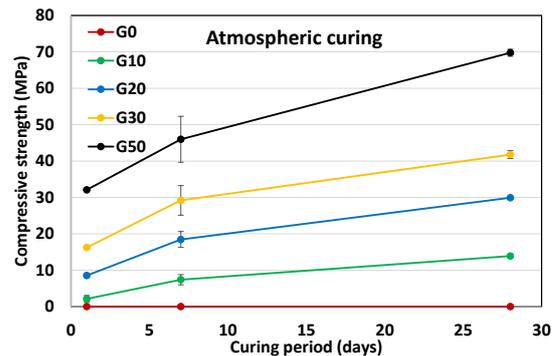


Fig.2 Compressive strength of geopolymers cured under ambient conditions

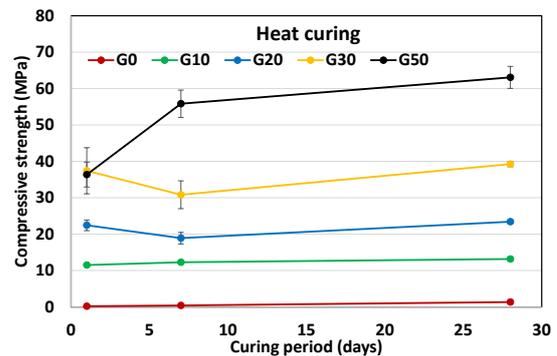


Fig.3 Compressive strength of geopolymers cured under oven dry heat

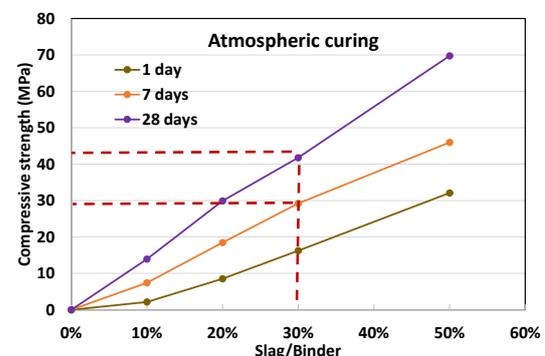


Fig.4 Compressive strength of geopolymers cured under ambient conditions

Study by Nath et al. showed no significant increase in strength of fly ash slag geopolymer if heat cured [18]. Similar trend is observed in slag Shirasu geopolymer if heat cured. The increase in compressive strength with increase in slag addition was confirmed

for both conditions of curing which is in line with other research [3,8,18-21]. Alkali activation of slag along with aluminosilicates elevates the strength development by combining effect of coexisting gel products [9,10]. Previous studies by Katpady et al. on Shirasu based geopolymer confirmed the slow reactivity and lower strength development [17]. Also it was concluded that even with continuous heat curing at high temperatures, high concentration and amount of alkaline activator, Shirasu geopolymer mortars begin hardening only after 3-5 days. With this knowledge, slag addition on Shirasu geopolymer clearly has an effect on the strength development. Hence, initial products of alkali activation of slag and combination of slag and Shirasu provides sufficient strength gain of mortars. In the present study, slag up to 50% is considered. With higher amounts of slag and high concentration of alkali activators, setting characteristics also gets affected. Mortars hardened quickly when amount of slag increased. Conversely, utilization of higher amounts of Shirasu requires higher amounts and concentration of alkali activators for dissolution of Shirasu particles. Therefore, to arrive at a balance between alkali activator amounts and concentration, amount of Shirasu and slag replacement, 30% replacement of slag is considered to be optimum in this study. It also serves in utilization of greater amounts of Shirasu, which is one of the purpose of this study. For instance, Fig.4 illustrates the compressive strength variation with slag replacement. In actual practice, if target compressive strength is decided, corresponding slag replacement can be determined. However, this is one of the cases with fixed alkaline activator amount and alkali activator to binder ratio. Likewise, for different parameters one can determine slag replacement for a target strength. For a strength requirement of 30MPa for 7 days and 40MPa for 28 days, 30% replacement of slag can be considered.

### 3.2 Sulfuric acid immersion test

The specimens subjected to sulfuric acid immersion test are sliced along the mid-section to determine depth of neutralization by phenolphthalein method. The depth of neutralization for all specimens under different curing conditions are shown in Fig.5. The figure also shows neutralization depth for OPC mortar cured under both ambient and water curing, immersed in sulfuric acid solution for 4 and 12 weeks. Since G0 developed no sufficient strength for sulfuric acid immersion test, results of G0 are not obtained. Increase in slag addition reduces the neutralization depth. Slag replacement of 50% shows about 1/2<sup>nd</sup> to 1/3<sup>rd</sup> neutralization compared to 10% replacement. No much difference is observed between curing conditions, which shows that ambient curing is sufficient to produce sulfate resistive geopolymer. It is also known that strength is higher for higher replacement of slag. Slag addition improves the quality of geopolymer and makes the matrix denser [22]. Hence acid penetration is reduced. Also, increase in GGBS increases calcium ions in the system. So even if calcium ions are used up by neutralization reaction, remaining calcium ions get

replenished.

According to Bakharev, breakage of polymers formed, exchange of sodium and potassium cations by hydrogen and hydronium ions are some of the reactions occurring during acid attack [23]. Since slag is used in the present study, C-A-S-H gel matrix is degraded to form calcium sulfates [22]. From the figure it is observed that OPC specimens show lesser neutralization depth than G10 and G20. Even though such case arise, all geopolymers show less degradation. On the other hand OPC specimens have severely degraded and lost almost entire mass.

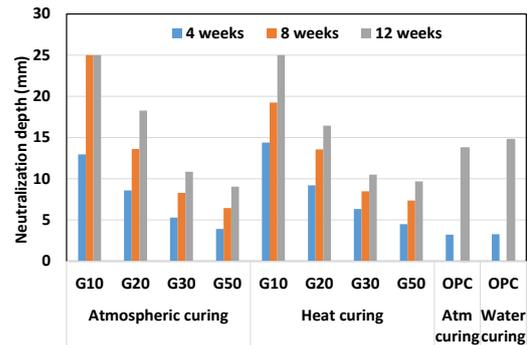


Fig.5 Neutralization depth of all geopolymers

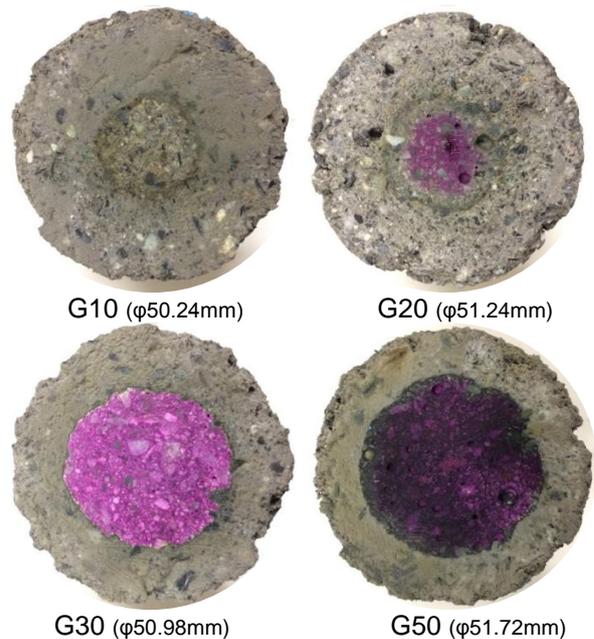


Fig.6 Neutralization depth indication for geopolymers cured under atmospheric condition

Fig.6, Fig.7 and Fig.8 show the condition after phenolphthalein spray for geopolymers under both curing conditions and for OPC immersed in sulfuric acid solution for 12 weeks. The size of pictures shown in Fig.6-8 are relative to the magnitude of actual condition. Fig.9 and Fig.10 show the mass loss rate for atmosphere cured and heat cured specimens respectively. Mass reduction is seen for all specimens irrespective of curing conditions. The mass reduction is less for higher slag replacement. OPC mortar specimens after 12 weeks of immersion have lost

almost 83.55% under atmospheric curing and 85.18% for water curing (Fig.8). Mass reduction of G30 is large compared to others only in case of atmosphere curing. This can be variation in experimental results. However, the order of mass reduction in all geopolymers is very less and not significant in comparison with OPC. Hence overall results show that geopolymer specimens with slag replacement show higher acid resistance. Atmosphere cured geopolymer shows similar resistance against acid attack compared to heat curing.

Fig.11 and Fig.12 show the geopolymer specimens after 12 weeks of sulfuric acid immersion.

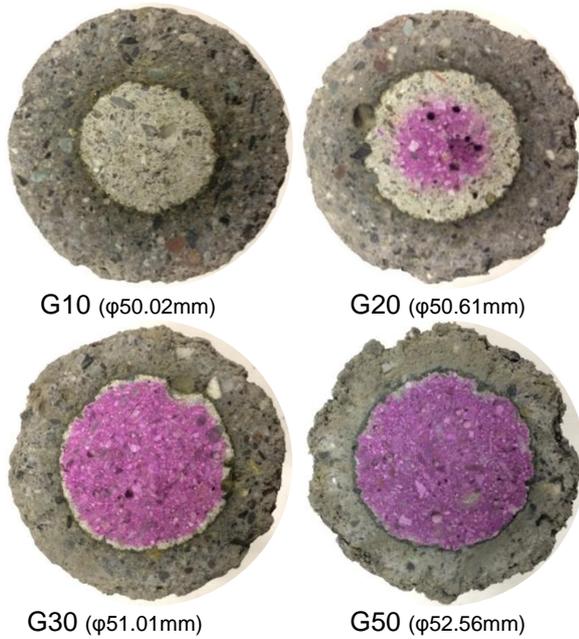


Fig.7 Neutralization depth indication for geopolymers cured under oven dry heat condition



Fig.8 Neutralization depth indication for OPC

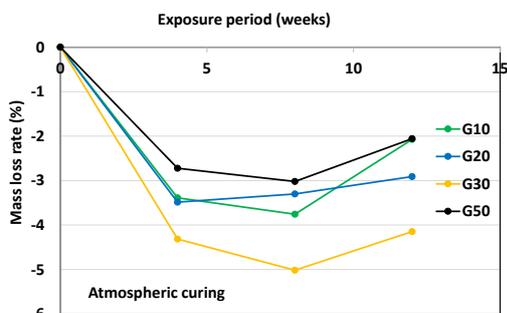


Fig.9 Mass loss rate of geopolymers immersed in sulfuric acid (atmospheric curing)

Even if the surface is rough, the specimens are

intact unlike OPC mortar. In the previous result on neutralization depth, OPC showed lesser neutralization depth compared to G10 and G20, but degradation is much higher for OPC. This shows that the C-A-S-H and N-A-S-H matrix formed in slag based Shirasu geopolymer renders mortar denser and prevents degradation due to acid attack. Geopolymers also show cracks developed. However, degradation is less in such extreme condition.

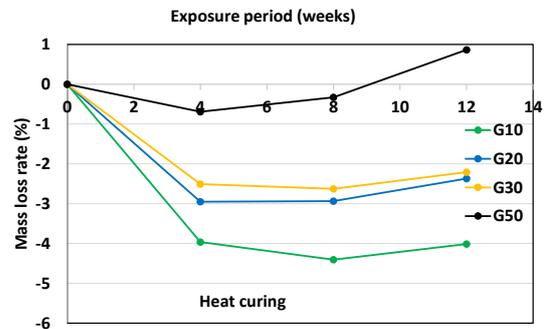


Fig.10 Mass loss rate of geopolymers immersed in sulfuric acid (oven dry heat curing)

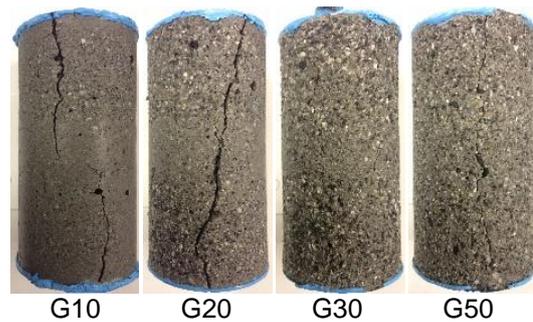


Fig.11 Pictures showing specimens immersed under sulfuric acid for 12 weeks (atmospheric curing)

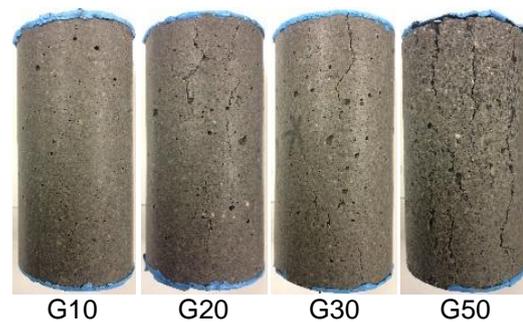


Fig.12 Pictures showing specimens immersed under sulfuric acid for 12 weeks (oven dry heat curing)

#### 4. CONCLUSIONS

An attempt is made in the study to produce Shirasu geopolymer under ambient curing conditions with the help of ground granulated blast furnace slag. Based on the experimental results following conclusions are drawn:

- (1) Compressive strength increase is observed as the

percentage addition of slag increases. Higher initial strength and rate of strength gain suggested that ambient curing is also possible for Shirasu geopolymer with slag.

- (2) Atmospheric curing and heat curing showed similar trend and the long term strength did not differ much. Low temperature curing requires longer curing periods to develop strength.
- (3) Slag addition improved the resistance of Shirasu geopolymer against acid. Heat curing and atmospheric showed similar resistivity.
- (4) To serve the purpose of utilization of Shirasu in abundance, addition of slag up to 30% is recommended to obtain optimum strength and resistance against acid attack.
- (5) Slag based Shirasu geopolymer showed better acid resistance compared to ordinary Portland cement mortar.

## REFERENCES

- [1] Duxson, P., Fernández-Jime'nez, A., Provis, J. L., Lukey, G.C., Palomo, A. and van Deventer, J. S. J., "Geopolymer technology: the current state of the art", *J. Mater. Sci.*, Vol. 42(9), 2007, pp. 2917-2933.
- [2] Hardjito, D., Wallah, S.E., Sumajouw, D.M.J. and Rangan, B.V., "On the development of fly ash-based geopolymer concrete", *ACI Mater. J.*, Vol. 101(6), 2004, pp. 467-472.
- [3] Puertas, F., MartõÁnez-RamõÁrez, S., Alonso, S. and VaÁzquez, T., "Alkali-activated fly ash/slag cement, Strength behaviour and hydration products", *Cem. Concr. Res.*, Vol. 30, 2000, pp. 1625-1632
- [4] Bakharev, T., "Geopolymeric materials prepared using class F fly ash and elevated temperature curing", *Cem. Concr. Res.*, Vol. 35, 2005, pp. 1224-1232
- [5] Li, X., Wang, Z. and Jiao, Z., "Influence of curing on the strength development of calcium-containing geopolymer mortar", *Materials*, Vol. 6, 2013, pp. 5069-5076
- [6] Nguyen, K.T., Lee, Y.H., Lee, J. and Ahn, N., "Acid resistance and curing properties for green fly ash-geopolymer concrete", *J. Asian Arch. Build. Eng.*, Vol. 12(2), 2013, pp. 317-322
- [7] Joshi, S.V. and Kadu, M.S., "Role of alkaline activator in development of eco-friendly fly ash based geo polymer concrete", *Int. J. of Environ. Sci. Dev.*, Vol. 3(5), 2012, pp. 417-421
- [8] Kumar, S., Kumar, R. and Mehrotra, S.P., "Influence of granulated blast furnace slag on the reaction, structure and properties of fly ash based geopolymer", *J. Mater. Sci.*, Vol. 45, 2010, pp. 607-615
- [9] Xu, H., Gong, W., Syltebo, L., Izzo, K., Lutze, W. and Pegg, I.L., "Effect of blast furnace slag grades on fly ash based geopolymer waste forms", *Fuel*, Vol. 133, 2014, pp. 332-340
- [10] Bernal, S.A., Provis, J.L., Walkley, B., Nicolas, R.S., Gehman, J.D., Brice, D.G., Kilcullen, A.R., Duxson, P. and van Deventer, J.S.J., "Gel nanostructure in alkali-activated binders based on slag and fly ash, and effects of accelerated carbonation", *Cem. Concr. Res.*, Vol. 53, 2013, pp. 127-144
- [11] Deb, P.S., Nath, P. and Sarker, P.K., "The effects of ground granulated blast-furnace slag blending with fly ash and activator content on the workability and strength properties of geopolymer concrete cured at ambient temperature", *Mater. Des.*, Vol. 62, 2014, pp. 32-39
- [12] Perna, I. and Hanzlìcek, T., "The setting time of a clay-slag geopolymer matrix: the influence of blast-furnace-slag addition and the mixing method", *J. Cleaner. Prod.*, Vol. 112, 2016, pp. 1150-1155
- [13] Temuujin, J., van Riessen, A. and Williams, R., "Influence of calcium compounds on the mechanical properties of fly ash geopolymer pastes", *J. Hazard. Mater.*, Vol. 167, 2009, pp. 82-88
- [14] Takewaka, K., "State-of-art-report on characteristics of shirasu concrete and its practical use", *Concr. J.*, Vol. 42(3), 2004, pp. 38-47
- [15] Takewaka, K. and Kawamata, K., "Durability of concrete using pyroclastic flow deposit for fine aggregates", *Proc. of Second Canada/Japan Workshop, Ottawa, 1991.*
- [16] Katpady, D.N., Takewaka, K., Yamaguchi, T., Moritaka, Y. and Tatara, Y., "Experimental study on deterioration monitoring of shirasu concrete in hot spring environment", *Int. J. Earth. Sci. Eng.*, Vol. 05(04), 2012, pp. 1020-1026
- [17] Katpady, D.N., Takewaka, K. and Yamaguchi, T., "Development of geopolymer with pyroclastic flow deposit called shirasu", *Adv. Mater. Res.*, Vol. 4(3), 2015, pp. 179-192
- [18] Nath, P. and Sarker, P.K., "Effect of GGBFS on setting, workability and early strength properties of fly ash geopolymer concrete cured in ambient condition", *Constr. Build. Mater.*, Vol. 66, 2014, pp. 163-171
- [19] Ushaa, T.G., Anuradha, R. and Venkatasubramani, G.S.W., "Performance of self-compacting geopolymer concrete containing different mineral admixtures", *Indian. J. Eng. Mater. Sci.*, Vol. 22, 2015, pp. 473-481
- [20] Gao, X., Yu, Q.L. and Brouwers, H.J.H., "Properties of alkali activated slag-fly ash blends with limestone addition", *Cem. Concr. Compos.*, Vol. 59, 2015, pp. 119-128
- [21] Kürklü, G., "The effect of high temperature on the design of blast furnace slag and coarse fly ash-based geopolymer mortar", *Compos. Part B*, Vol. 92, 2016, pp. 9-18
- [22] Lee N.K., Lee H.K., "Influence of the slag content on the chloride and sulfuric acid resistances of alkali-activated fly ash/slag paste", *Cem. Concr. Compos.*, Vol. 72, 2016, pp. 168-179
- [23] T. Bakharev, "Resistance of geopolymer materials to acid attack", *Cem. Concr. Res.*, Vol. 35, 2005, pp. 658-670.