Development of geopolymer with pyroclastic flow deposit called Shirasu

Dhruva Narayana Katpady^{*1}, Koji Takewaka² and Toshinobu Yamaguchi²

¹Kagoshima University, Department of Ocean Civil Engineering, 1-21-40, Korimoto, Kagoshima, Japan ²Department of Ocean Civil Engineering, Kagoshima University, 1-21-40, Korimoto, Kagoshima 890-0065, Japan

(Received August 14, 2015, Revised November 11, 2015, Accepted December 10, 2015)

Abstract. The study presents a preliminary investigation on the applicability of Shirasu (a pyroclastic flow deposit characterized by high percentage of volcanic glass) in geopolymer. Comparative study on compressive strength and internal pore structure has been done between geopolymers with alkali activated Shirasu and fly ash as aluminosilicates. Mortar mix proportions are selected based on variations in ratio of alkaline activators to aluminosilicate and also on silica to alkali hydroxide ratio. From the experimental study, Shirasu geopolymer exhibited fairly good compressive strength. Mix proportion based on silica to alkali hydroxide ratio is observed to have profound effect on strength development.

Keywords: aluminosilicate; alkali activation; geopolymer; polymerization; pyroclastic flow; Shirasu

1. Introduction

The contribution of cement to global CO2 increase has been a concern lately. A new technology called Geopolymer concrete has proved to solve this problem to a great extent if not completely. Geopolymerization involves the reaction of an aluminosilicate with a mixture of highly concentrated aqueous alkali hydroxide and silicate solution to produce a synthetic polymer, alkali aluminosilicate material (-Si-O-Al-O) (Duxson *et al.* 2007). These materials are comparable to traditional cementitious binders for a wide range of applications, but with the added advantage of significantly reduced greenhouse emissions as quoted by Turner and Collins (2013). According to Lloyd and Rangan (2010), geopolymer concrete can be potentially applicable in precast concrete. The most standard types of geopolymer concrete. However the production of the sodium silicate solution poses a different threat apart from global warming. Geopolymer concrete made from fly ashes or granulated blast furnace slags based usually require less of the sodium silicate solution for alkali activation (Habert *et al.* 2011) and hence friendlier to the environment. Geopolymers can exhibit a wide variety of properties and characteristics depending on the raw material selection, mix design and processing conditions. High compressive strength, low

Copyright © 2015 Techno-Press, Ltd.

http://www.techno-press.org/?journal=amr&subpage=7

^{*}Corresponding author, Ph.D, E-mail: dnkata@gmail.com

shrinkage, fast or slow setting and low thermal conductivity are some of the attributes proposed by Kong and Sanjayan (2010). Geopolymerization mechanism is very complex in nature and initially involves dissolution of silica and alumina in aluminosilicate source by alkaline hydrolysis which triggers polymerization at high pH conditions followed by gelation. The dissolution of silica and alumina especially from fly ash increases with increase in the concentration of sodium hydroxide used as activator according to the investigations by Rattanasak and Chindaprasirt (2009). Further rearrangement and reorganization of the gel increases the connectivity of the gel network resulting in the three-dimensional aluminosilicate network commonly attributed to geopolymer. There are several models proposed on different types of networks formed during polymerization. The characteristics and structure of polymers formed largely depends on aluminosilicate source used, alkalinity and temperature. The salient parameters affecting the compressive strength of geopolymer concrete are as listed below (Hardjito *et al.* 2004)

1. Silicon oxide (SiO₂) to aluminum oxide (Al₂O₃) ratio by mass of the source material.

- 2. Alkali activators to source material ratio by mass.
- 3. Molar concentration of sodium hydroxide (NaOH) (Molarity, M)
- 4. Sodium silicate to sodium hydroxide liquid ratio by mass.
- 5. Water to geopolymer solids ratio.
- $6. H_2O/Na_2O$ molar ratio.
- 7. Curing temperature.
- 8. Curing time and curing methods.

These parameters have profound influence on not only the compressive strength but also on the durability of geopolymer concrete. Chindaprasirt and Chalee (2014) showed that greater durability and higher resistance against chloride ingress can be possible by increasing the concentration of sodium hydroxide used in geopolymer which also results in higher compressive strengths. Joshi and Kadu (2012) showed the drastic increase in compressive strength when sodium hydroxide concentrations were changed from 12M to 14M. This is attributed to the fact that at higher NaOH concentration, dissolution of silica and alumina significantly improves. Hanjitsuwan *et al.* (2014) also showed that higher concentration of NaOH increases the setting time and compressive strength resulting from higher degree of fly ash reaction forming dense matrix. All these studies have proved the effect of NaOH on performance of geopolymer. Particularly on the study of selection and combination of alkali hydroxides by Bashir (2015), sodium hydroxide alone is confirmed to be the best suitable activator.

Recent advancements in research on the development of geopolymer concrete cured at ambient temperature further reduce the cost incurred on heat curing. Deb *et al.* (2014) showed that 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. Temuujin *et al.* (2009) stated that the calcium compounds are a factor for improved strengths for concretes cured at ambient temperatures. But if aluminosilicate source material is used as a sole binder, heat curing is a necessity and according to Joshi and Kadu (2012), strength of oven dry heat cured concrete is significantly higher than ambient cured concrete although the ambient curing is practically economical. The test results on durability by Shah *et al.* (2014) showed that oven dry heat cured fly ash based geopolymer concrete have an excellent resistance to sulfate attack, salt attack and acid attack. Oven dry heat curing can affect the properties of hardened concrete depending on temperature and duration. An increase in temperature between 60°C to 90°C increases the strength of concrete while temperatures beyond 100°C can have negative effect on strength development as investigated by Joseph and Mathew (2012). Hence,

180

these parameters with right proportioning can produce geopolymer concrete with outstanding characteristics. Olivia and Nikraz (2012) achieved 8-12% higher tensile strength, 1.4 times higher flexural strengths with less expansion and drying shrinkage than the ordinary Portland cement concrete. Major factors for a good performance of geopolymer concrete are alkali activators, their ratios and choice of activators. Higher amounts of alkaline activators are said to decrease sorptivity and increase the resistance of concrete against chloride ingress according to Shaikh (2014). The higher the ratio of sodium silicate to sodium hydroxide, the higher the strength is. And the strength is higher for sodium hydroxide than for potassium hydroxide (Motorwala et al. 2013). Addition of nanoparticles (MWCNTs) can enhance geopolymerization and contribute to strength gain. Even though higher dosages have negative effect on strength development, optimum addition can enhance properties like amorphousness and strength gain and decrease drying shrinkage according to Khater and Abd el Gawaad (2015). Apart from these, water to geopolymer solids ratio and alkali activators to aluminosilicates have major effects on fresh and hardened concrete properties. An increase in both factors can increase the workability of mix as investigated by Sanni and Khadiranaikar (2013). The bonding between the aggregate and the aluminosilicates have considerable impact on the strength. Higher amount of aggregates reduces the degree of polymerization but has less significance of strength reduction. Hence incorporating higher volume of aggregate can be made possible by optimizing alkali activators (Temuujin et al. 2010). Apart from compressive strength, fiber reinforced geopolymer concrete exhibits higher tensile strength and modulus of elasticity (Ganesan et al. 2013). Collectively, the performance of geopolymer depends on choice of materials and their proportioning. And the advancements on geopolymers with established combination of materials encourages trying new materials.

1.1 Shirasu as aluminosilicate source in geopolymer

Extensive research is carried out on geopolymer with fly ash, metakaolin and blast furnace slags as aluminosilicates. The present study is an attempt to utilize unused natural resource called Shirasu as aluminosilicate source in geopolymer. "Shirasu", a kind of volcanic ash abundantly deposited due to a big pyroclastic flow in the southern part of Kyushu Island, Japan, in 20 to 100 thousand years ago, is one of the unused natural resources. 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. 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 well in hot conditions and is resistant to sulfate attacks (Takewaka and Kawamata (1991)). Laboratory tests on Shirasu concrete by Katpady (2012) proved that Shirasu concrete is highly resistant to chemical attacks and possess higher capabilities in corrosion protection of reinforcement. As Shirasu is rich in silica and alumina, it can be potentially used as aluminosilicate source in geopolymer. The present investigation is an attempt to study the performance of geopolymer with Shirasu as aluminosilicate source. The behavior of Shirasu geopolymer is compared with that of geopolymer mortars prepared with fly ash. Past researches have proved that fly ash geopolymer are generally stronger and durable (Duxson et al. 2007). With this knowledge, Shirasu geopolymer with different mix proportions is tried. As Shirasu and fly ash have different characteristics, an attempt to study the strength development of mortars and to obtain optimum strength is done assuming silica to alkali hydroxide ratio

Meas0/	Aluminosilicate source		
Mass%	Shirasu	Fly ash	
SiO ₂ (%)	76.6	63.3	
Al ₂ O ₃ (%)	12.2	22.41	
CaO (%)	1.08	1.93	
Na ₂ O (%)	3.43	-	
K ₂ O (%)	3.54	-	
MgO (%)	-	1.01	
$Fe_2O_3(\%)$	1.48	5.74	
Specific gravity	2.4	2.25	
Blaine specific surface area (cm ² /g)	2200 (-75µm)	3990	
Water absorption (%)	7.52	-	

Table 1 Properties of aluminosilicates used



Fig. 1 Particle size distribution of aluminosilicates

(here-in-after called "Si/NH") in the mix to be one of the important parameters. This study being the first attempt on the development of Shirasu in geopolymer provides evidence on utilization of natural source as a building material.

2. Materials and methods

Geopolymer mortars are made with following materials

1. Aluminosilicate source (Binder): Shirasu of size under 75 μ m and fly ash are used. The physical and chemical characteristics of Shirasu and fly ash are shown in Table 1.

2. Fine aggregate: river sand with a specific gravity of 2.6.

3. Alkaline activators: Sodium hydroxide solution (14N) and sodium silicate solution (52% as

say) are used under the condition of sodium silicate to sodium hydroxide of 2.5 by volume. Two main types of geopolymer mortars are made, namely

4. Shirasu geopolymer (GSH): Shirasu as aluminosilicate source and river sand as fine aggregate.

Table 2 Mix proportion for Shirasu geopolymer mortar

				Materials (kg/m ³)	
Mix No.	Alkali activators/Shirasu	Shirasu	Sand	Sodium hydroxide solution (14N NaOH)	Sodium silicate
*GSH-1	0.55	457	1655	78	176
GSH-2	0.7	365	1756	78	176
GSH-3	0.85	299	1829	78	176

^{*}GSH: Shirasu Geopolymer mortar

Table 3 Mix proportion for fly ash geopolymer mortar

		Materials (kg/m ³)			
Mix No.	Alkaline activators/fly ash	Fly ash	Sand	Sodium hydroxide solution 14N NaOH	Sodium silicate
*GFA-1	0.55	456	1624	78	176
GFA-2	0.7	365	1729	78	176
GFA-3	0.85	299	1805	78	176

^{*}GFA: Fly Ash Geopolymer mortar

5. Fly ash geopolymer (GFA): Fly ash as aluminosilicate source and river sand as fine aggregate.

The particle size distributions of Shirasu (particle size under 75 μ m) and fly ash measured by Laser Diffraction Particle Size Analyzer are shown in Fig. 1. Fly ash is observed to be finer than Shirasu since Shirasu used in the study is sieved under 75 μ m sieve. Particles passing this sieve are used as aluminosilicate.

The mix proportions for geopolymer mortars with Shirasu and fly ash as aluminosilicate sources are shown in Table 2 and Table 3 respectively. The total amount of alkaline activators is kept constant in all the mix while the ratio of alkaline activators to aluminosilicate (either fly ash or Shirasu) is varied, as, 0.55, 0.7 and 0.85. The ratios were selected based on trials to obtain consistent mix for easy handling since geopolymer mortars are generally very sticky in nature. Shirasu geopolymer is named as "GSH" and fly ash geopolymer as "GFA" in the experimental study. The required water is contained in the alkaline activator solutions and no extra water is added. All mix proportions are in unit weight to volume basis.

The alkaline activators are prepared 24 hours prior to mixing. Initially, mixture of aluminosilicate source and sand are dry mixed followed by addition of alkaline activators. The total time for mixing is 4 minutes after which the mixture is poured on to the cylindrical molds of diameter 5 cm and length 10 cm. Table vibrator is used while casting to achieve optimum compaction of the mortar in molds. After casting of mortar, the top exposed portion of the molds is wrapped with a combination of polymer plastics and aluminum foil to prevent evaporation of water. Wrapped molds are kept under room temperature condition for 1 hour and then subjected to temperatures of 80°C and 90°C in oven dry condition for all mix proportions.

2.1 Silica to alkali hydroxide ratio (Si/NH) for mix proportion

Dhruva Narayana Katpady, Koji Takewaka and Toshinobu Yamaguchi

Shirasu and Fly ash are two different materials with different origin, chemical and physical characteristics. The amount of silica contained in Shirasu and fly ash is different. Hence, the mix proportion based on silica to alkali hydroxide ratio by making the ratios equal is thought to provide better comparison of their strength properties. Silica to alkali hydroxide ratio of GSH and GFA are varied from 6 to 12. Silica to alkali hydroxide was calculated as follows

Si = (Silica in Shirasu/fly ash) + (Silica in sodium silicate), grams

NH = NaOH solution, grams

That is,

184

(Silica in Shirasu or fly ash + Silica in sodium silicate) / NaOH

The mix proportions based on Si/NH in GSH and GFA are shown in Table 4 and Table 5 respectively. The paste volume in all the mixes is kept constant. The compressive strength tests are carried in accordance with JIS A1108 for both GSH and GFA mortars heat cured at 90°C. After having chosen the optimum mix among various ratios of silica to alkali hydroxide, mix proportion with variation in ratio of aggregate to aluminosilicate is considered so as to vary the paste volume in the mix. The mix proportion for the same is shown in Table 6.

Table 4 Mix proportion base	d on silica to hydroxide ratio for	or Shirasu geopolymer morta
-----------------------------	------------------------------------	-----------------------------

			Materials (kg/m ³)	
Si/NH*	Shirasu	Sand	Sodium hydroxide solution 14N NaOH	Sodium silicate
12	401	1716	78	177
10	354	1716	87	195
9	326	1716	92	207
8	295	1716	97	219
6	221	1716	110	249

*Si/NH: Silica to alkali hydroxide mass ratio

Table 5 Mix proportion based on silica to hydroxide ratio for fly ash geopolymer mortar

	Materials (kg/m^3)				
Si/NH*	Fly ash	Sand	Sodium hydroxide solution 14N NaOH	Sodium silicate	
12	414	1716	71	160	
10	369	1716	80	179	
9	343	1716	85	191	
8	313	1716	90	204	
6	238	1716	105	236	

*Si/NH: Silica to alkali hydroxide mass ratio

Table 6 Mix proportion with variation in aggregate to Shirasu ratio keeping Si/NH constant at 9

Materials (kg/m ³)					
Si/OH*	Sand/Shirasu	Shirasu	Sand	Sodium hydroxide solution 14N NaOH	Sodium silicate
	5	337	1686	95	213
9	4	386	1546	109	245
	3	452	1360	127	286

*Si/NH: Silica to alkali hydroxide mass ratio

2.2 Compressive strength test

Compressive strength testing is done for heat cured geopolymer mortars in accordance with method specified by JIS A1108 (Method of test for compression strength of concrete). Three samples each for specified curing period and mix proportion are tested for compressive strength and the average of the compressive strengths of three samples are taken for projecting the results.

2.3 Porosity test for geopolymer mortars

The geopolymer mortars are analyzed for porosity based on the principle of mercury intrusion porosimetry. The tests are conducted on all samples subjected to a temperature of 90°C for 7 days. Three specimens for each mix proportion are taken for analysis of porosity from which samples of about 1 cm³ are obtained. One cubic sample from each specimen is chosen for porosity test and finally the average of three samples is considered for analyzing the internal pore structure.

3. Results and discussion

3.1 Compressive strength of Shirasu geopolymer mortar (GSH)

Geopolymer mortar with Shirasu of size under 75 μ m as aluminosilicate source is made with mix proportions given in Table 2 and heat cured at 90°C and 80°C. Compressive strength test is carried out for specimens for each set of mix proportions. The compressive strength variation is shown in Fig. 2 and Fig. 3 for specimens heat cured at 90°C and 80°C respectively. At all ages of heat curing, higher the alkali activator to aluminosilicate ratio lower the compressive strength is. However, the strength develops only after 6 days at 90°C heat curing. Shirasu shows lower reactivity and initiation of hardening. This may be attributed to the fact that Shirasu has been deposited over thousands of years. Hence, impurities and oxides coating on the surface of particles reduces the rate of polymerization and delays initiation of hardening. Even though such case arises, Shirasu clearly shows good performance in polymerization and the maximum compressive strength is up to 20 MPa. Degree of amorphousness and alumina content are also the main factors



Fig. 2 Compressive strength variation with age for Shirasu geopolymer mortar heat cured at 90°C



Fig. 3 Compressive strength variation with age for Shirasu geopolymer mortar heat cured at 80°C



Fig. 4 Compressive strength variation with age for fly ash geopolymer mortar heat cured at 90°C

governing the development of strength. Shirasu particles may be less amorphous in nature and percentage of reactive silica in Shirasu may also affect the strength gain. Decrease in the compressive strength of Shirasu geopolymer is observed with increase in ratio of alkaline activators to Shirasu, unlike fly ash geopolymer. But, the decrement is insignificant. One of many other possibilities of delayed hardening and strength gain of Shirasu mortar is the fineness. Shirasu particles of size under 75 μ m has Blaine specific surface area of 2200 cm²/g which is much lower than that of fly ash with 3990 cm²/g. Change in temperature of heat curing also affects the development of strength. As an illustration, Fig. 3 shows a clear decrease in compressive strength of mortars. Moreover, the initiation of hardening delays further when the temperature of heat curing is reduced.

3.2 Compressive strength of fly ash geopolymer mortar (GFA)

Fly ash geopolymer mortar is prepared with mix proportion as shown in Table 4. The amount of alkaline activators is kept constant similar to Shirasu geopolymer to study the relative performance of Shirasu polymerization when compared to fly ash. The compressive strengths of



Fig. 5 Compressive strength variation with age for fly ash geopolymer mortar heat cured at 80°C

fly ash geopolymers heat cured at 90°C and 80°C are given in Fig. 4 and Fig. 5 respectively. Increase in ratio of alkaline activators to aluminosilicate shows increase in strength, unlike Shirasu geopolymer which showed inverse relation. Also, increase in temperature of heat curing increases the compressive strength. The results are compliant with several other researches carried out on fly ash geopolymer. As the alkaline activators increase, dissolution of aluminosilicates in pozzolans becomes easier. Also, fly ash is more amorphous in nature than Shirasu and silica and alumina are readily available for reaction in the case of fly ash. Even though the amount of silica in fly ash is lesser than Shirasu, reactive silica and alumina in fly ash are higher in content. Maximum strength of around 35MPa is achieved. But maximum strength of Shirasu geopolymers are comparable to fly ash geopolymers. The only major difference between Shirasu and fly ash geopolymer is that the fly ash geopolymer gains strength within 1 day of heat curing, whereas strength development of Shirasu geopolymer is after 6 days. The contrast in result is the effect of the nature of Shirasu and fly ash. Even if both are pozzolans and have similar characteristics, Shirasu is a deposit and fly ash is a by-product. Shirasu was deposited several thousand years ago and has been subjected to various natural conditions which change the particle surface nature. The demand for sufficient alkali may not have been met in these mix designs. Moreover, Blaine specific surface area of Shirasu used is much less than fly ash. The fineness affects the reactive, overall strength and initiation of hardening. The reason for high initial reactivity is the content of alumina in aluminosilicates. This high percentage of alumina is seen in fly ash. However, overall results show that Shirasu can be potentially used in geopolymer if the parameters like fineness, characteristics of alkali activators and addition of chemical admixtures like slag are considered.

3.3 Porosity of geopolymer mortars

Porosity of GSH and GFA subjected to 90°C for 7 days was determined for clear understanding of the variation in strengths. The pore distributions are given in Fig. 6. GSH mortars have highest volume of pores at 100 μ m and above. On the other hand, GFA-1 has high volume of pores at 100 μ m, GFA-2 at 1 μ m and GFA-3 at 10 nm. Therefore, as the ratio of alkaline activators to aluminosilicate increases, porosity reduces while reducing large pores and simultaneously increasing micro pores. Geopolymer mortars where Shirasu is used as aluminosilicate source



Fig. 6 Pore distribution of all geopolymer mortars subjected to temperature of 90°C up to 7 days



Fig. 7 Compressive strength variation with Si/OH for Shirasu geopolymer mortar

(GSH) show higher porosity compared to that of fly ash geopolymer (GFA). This trend in porosity of mortars is similar to the trend in strength development. The pore volumes and pore distribution in each mix of GSH and GFA match with the compressive strength results and explain the contradicting results of strength.

3.4 Effect of silica to alkali hydroxide ratio (Si/NH) on strength development of geopolymer mortars

In the previous investigations of geopolymer mortars with Shirasu and/or fly ash, it was observed that changes in compressive strength with variation in ratio of alkaline activators to aluminosilicate were not similar. Difference in nature of Shirasu and fly ash, like, amount of silica and reactive silica content, degree of amorphousness and origin, processing of aluminosilicates and specific surface area are governing factors. For this purpose, the ratio of silica to sodium



Fig. 8 Compressive strength variation with Si/OH for fly ash geopolymer mortar



Fig. 9 Pore distribution of all geopolymer mortars subjected to temperature of 90° C up to 7 days for mix with Si/NH=9

hydroxide in the mix is made equal for both Shirasu and fly ash geopolymers and compressive strengths are compared. In this way, by creating a balance in silica and alkaline conditions in the mix, comparative study can be easily possible. The compressive strength results of GSH and GFA mortars with mix proportions are shown in Tables 4 and 5, heat cured at 90°C are also shown in Fig. 7 and Fig. 8 respectively.

The graphs illustrating the compressive strength depending on Si/NH clearly show that it has a great influence on the strength properties of mortar. The peak compressive strength is obtained at Si/NH=9 in both aluminosilicates. This indicates a clear effect of silica to hydroxide balance in the mix. The condition of Si/NH<9 has fewer amount of aluminosilicate source necessary for polymerization. On the contrary, the condition of Si/NH>9 has higher amount of alkaline activators in the mix which does not have enough aluminosilicate source necessary for polymerization. Higher amount of alkaline activators also increase the cost of preparation of mortars and causes adverse conditions like expansion and cracking.



Fig. 10 Pore distribution of all geopolymer mortars subjected to temperature of 90⁰C up to 7 days for mix with Si/NH=9

The porosity of both geopolymers with mix proportion having Si/NH=9 is clearly lesser than the previous mix proportions as illustrated by the pore distributions in Fig. 9. Also, the difference in porosity between Shirasu and fly ash geopolymer mortars is reduced justifying the insignificant difference in compressive strength. Hence, silica to alkali hydroxide is an important parameter for development of strength and also one of the factors to be considered for design of mix proportions. Further, keeping silica to alkali hydroxide ratio constant at 9, aggregate to Shirasu ratio is varied to examine the changes in compressive strength and to achieve optimum mix. By doing so, the paste volume in the mix varies. This means, a lower ratio increases the paste volume since the silica to alkali hydroxide ratio is kept constant. Fig. 10 shows, decrease in aggregate to Shirasu ratio increases the compressive strength. A ratio greater than 3 is thought to be a lean mix. Hence, the ratio around 3 is observed to have sufficient paste volume and aggregate volume.

4. Conclusions

Utilization of Shirasu as an aluminosilicate material in making geopolymer has been attempted successfully.

• Shirasu in geopolymer has given considerably good results when compared to conventional fly ash.

• The variations in ratio of alkaline activators to aluminosilicate show contrasting results between different geopolymers. These contrasting results are attributed to the effect of parameters like property of silica and alumina, and their content in Shirasu or fly ash, specific surface area of particles and also the balance between aluminosilicates and alkalinity.

• Silica and alumina in Shirasu particles may not be easily available for dissolution process with alkaline medium to form polymer even at high temperatures. Silica to alkali hydroxide balance in the mix has an effect on the compressive strength of the mortar. It can be considered as one of the important factors in formulations of mixes.

• Though strength of Shirasu geopolymer is lesser when compared to fly ash geopolymer, the peak compressive strength for silica to alkali hydroxide ratio of 9 matches with the strength of fly ash geopolymer.

• The initial hardening of Shirasu geopolymer is delayed up to 5 to 6 days of heat curing. This delay may be attributed to the lower dissolution process in the case of Shirasu because of possible impurities and oxide content over the years of deposition and less alumina content which further contributes to delays in gelation and polymerization process.

• Processing Shirasu to Blaine specific area greater than 4000 cm²/g and partial addition of slag are likely to increase the reactivity in polymerization and hence needs consideration for potential utilization.

References

- Bashir, S.U. (2015), "Effect of alkali materials on geo polymer concrete", *Int. J. Civil Eng. Tech.*, 6(1), 1-13. Chindaprasirt, P. and Chalee, W. (2014), "Effect of sodium hydroxide concentration on chloride penetration and steel corrosion of fly ash-based geopolymer concrete under marine site", *Constr. Build. Mater.*, 63, 303-310.
- Deb, P.S., Nath, P. and Sarker, P.K. (2014), "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.*, **62**, 32-39.
- Duxson, P., Fernández-Jiménez, A., Provis, J. L., Lukey, G.C., Palomo, A. and Van Deventer, J.S.J. (2007), "Geopolymer technology: the current state of the art", *J. Mater. Sci.*, **42**(9), 2917-2933.
- Ganesan, N., Indira, P.V. and Santhakumar, A. (2013), "Engineering properties of steel fibre reinforced geopolymer concrete", *Adv. Concr. Constr.*, **1**(4), 305-318.
- Habert, G. d'Espinose de Lacaillerie, J.B. and Roussel, N. (2011), "An environmental evaluation of geopolymer based concrete production: reviewing current research trends", J. Clean. Prod., 19(11), 1229-1238.
- Hanjitsuwan, S., Hunpratub, S., Thongbai, P., Maensiri, S., Sata, V. and Chindaprasirt, P. (2014), "Effects of NaOH concentrations on physical and electrical properties of high calcium fly ash geopolymer paste", *Cement Concr. Comp.*, 45, 9-14.
- Hardjito, D., Wallah, S.E., Sumajouw, D.M. and Rangan, B.V. (2004), "On the development of fly ash-based geopolymer concrete", *ACI Mater. J.*, **101**(6), 467-472.
- Joseph, B. and Mathew, G. (2012), "Influence of aggregate content on the behavior of fly ash based geopolymer concrete", *Scient. Iranica*, **19**(5), 1188-1194.
- Joshi, S.V. and Kadu, M.S. (2012), "Role of alkaline activator in development of eco-friendly fly ash based geo polymer concrete", *Int. J. Environ. Sci. Dvlp.*, **3**(5), 417-421.
- Katpady, D.N., Takewaka, K., Yamaguchi, T., Moritaka, Y. and Tatara, Y. (2012), "Experimental study on deterioration monitoring of shirasu concrete in hot spring environment", *Int. J. Earth Sci. Eng.*, 05(04), 1020-1026.
- Khatera, H.M. and Abd el Gawaad, H.A. (2015), "Characterization of alkali activated geopolymer mortar doped with MWCNT", *Adv. Mater. Res.*, **4**(1), 45-61.
- Kong, D.L.Y. and Sanjayan, J.G. (2010), "Effect of elevated temperatures on geopolymer paste, mortar and concrete", *Cement Concr. Res.*, **40**(2), 334-339.
- Lloyd, N.A. and Rangan, B.V. (2010), "Geopolymer concrete with fly ash", *Second International Conference on Sustainable Construction Materials and Technologies*, Università Politecnica delle Marche, Ancona, Italy.
- Motorwala, A., Shah, V., Kammula, R., Nannapaneni, P. and Raijiwala, D.B. (2013), "Alkali activated fly-ash based geopolymer concrete", *Int. J. Emerg. Tech. Adv.Eng.*, **3**(1), 159-166.

- Olivia, M. and Nikraz, H. (2012), "Properties of fly ash geopolymer concrete designed by Taguchi method", *Mater. Des.*, **36**, 191-198.
- Rattanasak, U. and Chindaprasirt, P. (2009), "Influence of NaOH solution on the synthesis of fly ash geopolymer", *Miner. Eng.*, 22(12), 1073-1078.
- Sanni, S.H. and Khadiranaikar, R.B. (2013), "Performance of alkaline solutions on grades of geopolymer concrete", Int. J. Res. Eng. Tech., IC-RICE Conference Issue, 366-371.
- Shah, K.C., Parikh, A.R. and Parmar, K.J. (2014), "Study of strength parameters and durability of fly ash based geopolymer concrete", *Paripex Indian J. Res.*, **3**(7), 207-210.
- Shaikh, F.U.A. (2014), "Effects of alkali solutions on corrosion durability of geopolymer concrete", *Adv. Concr. Const.*, **2**(2), 109-123.
- Takewaka, K. (2004), "State-of-art-report on characteristics of shirasu concrete and its practical use", *Concr. J.*, **42**(3), 38-47. (in Japanese)
- Takewaka, K. and Kawamata, K. (1991), "Durability of concrete using pyroclastic flow deposit for fine aggregates", *Proceedings of Second Canada/Japan Workshop*, Ottawa.
- Temuujin, J., van Riessen, A. and MacKenzie, K.J.D. (2010), "Preparation and characterisation of fly ash based geopolymer mortars", *Constr. Build. Mater.*, **24**(10), 1906-1910.
- Temuujin, J., van Riessen, A. and Williams, R. (2009), "Influence of calcium compounds on the mechanical properties of fly ash geopolymer pastes", *J. Hazard. Mater.*, **167**, 82-88.
- Turner, L.K. and Collins, F.G. (2013), "Carbon dioxide equivalent (CO₂-e) emissions: a comparison between geopolymer and OPC cement concrete", *Constr. Build. Mater.*, **43**, 125-130.