Development of slag based Shirasu geopolymer

Dhruva Narayana Katpady[*], Koji Takewaka and Toshinobu Yamaguchi

Department of Ocean Civil Engineering, Kagoshima University, 1-21-40, 8900065, Korimoto, Kagoshima, Japan

Abstract. Shirasu, a pyroclastic flow deposit, showed considerable performance as aluminosilicate source in geopolymer, based on past research. However, the polymerization reactivity was somewhat lower compared to the traditional fly ash based geopolymer even though the long-term strength was fairly good. The present study concentrates on the development of higher initial strength performance of Shirasu based geopolymer by utilizing ground granulated blast furnace slag as an admixture. Mortars with various mix proportions were adopted to study the effect of parametric changes on strength development along with the addition of slag in different percentages. A combination of sodium hydroxide and sodium silicate was used as alkaline activators considering parameters like molar ratios of alkali to geopolymer water and silica to alkali molar ratio. The mortars were cured at elevated temperatures under different curing conditions to analyze the effect on strength development. Compressive strength test, mercury intrusion porosimetry and X-ray powder diffraction were carried out to assess the strength performance and microstructure of slag-Shirasu based geopolymer. Based on the experimental study, it was observed that the initial and long-term strength development of Slag-Shirasu geopolymer were improved by the addition of slag.

Keywords: Shirasu; pyroclastic flow; geopolymer; alkali activation; polymerization; ground granulated blast furnace slag

1. Introduction

Geopolymer concrete has gained considerable attention as a sustainable concrete of the future. Vast research on geopolymer using industrial wastes or byproducts like fly ash, ground granulated blast furnace slag (here-in-after referred as "slag"), metakaolin and silica fume as aluminosilicates showed potential characteristics and beneficial applications of such materials. Among these notable materials, fly ash based geopolymer has been extensively studied and immense data on its performance and durability has been accumulated. Adding to this, fly ash geopolymer has been regarded as more strong and durable in general (Duxson *et al.* 2007). With regard to traditional geopolymers, a 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 a profound effect on the performance of geopolymer concrete (Hardjito *et al.* 2004). Therefore, if aluminosilicate (especially fly ash) is used as a sole binder, effective polymerization can be achieved only at elevated temperatures due to its lower reactivity at lower temperatures leading to increased amount of unreacted fly ash before final hardened structure is formed (Puertas *et al.* 2000, Bakharev 2005). Fly ash geopolymer showed higher compressive strength when heat cured than ambient cured (Li *et al.* 2013, Nguyen *et al.* 2013, Joshi and Kadu 2012) and addition of slag is required to obtain better strength under ambient curing conditions. Requirement of elevated temperatures for heat curing contributes to high cost in the 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.* (2010) also considered the addition of slag. Their study on combination of fly ash and slag proved that at room temperatures slag dominated the reaction forming C-S-H 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 forms are also confirmed in fly ash slag based geopolymers (Xu *et al.* 2014, Bernal *et al.* 2013) 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 an increase in slag content (Deb *et al.* 2014, Perna *et al.* 2016, Temuujin *et al.* 2009) stated that the calcium compounds are a factor for improved strengths for concretes cured at ambient temperatures.

1.1 Shirasu as a potential source for geopolymer

∗Corresponding author, Ph.D.
 E-mail: drunarkat@gmail.com

Table 1 Physical and chemical characteristics of binder materials used

| | Specific gravity | Blaine specific surface area (cm²/g) | Mass % | | | | | |
			SiO_2	CaO	Al_2O_3	SO_3	Fe_2O_3	MgO
Shirasu	2.48	4500	70.2	4.55	13.9	0.07	3.92	0.395
Fly ash	2.29	4614	65	5.03	19.2	0.73	5.73	1.12
GGBS	2.9	4189	30.7	44.1	14.1	1.68	0.4	7.39

Table 2 Mix proportion for geopolymer mortars (kg/m³)

| Mix No. | GPW/B (%) | G/B (%) | Na_2O/H_2O molar ratio | SiO_2/Na_2O molar ratio | Materials (kg/m³) | | | | |
| | | | | | Binder (B) | | | | |
					Water (GPW)	Shirasu (S)	Fly ash (F)	Slag (G)	Sand
S45G5		5				560	-	29	1206
S45G15	45	15	0.09		265	501	-	88	1215
S45G30		30				412	-	177	1228
S42G5		5				560	-	29	1258
S42G15	42	15	0.095		245	501	-	88	1267
S42G30		30				412	-	177	1281
S38G5		5				560	-	29	1311
S38G15	38	15	0.1	0.47	225	501	-	88	1320
S38G30		30				412	-	177	1334
F45G5		5				-	560	29	1156
F45G15	45	15	0.09		265	-	501	88	1170
F42G5		5				-	560	29	1209
F42G15	42	15	0.095		245	-	501	88	1223
F38G5		5				-	560	29	1262
F38G15	38	15	0.1		225	-	501	88	1276

Fig. 1 Particle size distribution of materials

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 based on density current and origin. The density of Shirasu available ranges from 2.1 to 2.7 g/cm³. Shirasu is sandy but porous material with a 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 performs well in hot conditions and is resistant to sulfate attacks (Takewaka and Kawamata 1991). Laboratory tests on Shirasu concrete by Katpaddy *et al.* (2012) proved that Shirasu concrete is highly resistant to chemical attacks and possess high capabilities in corrosion protection of reinforcement. 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
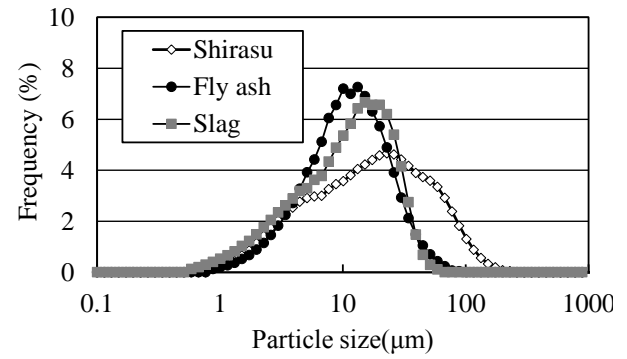
can be potentially used as aluminosilicate source in geopolymer. Studies on Shirasu as aluminosilicate has been tried with various mix proportions in the past. It was observed that Shirasu geopolymer showed lower reactivity and delayed strength development compared to that of fly ash. Shirasu geopolymer exhibited no strength gain at the first 24 hours to 48 hours of oven dry heat curing at 90°C and required continuous curing at elevated temperatures (in this case 90°C) up to 10-12 days to gain a compressive strength of around 20 MPa (Katpady *et al.* 2015). Many factors influence the strength gain of geopolymer concrete. In this case, fineness of Shirasu particles and its mineral composition is found to have an immense effect on the performance of Shirasu geopolymer. Milling of aluminosilicate particles has an effect on the dissolution. However, the effect is different for different aluminosilicate (Hajimohammadi and Van Deventer 2016). In this study, milled Shirasu is used as an aluminosilicate. 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% by mass against 22-25% in fly ashes generally used worldwide. It is a well-established fact that alumina is important for strength development of geopolymer by producing A-S-H in complex polymer structures. Moreover, difference in physical nature of Shirasu and fly ash particles may affect the reactivity. Therefore, to improve the initial strength development of Shirasu geopolymer, investigation on strength properties with the addition of slag is considered. The behavior of slag-Shirasu geopolymer is compared with that of geopolymer mortars prepared with slag-fly ash.

2. Experimental investigation

2.1 Materials

Two component binder mixes were adopted in the study. Shirasu and/or fly ash as primary binders with partial addition of slag were used. Milled Shirasu with Blaine specific surface area of 4500 cm²/g and specific gravity of 2.48 was used. Fly ash with Blaine specific surface area of 4614 cm²/g and specific gravity of 2.29 was also used for comparative study. Slag with a Blaine specific surface area of 4189 cm²/g was used as an additive. Table 1 shows the physical and chemical properties of materials used and Fig.
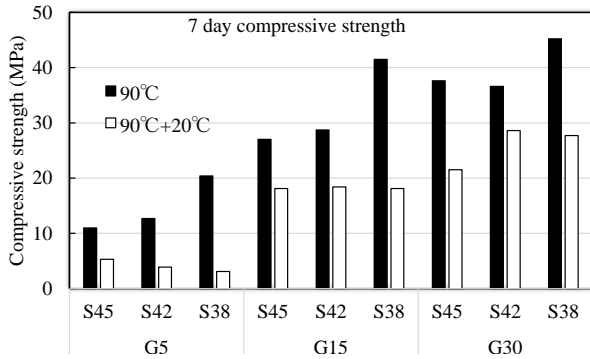
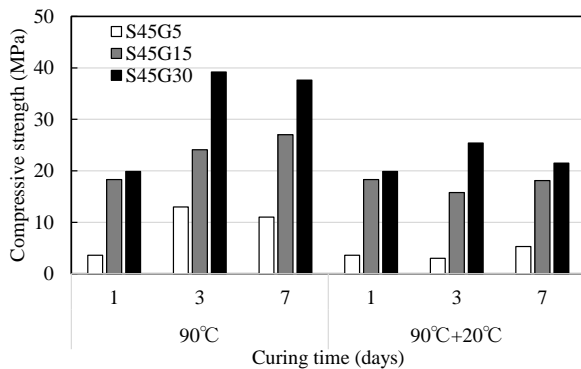Fig. 2 Compressive strength versus (GPW/B) and (Na$_2$O/H$_2$O) after 7 days of curing

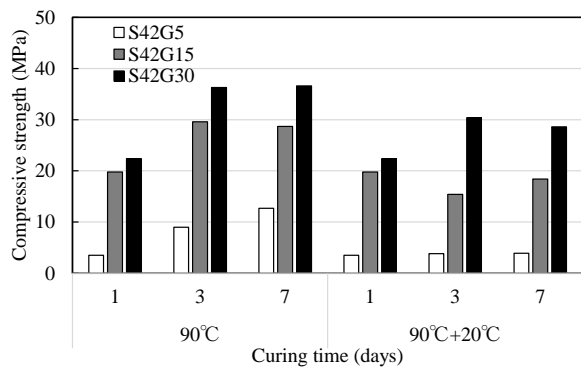Fig. 3 Effect of curing condition on compressive strength development of S45 geopolymer

Fig. 4 Effect of curing condition on compressive strength development of S42 geopolymer

1 shows particle size distribution of slag, Shirasu and fly ash used in the study by Laser Diffraction Particle Size Analyzer. River sand was used as fine aggregate having a specific gravity of 2.64. Alkaline activator solution was a combination of sodium hydroxide (pellets of 98% purity) and sodium silicate (55% assay, SiO$_2$/Na$_2$O=2.2).

2.2 Mix proportion

Mix proportions of geopolymer mortars were developed based on two important parameters. One is the geopolymer water to binder ratio (here-in-after referred as "GPW/B") set at 45%, 42% and 38% (GPW of 265, 245 and 225 kg/m^3 respectively). GPW includes water contained in sodium silicate solution and additional water in the system.

Therefore, an increase in GPW means an increase in water content (shown in Table 2) as the total amount of alkaline activators was kept constant. Another parameter considered was Na$_2$O/H$_2$O. Alkaline activator was prepared by mixing sodium silicate solution and sodium hydroxide pellets such as to obtain Na$_2$O/H$_2$O equal to 0.09, 0.095 and 0.1 and SiO$_2$/Na$_2$O constant at 0.47 for all mix. Partial addition of slag (represented as "G") in the place of total binder content (represented as "B") was set at 5%, 15% and 30%. The total binder content in both cases of Shirasu and fly ash geopolymers were constant with varying GPW/B and Na$_2$O/H$_2$O. Mix proportions employed in the study are shown in Table 2. Similar mix proportions were used for both Shirasu and fly ash for comparative study. Specimen referencing is done based on GPW/B and percentage replacement of slag. For instance, S45G30: S-Shirasu, GPW/B=45%, G-slag, slag replacement of 30%. GPW/B=45%, GPW/B=42% and GPW/B=38% also correspond to Na$_2$O/H$_2$O=0.09, Na$_2$O/H$_2$O=0.095 and Na$_2$O/H$_2$O=0.1, respectively.

2.3 Casting and curing methods

Initially, dry mixture of binders and aggregate was mixed for up to 1 minute. After dry mix, the alkaline activator was introduced and mixed for another 3 minutes. Fresh mortar was cast on to moulds of 5 cm in diameter and 10 cm in length and then vibrated for 30 seconds on a table vibrator. Cast moulds were wrapped with polyvinylidene chloride film over which aluminum tapes were wrapped to prevent water loss during heat curing. After the preparation, cast moulds were kept in the room temperature condition for 2 hours prior to heat curing. Two different curing conditions were employed. One set of specimens were subjected to oven dry heat curing at 90℃ throughout the test period and demoulded subsequently until predetermined curing period was achieved for the compressive strength test. This curing condition was employed to simulate hot spring environment condition where temperatures can go beyond 90℃. Another set of specimens were initially oven dry heat cured at 90℃ for 24 hours (1 day) and then subjected to ambient curing until predetermined exposure period.

2.4 Experimental tests

Compressive strength test was carried out for all specimens cured under different conditions at predetermined curing periods of 1 day, 3 days and 7 days. Mercury intrusion porosimetry was also done for specimens cured at 90℃ for 7 days. X-ray diffraction (XRD) analysis was done to study the microstructures.

3. Results and discussion

3.1 Effect of geopolymer water to binder ratio and Na$_2$O/H$_2$O on the compressive strength

The effect of GPW/B on compressive strength is shown in Fig. 2. The result shows the 7 days compressive strength

of slag-Shirasu geopolymer subjected to both types of curing conditions. The compressive strength was observed to increase with decrease in GPW/B in the mixture. It also shows that increase in Na_2O/H_2O increases the compressive strength. Higher alkali concentration increases the solubility of aluminosilicate and enhances strength (Guo *et al.* 2010, Hajimohammadi and Van Deventer 2016). Usually, minimal extra water is added in geopolymer mix proportion only to increase the workability of the fresh concrete, which is also seen in the study by Nguyen *et al.* (2013). Also, water acts as a medium for polymerization reaction and shall not participate in the chemical reaction (Duxson *et al.* 2007). Hence, water resides in the pores increasing the porosity. If the total water content is high, the voids or pores in the mortar increase resulting in strength reduction. This trend is also observed in the experimental investigation on the porosity of the mortars. Increase in water content increases the relative porosity. A compressive strength of about 45 MPa was achieved for geopolymer mortar with GPW/B=38% and slag addition of 30% (S38G30) subjected to continuous heat curing up to 7 days. Heat curing for 24 hours and further ambient curing up to 7 days also showed lower compressive strength with a maximum strength of about 28 Pa. Shirasu geopolymer with no slag addition showed a compressive strength of around 8-9 MPa for S42 and S38 when continuously cured at 90℃ up to 7 days (data not shown)

3.2 Effect of curing condition on compressive strength

Figs. 3, 4, and 5 show the effect of curing conditions on compressive strength of Shirasu geopolymer with slag addition. Continuous heat curing up to 7 days showed higher development of strength for all cases of geopolymer mortars with varying GPW/B and Na_2O/H_2O. The incremental increase in compressive strength with age was high. The strength development of mortars with initial heat curing for 24 hours and subsequent ambient curing was about 50% compared to continuous heat curing. The compressive strength increase with age was not found to be significant but kept constant. Geopolymer with Shirasu as aluminosilicate source showed low reactivity compared to that of fly ash geopolymer in previous experimental investigations. Strength development was not achieved at first 24 hours of heat curing even at 90℃. However, compressive strength of around 20 MPa was achieved with prolonged heat curing. In the present case, strength development after 24 hours of heat curing could be achieved with the addition of slag. Studies on metakaolin based geopolymer subjected to different curing profiles Heah *et al.* (2011) found that curing at ambient temperature was not feasible while increase in temperature from 40℃ to 100℃ favored the strength gain after 1 to 3 days. It was also observed that curing at higher temperature for a longer period of time caused failure of samples at a later age due to the thermolysis of -Si-O-Al-O- bond. In the previous studies on Shirasu based geopolymers, lower reactivity and lack of strength gain even after 3 days of continuous heat curing were confirmed. Similar performance of Kaolin-based geopolymer was reported by Heah *et al.* (2011). Several other studies on volcanic ash also confirmed low reactivity and strength gain due to lower content of
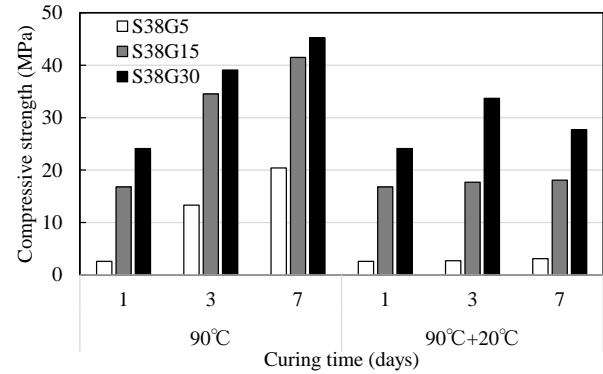

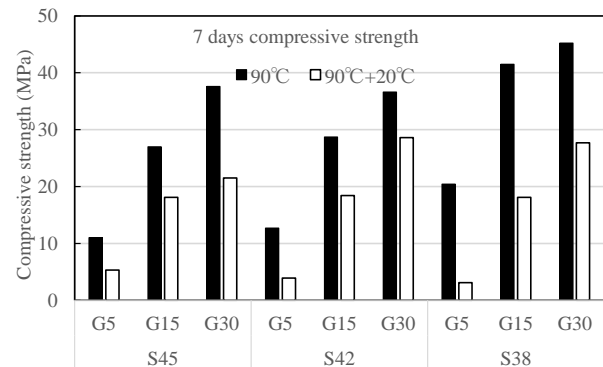Fig. 5 Effect of curing condition on compressive strength development of S38 geopolymer

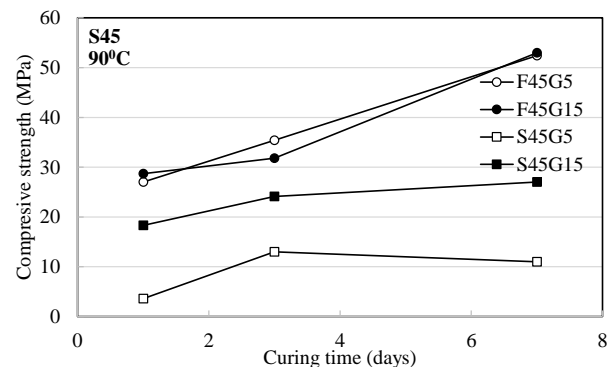Fig. 6 Effect of slag addition on compressive strength

Fig. 7 Comparison of compressive strength between Shirasu and fly ash geopolymer subjected to continuous heat curing at 90℃

amorphous alumina (Djobo *et al.* 2014, Tchakoute *et al.* 2013). Based on these facts, slag addition in Shirasu geopolymer was considered along with the heat treatment. From the results, heat curing even up to 7 days kept on increasing the compressive strength confirming continued reaction at later stages. Particularly, heat curing for 24 hours and then ambient curing showed no increase in strength with age. A study by Nath *et al.* (2014) showed no significant increase in strength of fly ash slag geopolymer if heat cured. These results show the slow and gradual increase of strength gain by Shirasu if heat cured for a longer time.

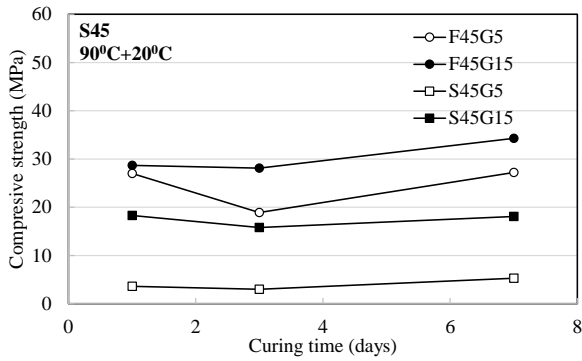### 3.3 Influence of slag addition on compressive strength

Fig. 8 Comparison of compressive strength between Shirasu and fly ash geopolymer subjected initial heat curing at 90℃ for 24 hours
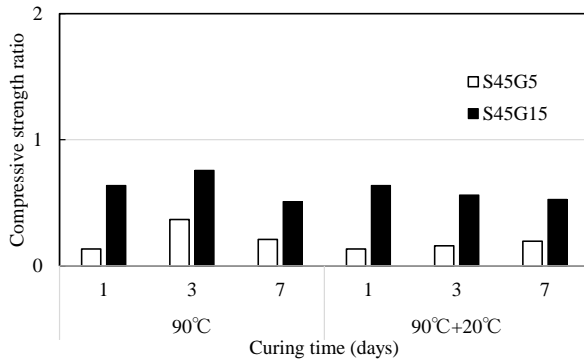

Fig. 9 Reactivity index for S45

Fig. 10 Reactivity index for S42

Fig. 11 Reactivity index for S38

Fig. 12 Pore size distribution for all slag-Shirasu geopolmers subjected to continuous heat curing for 7 days

The effect of slag addition on compressive strength development of mortars subjected to both curing conditions is shown in Fig. 6. The increase in compressive strength with increase in slag addition was confirmed for both conditions of curing regardless of the GPW/B and Na_2O/H_2O in the mix and curing profile which is in line with other research (Ushaa *et al.* 2015), Kumar *et al.* 2010, Nath *et al.* 2014, Puertas *et al.* 2000, Gao *et al.* 2015, Kürklü 2016). Especially the higher incremental increase in compressive strength is seen clearly between 5% and 15% of slag addition in all mortars. Alkali activation of slag along with aluminosilicates elevates the strength development by combining effect of coexisting gel products (Xu *et al.* 2014, Bernal *et al.* 2013). Previous studies by Katpady *et al.* (2015) on Shirasu based geopolymer confirmed the slow reactivity and lower strength development. Also, it was concluded that even with continuous heat curing at high temperatures, Shirasu geopolymer mortars begin hardening only after 3-5 days. With this knowledge, slag addition on Shirasu geopolymer clearly has an effect on the initial strength development. The compressive strength results from Figs. 2-6 show that slag addition helps in initial strength gain and prolonged curing at elevated temperatures favors dissolution of Shirasu which further increases the strength.

3.4 Compressive strength comparison between Shirasu and fly ash geopolymer

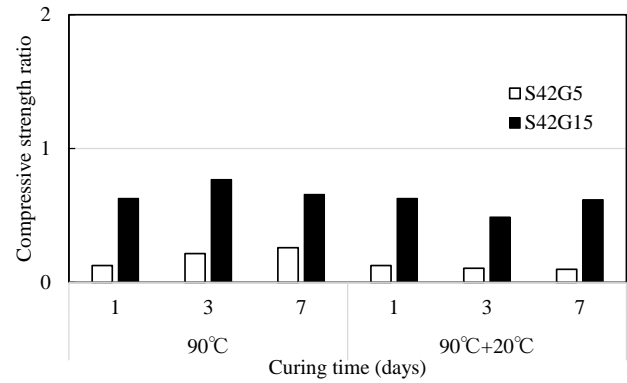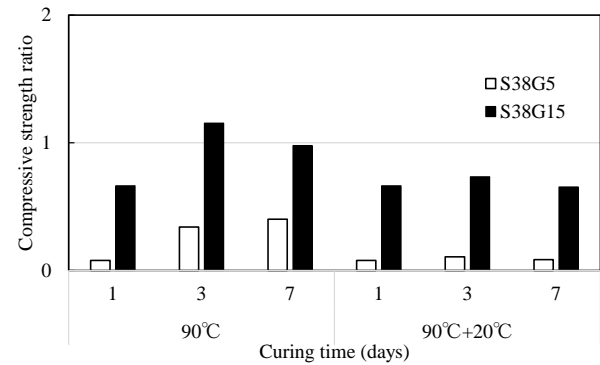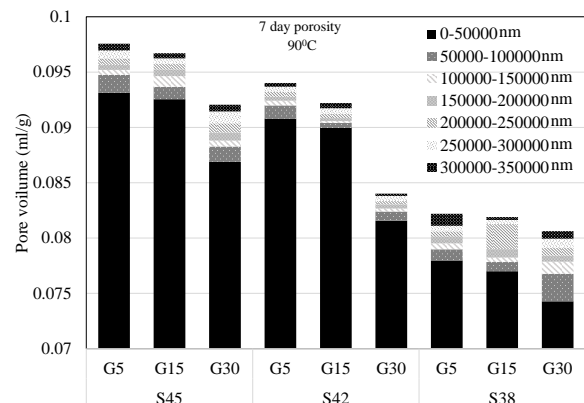A comparative study on compressive strength of slag-Shirasu and slag-fly ash based geopolymer mortar of

GPW/B=45% and Na_2O/H_2O=0.1, heat cured at 90℃ up to 7 days and 90℃ for 24 hours are shown in Figs. 7 and 8 respectively. The compressive strength of fly ash geopolymer mortar was higher compared to Shirasu geopolymer. One of the reasons for the higher strength of fly ash over Shirasu is the alumina content of the pozzolans. Shirasu is less in alumina content than fly ash. Also, physical nature of particles may affect strength development. Shirasu is irregular and porous, whereas fly ash is smooth and spherical. All these factors contribute to lesser reactivity and strength gain for Shirasu geopolymer. High difference in compressive strength between Shirasu and fly ash geopolymer was seen for low percentage of slag addition. Increase in slag addition reduced the difference in compressive strength. This confirms the effect of slag
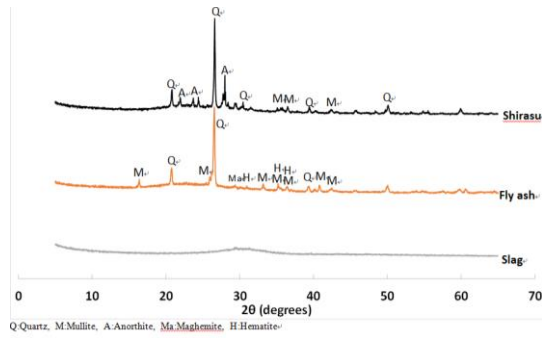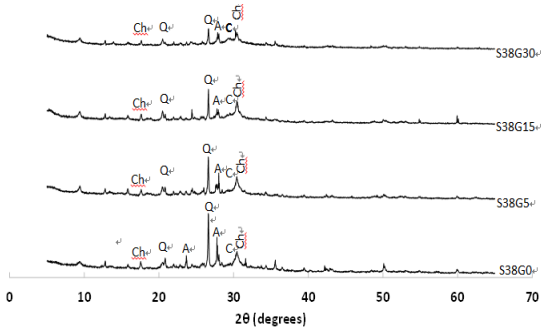
Fig. 13 XRD patterns of geopolymer precursors

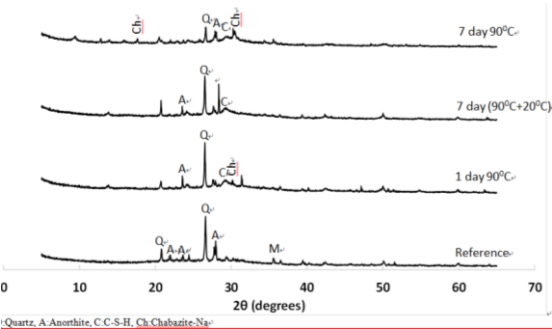Fig. 14 XRD patterns of S38 geopolymer cured at 90℃ up to 7 days

Fig. 15 XRD pattern of S38G30 under different curing conditions

addition. For a clear understanding of the effect of slag addition, ratio of the compressive strength of slag-Shirasu to slag-fly ash based geopolymer mortar (reactivity index of Shirasu geopolymer) for different GPW/B are shown in Figs. 9, 10 and 11. The index is lower in the case of 5% slag addition. However, for 15% slag addition the index increases drastically. As the GPW/B decreases the index increases clearly. But, increasing slag addition to 15% significantly increased the strength of Shirasu geopolymer. Especially for GPW/B=38% cured continuously at 90℃, the reactivity index is close to 1 for higher slag addition. These results show that, prolonged heat curing triggers the reaction of Shirasu.

3.5 Pore distribution

The pore distribution of slag-Shirasu geopolymer mortars are shown in Fig. 12. It was observed that there is a typical trend of pore distribution dependent on the GPW/B

in the mixture and also on the percentage addition of slag. As GPW/B increases there was an increase in internal pore volume. Conversely, decrease in Na_2O/H_2O increases porosity. Also, as the percentage addition of slag increases, there is a clear reduction in pore volume. With the combination of reduction in total water content and increase in slag addition, pores of size less than $50\mu m$ and total pore volume decrease. The results of pore distribution also relate to the compressive strength test results, where reduction in GPW/B and increase in both Na_2O/H_2O and slag addition increased compressive strength due to reduction in total pore volume.

3.6 X-ray powder diffraction

Fig. 13 shows XRD patterns of precursor materials (Shirasu, fly ash and slag) used in the study. Shirasu, as discussed earlier contains a large amount of volcanic glass. XRD pattern of Shirasu shows the presence of peaks corresponding to Quartz ($2SiO_2$), Anorthite ($CaO.Al_2O_3.2SiO_2$) and Mullite. Fly ash mainly exhibits peaks corresponding to quartz, mullite, Maghemite, Haematite. GGBS has a smooth curve almost showing no major peaks, but a broad diffuse halo somewhere between 25 and $35(2\theta^0)$. Fig. 14 shows XRD pattern of slag-Shirasu geopolymer with different percentages of slag, cured up to 7 days under constant oven dry heat curing at 90℃. The peaks of quartz and anorthite from Shirasu were found to be decreasing with the addition of slag. The increase in slag shows a decrease in intensity of crystalline phases similar to that observed by Kumar *et al*. (2010). Some new peaks are formed around $29\text{-}31(2\theta^0)$ corresponding to C-S-H and Chabazite-Na. Similar observations on the formation of C-S-H with slag addition were made in other research (Lee *et al*. 2016, Gao *et al*. 2015, and Bernal *et al*. 2013). It is also known that aluminosilicate gel and C-S-H coexist in certain conditions and in the presence of sufficient calcium in the system (Oh *et al*. 2012). Since the sodium hydroxide dosage is high in the present study, formation of C-S-H may be hindered as the amount of slag increases. This may result in higher calcium content leading to the formation of calcium hydroxide crystals (Yip *et al*. 2005). Hence the presence of carbonates due to carbonation of calcium hydroxide or C-S-H is difficult to infer. Since samples were oven dry heat cured, possibility of $CaCO_3$ formation is less. Fig. 15 shows XRD patterns of geopolymer (S38) cured at different conditions. Chabazite-Na peak is not clearly observed. This can be a reason for lowered compressive strength. Geopolymers subjected to 90℃ either for 24 hours or continuously up to 7 days show characteristic peaks of C-S-H and Chabazite-Na. Coexistence of C-S-H and N-A-S-H/zeolites systems contributing to strength has been discussed by previous studies (Xu *et al*. 2014, Moon *et al*. 2014, Yip *et al*. 2005). And in the present study, longer duration of heat curing showed the co-existence of C-S-H and Chabazite-Na. Hence it can be concluded that Shirasu requires prolonged heat curing for geopolymerization.

4. Conclusions

An attempt was made in this particular study to improve the reactivity and strength development of Shirasu geopolymer by the addition of ground granulated blast furnace slag and varying other parameters involving mix proportions and curing conditions. Based on the experimental results following conclusions are drawn:

1. Increase in ratio of geopolymer liquid to binder ratio (increase in total water content) showed decrease in compressive strength. Also, the total pore volume increased with increase in the ratio.

2. The strength of slag-Shirasu geopolymer increased with increase in Na_2O/H_2O molar ratio.

3. Compressive strength increase was observed as the percentage addition of slag increased. Addition of slag also increased the reactivity of Shirasu, confirming development of strength after 24 hours of heat curing. The porosity of geopolymer mortars reduced with an increase in slag addition.

4. A significant difference in strength was observed with different curing methods. Continuous heat curing for longer durations increased the compressive strength. Ambient curing after 24 hours of heat curing did not show much increase in compressive strength.

5. The comparative study on strength development between Shirasu and fly ash based geopolymer showed that fly ash has higher reactivity than Shirasu. Lower percentage of alumina content and particle nature of Shirasu is thought to decrease its reactivity. However, higher percentage of slag addition and lower geopolymer water to binder ratio in Shirasu geopolymer decreased the difference in strength between Shirasu and fly ash based geopolymer. Moreover, longer duration of heat curing for Shirasu geopolymer is necessary to achieve higher strengths similar to fly ash.

References

Bakharev, T. (2005), "Geopolymeric materials prepared using class F fly ash and elevated temperature curing", *Cement Concrete Res.*, **35**(6), 1224-1232.

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. (2013), "Gel nanostructure in alkali-activated binders based on slag and fly ash, and effects of accelerated carbonation", *Cement Concrete Res.*, **53**, 127-144.

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.

Djobo, J.N.Y., Tchadjié, L.N., Tchakoute, H.K., Kennea, B.B.D., Elimbi, A. and Njopwouo, D. (2014), "Synthesis of geopolymer composites from a mixture of volcanic scoria and metakaolin", *J. Asian Ceram. Soc.*, **2**(4), 387-398.

Duxson, P., Fernandez-Jimenez, 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.

Gao, X., Yu, Q.L. and Brouwers, H.J.H. (2015), "Properties of alkali activated slag-fly ash blends with limestone addition", *Cement Concrete Compos.*, **59**, 119-128.

Guo, X., Shi, H. and Dick, W.A. (2010), "Compressive strength and microstructural characteristics of class C fly ash geopolymer", *Cement Concrete Compos.*, **32**(2), 142-147.

Hajimohammadi, A. and Van Deventer, J.S.J. (2016), "Dissolution behaviour of source materials for synthesis of geopolymer binders: A kinetic approach", *J. Min. Proc.*, **153**, 80-86.

Hardjito, D., Wallah, S.E., Sumajouw, D.M.J. and Rangan, B.V. (2004), "On the development of fly ash-based geopolymer concrete", *ACI Mater. J.*, **101**(6), 467-472.

Heah, C.Y., Kamarudin, H., Mustafa Al Bakri, A.M., Binhussain, M., Luqman, M., Nizar, I.K., Ruzaidi, C.M. and Liew, Y.M. (2011), "Effect of curing profile on kaolin-based geopolymers", *Phys. Proc.*, **22**, 305-311.

Joshi, S.V. and Kadu, M.S. (2012), "Role of alkaline activator in development of eco-friendly fly ash based geo polymer concrete", *J. Environ. Sci. Develop.*, **3**(5), 417-421.

Katpady, D.N., Takewaka, K. and Yamaguchi, T. (2015), "Development of geopolymer with pyroclastic flow deposit called shirasu", *Adv. Mater. Res.*, **4**(3), 179-192.

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", *J. Earth Sci. Eng.*, **5**(4), 1020-1026.

Kumar, S., Kumar, R. and Mehrotra, S.P. (2010), "Influence of granulated blast furnace slag on the reaction, structure and properties of fly ash based geopolymer", *J. Mater. Sci.*, **45**(3), 607-615.

Kürklü, G. (2016), "The effect of high temperature on the design of blast furnace slag and coarse fly ash-based geopolymer mortar", *Compos. Part B*, **92**, 9-18.

Lee, N.K., An, G.H., Koh, K.T. and Ryu, G.S. (2016), "Improved reactivity of fly ash-slag geopolymer by the addition of silica fume", *Adv. Mater. Sci. Eng.*, **6**, 1-11.

Li, X., Wang, Z. and Jiao, Z. (2013), "Influence of curing on the strength development of calcium-containing geopolymer mortar", *Mater.*, **6**(11), 5069-5076.

Moon, J., Bae, S., Celik, K., Yoon, S., Kim K.H., Kim, K.S. and Monteiro, P.J.M. (2014), "Characterization of natural pozzolan-based geopolymeric binders", *Cement Concrete Compos.*, **53**, 97-104.

Nath, P. and Sarker, P.K. (2014), "Effect of GGBFS on setting, workability and early strength properties of fly ash geopolymer concrete cured in ambient condition", *Constr. Build. Mater.*, **66**, 163-171.

Nguyen, K.T., Lee, Y.H., Lee, J. and Ahn, N. (2013), "Acid resistance and curing properties for green fly ash-geopolymer concrete", *J. Asian Architect. Build. Eng.*, **12**(2), 317-322.

Oh, J.E., Moon, J., Oh, S.G., Clark, S.M.P. and Monteiro, J.M. (2012), "Microstructural and compositional change of NaOH-activated high calcium fly ash by incorporating Na-aluminate and co-existence of geopolymeric gel and C-S-H(I)", *Cement Concrete Res.*, **42**(5), 673-685.

Perna, I. and Hanzlícek, T. (2016), "The setting time of a clay-slag geopolymer matrix: The influence of blast-furnace-slag addition and the mixing method", *J. Clean. Prod.*, **112**, 1150-1155.

Puertas, F., MartõÂ nez-RamõÂ rez, S., Alonso, S. and VaÂ zquez, T. (2000), "Alkali-activated fly ash/slag cement, strength behaviour and hydration products", *Cement Concrete Res.*, **30**(10), 1625-1632.

Takewaka, K. (2004), "State-of-art-report on characteristics of shirasu concrete and its practical use", *Concrete J.*, **42**(3), 38-47.

Takewaka, K. and Kawamata, K. (1991), "Durability of concrete using pyroclastic flow deposit for fine aggregates", *Proceedings of the 2nd Canada/Japan Workshop*, Ottawa, Canada.

Tchakoute, H.K., Elimbi, A., Yanne, E. and Djangang, C.N. (2013), "Utilization of volcanic ashes for the production of geopolymers cured at ambient temperature", *Cement Concrete Compos.*, **38**, 75-81.

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**(1), 82-88.

Ushaa, T.G., Anuradha, R. and Venkatasubramani, G.S.W. (2015), "Performance of self-compacting geopolymer concrete containing different mineral admixtures", *Ind. J. Eng. Mater. Sci.*, **22**, 473-481.

Xu, H., Gong, W., Syltebo, L., Izzo, K., Lutze, W. and Pegg, I.L. (2014), "Effect of blast furnace slag grades on fly ash based geopolymer waste forms", *Fuel*, **133**, 332-340.

Yip, C.K., Lukey, G.C. and Van Deventer, J.S.J. (2005), "The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation", *Cement Concrete Res.*, **35**(9), 1688-1697.

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