

Effect of Water Content on the Development of Fly Ash-based Geopolymers in Heat and Ambient Curing Conditions

Jiting Xie^{1,*}, Obada Kayali¹

¹*School of Engineering and Information Technology, University of New South Wales
Canberra, Australia*

**the Australian Defence Force Academy, Northcott Drive, Canberra ACT 2600, Australia
Email: <Jiting.Xie@student.adfa.edu.au>, <O.Kayali@adfa.edu.au>*

ABSTRACT

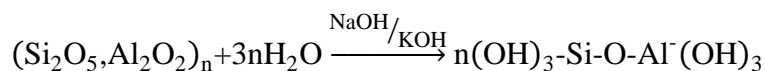
This paper presents a study of the role of water content in the development of heat cured and of controlled ambient-cured fly ash-based geopolymers. Compressive strength and SEM test were performed. It was concluded that lower initial water content would result in higher strength in both curing conditions. It was however found, that in the case of ambient curing, lower water content results in increased rate of strength gain. However, in the case of heat curing, the lower water content, although resulted in higher strength and denser microstructure, it did not significantly increase the rate of strength gain. Thus, ambient-cured geopolymer coupled with lower water content can achieve comparable strength and adequate structural performance as the short-term heat-cured geopolymer.

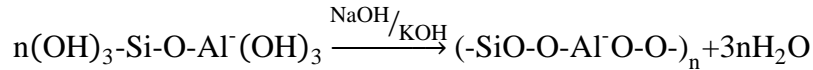
Keywords. Fly ash; Geopolymer; Water; Curing; Strength

1. INTRODUCTION

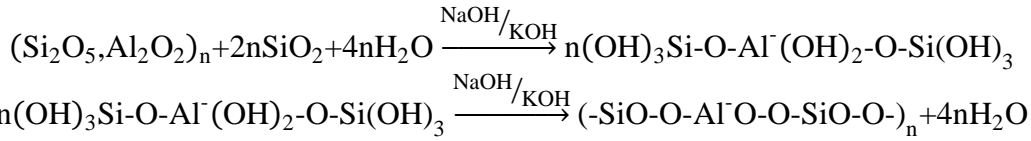
‘Geopolymer’ is a given name to describe a new class of synthetic materials that has been researched and applied mainly in recent decades. According to the newest definition by the Geopolymer Institute, geopolymer refers to the ambient X-ray amorphous materials that are composed of mineral molecule chains or 3-D networks linked with covalent bonds (G. I., 2012). In this paper, the aluminosilicate-based type of geopolymer that is dominantly composed of SiO₄ and AlO₄ tetrahedra are chosen as the basis of this research. The empirical formula given for this type of geopolymers is M_n-(SiO₂)_z-AlO₂)_n·H₂O, where n is the degree of polycondensation; M is the monovalent cation like K⁺ or Na⁺; z is the ratio of Si/Al and can be 1, 2 or 3. This geopolymer can be synthesized from fly ash and alkali activating solution. The basic principles on the synthetical reactions and hardening process have been concluded into two series as below (Davidovits, 1989):

Series 1:





Series 2:



Under the strong alkali attack, the silicon and aluminum oxides from the raw fly ashes are dissolved and form into the aluminosilicate ions shown in the first equation of each series above. At this moment, the mixtures appear to be a gel or dough-like phase due to the relative less water content inside. Then, these aluminosilicate ions accumulate and form into the polycondensed products and water as shown in the second equations. These polycondensed products could precipitate from the original gel or dough-like phase and turn into the hardened 3-D molecule networks, which provides the required strength and durability for geopolymer products (Davidovits, 2008).

The aluminosilicate-based geopolymer has been recommended as a new construction material performing similarly to cement in concrete. More advanced properties derived from geopolymers, such as higher early strength, better thermal and chemical resistance, much less CO₂ emission and more efficient consumption of fly ash wastes, provide a possibility to replace the traditional Portland cement in future sustainable concrete production (Davidovits, 2008, Duxson et al., 2007, Palomo et al., 1999, Rangan et al., 2005). To achieve this, more research is still needed to further understand the principles of geopolymer reactions. Several investigations into ingredients composition and curing conditions have been done. It can be generally concluded that the strength development of geopolymer products can be improved by increasing the reactivity of fly ash, the concentration of alkali activator, and the curing temperature and period (Duxson et al., 2007, Rangan, 2007, Khale and Chaudhary, 2007, Kumar and Kumar, 2010).

However, investigation into the role of water in producing geopolymers has been relatively rare. It has been known that water content in a geopolymer mixture determines the initial workability while mixing, which can affect the relative properties of final products (Provis et al., 2009, Rangan, 2007). Water can exist inside the final products as free or bound water, and have an influence on the strength and microstructure (Lizcano et al., 2012, Zuhua et al., 2009). According to reaction models previously proposed, water acts as the medium and participates in the geopolymer reactions (Davidovits, 1989, Provis et al., 2005). Research on the kinetics indicates that water content is critical to geopolymer reactions (Provis and van Deventer, 2007). Through the measurement of heat evolution, it is also proposed that water may have different effects on the different reaction stages (Zuhua et al., 2009). This implies that water may be able to affect the progress of geopolymer reactions in ways that can possibly be as important as those attributed to the activators. To investigate this possibility, the geopolymer syntheses with different water contents, specified at different stages like either initial design or curing process, were compared. In this paper, mixture designs that express applied water differences are illustrated. In addition to the traditional heat curing process, three types of ambient curing were investigated. These were applied in order to investigate the effect of changes in water content as induced by curing condition. Since heat is regarded as more like an acceleration process rather than a necessity (Rovnaník, 2010, Davidovits, 2008), removing of heat treatment may be a possibility that could reduce cost and improve practical usage of geopolymer concrete. In this paper, evaluation of the water

role is done by observing the relative characteristics of strength and microstructural development under different conditions.

2. EXPERIMENTAL DETAILS

2.1 Materials

Geopolymer pastes made with fly ash and alkali solutions were investigated here. ASTM Class F (low-calcium) fly ash whose chemical composition is listed in Table 1, was obtained from Eraring thermal power station and was chosen as the solid base. The crystalline and amorphous phases of this fly ash have been characterized to be 83.2% glass, 11.8% mullite and 5% quartz. The large content of amorphous phase can lead to good geopolymerisation reactivity (Fang and Kayali, 2012). For the liquid base, NaOH flakes (>98% purity), Grade D Na_2SiO_3 solution with the weight ratio of $\text{SiO}_2/\text{Na}_2\text{O}=2$ (29.4% SiO_2 , 14.7% Na_2O), and deionized water were used. The physical specific gravity of the applied ingredients, including both the fly ash and the liquids, are listed in Table 2.

Table 1 Chemical Composition in Percentage of Fly Ash by XRF Analysis

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	Na ₂ O	K ₂ O	SrO	TiO ₂	P ₂ O ₅	Mn ₂ O ₃
3.20	59.60	29.10	3.30	0.20	0.40	0.28	0.48	0.10	1.10	0.70	< 0.10

Table 2 Specific Gravity of Applied Ingredients

	Fly Ash	NaOH flakes	D Na ₂ SiO ₃	Water
Specific Gravity	2.21	2.13	1.52	1.00

2.2 Mix Designs

Fly ash is applied directly without further modification, so the mix design was mainly decided by the activator composition. The activator composition is expressed as $\text{Na}_2\text{O} \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ to emphasize the molar proportion of water and other solutes inside, which has been applied by Provis *et al.* before. Variation in the design of the activators can be made by mixing different amounts of NaOH flakes, Na_2SiO_3 solution and deionized water based on known or assumed values of x and y. The ' Na_2O ' that appears in the formula above, comes from both the NaOH flakes and Na_2SiO_3 solution, so the value of x is from 0 (no Na_2SiO_3) to about 2 (no NaOH). Following the optimum range proposed by Provis *et al.*, $x=1.25$ was applied here (Provis *et al.*, 2009). The values of y taken as y=11, 12 and 13 were set to result in different water content in the activator.

To control the diversity of water content of each design as required by this research, the parameter 'Water-to-Geopolymer Solids Mass Ratio' (W/G) proposed by Rangan is also introduced. The 'Water' refers to the mass of water in the fly ash and the activator solutions, and the 'Geopolymer Solids' term refers to the total mass of the materials in solid phase when mixing and the solid part in the liquids (the solutes), that is; the mass of fly ash, Na_2O and SiO_2 (Rangan, 2007). In this research, the mass ratio of fly ash to activator solutes in the 'Geopolymer Solids' was made constant for each mix design. Then, the variation in the y values could cause variation in the (W/G) values, leading to different water content between the various mix designs. With known (W/G) values, the relevant 'Fly Ash-to-Activator Mass

Ratio' (F/A) that commonly applied for geopolymer practical mix would be obtained step by step (Rangan, 2007). The calculated results of the three mix designs are listed in Table 3. The calculations with the generalized equations relating to the values of y, (W/G) and (F/A) will be presented in another paper by the authors.

Table 3 Mix Designs for Geopolymer Synthesis with Different Water Content

No.	x	y	W/G	F/A	Liquid			
					Fly Ash	NaOH flakes	D Silicates Solution	Water
(kg/m ³)								
1	1.25	11	0.22	2.28	1324.00	54.88	442.67	83.77
2		12	0.24	2.16	1283.77	53.22	429.24	111.54
3		13	0.26	2.06	1246.01	51.62	416.59	137.65

2.3 Specimen Preparation

Initially, the activator was prepared through a two-step method. At first, the NaOH solution with required concentration was prepared by mixing the NaOH flakes and deionized water. The mixed solution was placed without disturbance for at least one day to cool down and become uniformly homogeneous. The NaOH solution was cover sealed to prevent the reaction with CO₂ from the atmosphere. The final phase of the activator preparation was done by adding Na₂SiO₃ solution into the prepared NaOH solution just before the geopolymer synthesis. The activator was then stirred manually for 3-5 minutes and kept still for further 5 minutes to become uniform.

After the materials preparation, the activator was poured onto the dry fly ash and mixed using a Hobart Mixer for 5 minutes. The mixture displayed a uniform phase with certain viscosity which resembled that of a slurry or plasticine depending on the different water contents. Then the mixture was cast into the 50*50*50mm plastic cubic moulds with 10 seconds to 1 minute vibration on a vibration table. The vibration stopped when the surface was level and no significant bubbles appeared. The moulds were sealed with a lid to prevent water evaporation. The samples were stored in the environmental control room (ER) at 20°C and 50% relative humidity, for 6 hours as the resting time. This was followed by certain prescribed curing regime designated for the specific mixes. Following the end of the specified curing, the samples were returned to the ER until further tests were performed.

Both heat curing and controlled ambient curing procedures were administered. For heat curing process, 60°C was used as recommended by previous research work (Rangan, 2007). Sealed moulds were heated for 4 or 24 hours to investigate the development of the geopolymer. After that, the samples were demoulded and kept in the ER. Tests began at 7 days after casting which is the common practice for geopolymer synthesis.

Controlled ambient curing procedure was investigated to explore the possibility of a method more economical than heat curing. This procedure was done as follows: After resting time, sealed moulds were kept in the ER and demoulded after hardening. All specimens were demoulded after 5 days of casting to guarantee that every specimen was hardened enough. After demoulding, the specimens were left in a sealed condition until the age of 7 days since casting. After that, the samples were either tested or cured in the ER for further 7 days under different conditions, namely; (1) unsealed (2) Sealed or (3) desiccated inside a vacuum desiccator. The sealed curing aimed to retain the water during the 7-14 days after casting,

while the desiccated curing aimed to accelerate the water release. These three methods are coded as group A, AS and AD.

The curing regimes applied in this investigation are summarised in Table 4 and 5.

Table 4 Heat Curing Procedures on Synthesized Geopolymers

Mix No.	Resting Time (hours)	Heating Temp. (°C)	Heating Time (hours)	Age at Test (days)
1	6	60	4	7
			24	
2			4	
			24	
3			4	
			24	

Table 5 Controlled Ambient Curing Procedures on Synthesized Geopolymers

Mix No.	Resting Time (hours)	Demoulding Time (days)	Unsealed (A)	Sealed (AS)	Desiccated (AD)	Age at Test (days)
1	6	5	Yes	-	-	7
2			Yes	-	-	7
3			Yes	-	-	7
1			Yes	-	-	14
2			Yes	-	-	14
3			Yes	-	-	14
1			-	Yes	-	14
1			-	-	Yes	14
1			-	-	-	Yes

2.4 Testing

The testing reported in this paper mainly concentrates on the strength and microstructural development of different geopolymer samples. Compressive strength testing was done on a TECNOTEST compressive machine (3000 kN capacity) at the speed of 0.33MPa/s. Each condition was represented by three specimens. The measurements were taken for each specimen and the average for the three was then determined. The microstructure was inspected using a HITACHI TM 3000 tabletop scanning electron microscope (SEM). The SEM testing was done immediately following the strength test.

3. RESULTS AND DISCUSSION

3.1 Heat Curing

According to the traditional synthetic method for fly ash-based geopolymers, mild-temperature heat curing is always used where the operated temperature and time are between 50-90°C and 6-48h, respectively (Provis et al., 2009, Rangan, 2007, Palomo et al., 1999). Such heat would accelerate the whole geopolymer reaction process, and lead to relatively more generated geopolymers within a short time, and subsequently better properties like higher strength and more stable structure (Rovnaník, 2010, Davidovits, 2008). For this reason, mild-temperature heat curing can be applied to increase the difference in short term

among various geopolymer syntheses. In this paper, the geopolymer mixes that were destined for heat curing were subjected to a temperature of 60°C for either 4 or 24 hours. These mixes possessed different initial water content so as to investigate the effect of such difference on the heat cured samples.

The 7-day compressive strength of the geopolymer samples with different W/G values has been determined, and the results are shown in Figure 1(a). The compressive strength values for the 24 hour cured samples were larger than those for the 4 hours cured. Both the 4-hour and 24-hour cured samples behaved in the trend that the lower the value of W/G, the higher the compressive strength obtained. This corresponded well with the previous research on the effect of initial mix designs for geopolymer concretes (Rangan, 2007). However, there was no significant difference to be observed between the slopes of the three lines, indicating that the water content might have little obvious effect on the rate of strength development under heat curing conditions.

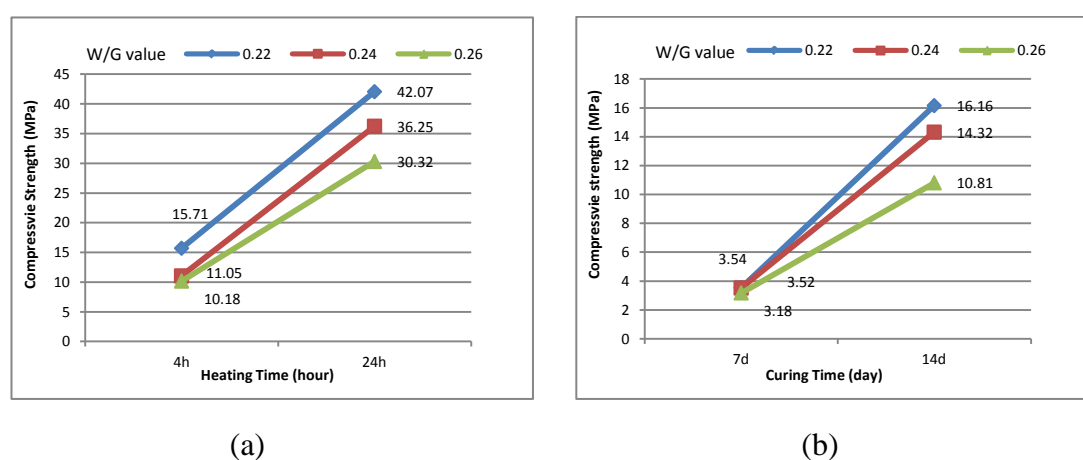


Figure 1. 7-Day Compressive Strength of 4-hour & 24-hour Heat-cured Geopolymers (a), and 7 & 14-Day Compressive Strength of Controlled Ambient-cured Geopolymers (b) with Different W/G Values

3.2 Ambient Curing

Controlled ambient ER curing process (at 20°C and 50% RH) was applied in contrast with the traditional heat curing process. It aimed to eliminate the exterior heat application during the synthesis of geopolymers. Thus, cost would obviously be reduced and the manufacture would be simplified. However, the rate of strength and microstructural development may be significantly delayed without heat application. To deal with this situation, modification may focus on the mix design and curing process. Two possibilities of difference in water content will be discussed here. The first is the different water content specifically actioned through the mix design. The second would be occurring as a result of changes in water content after initial hardening and caused by either gain or loss of water depending upon the curing conditions.

The ambient-cured geopolymer group A (which was unsealed) with different W/G values was synthesized first. The 7 and 14 day compressive strength of the ambient-cured geopolymer samples are presented in Figure 1(b). From this Figure, we can see a similar

trend in strength development under different curing time, to that shown in Figure 1(a). After 7 days, the compressive strength values of the samples were low and there was very little difference between the three mixes. While after 14 days, the strength values increased and were significantly different for the three different mixes. In this case, however, the slope values of the three lines representing the three mixes are significantly different. Hence, the rate of strength gain of the samples with less water content was faster than the rate of the samples with higher water content. Moreover, the 14 day compressive strength values were even comparable with the 4-hour heat-cured samples shown in Figure 1(a). Thus it could be concluded that the long curing time and lower water content have resulted in similar effect on strength development as the effect of heat application.

As shown in Figure 1(b) and discussed in the previous paragraph, the initial water content has had a significant effect on the final strength of ambient cured geopolymers. As introduced earlier, two further curing regimes were applied in order to investigate the effect of influencing water content during curing, on the final strength value. To further explore this effect, the water content of the initial design was kept constant at 0.22. The mixing, moulding and demoulding procedures remained the same for all the mixes. However, the curing condition after 7 days was changed. The three curing regimes defined earlier as A, AS and AD were applied. The compressive strength results after 14 days are presented in Figure 2.

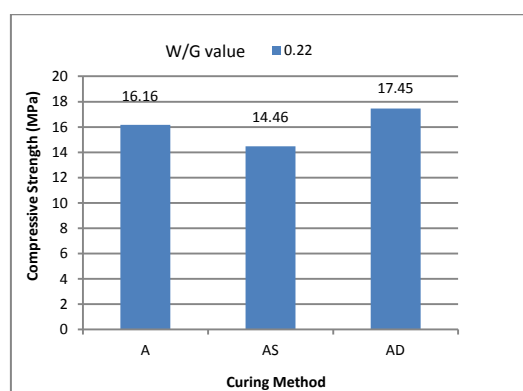


Figure 2. Compressive Strength of 14 Days Ambient-cured Geopolymers Coded as A, AS and AD with W/G=0.22

In Figure 2, the order of the compressive strength was: AD>A>AS, indicating that the desiccation method could enhance the strength development but the surface-seal would decrease the strength. In the AS samples, the surface seal prevented the water from evaporating. From these results it seems that the retention of initial water content as manifested in the AS regime results in lower strength than in the cases when water was allowed to escape. As shown in the Figure 2, the vacuum aided desiccation process would cause relatively poor internal water atmosphere and it seems that this condition has resulted in higher strength gain. The authors would not at this moment rush into a generalised conclusion based on this observation. The phenomenon of apparent compressive strength superiority exhibited by dried specimens over wet ones is well known in the concrete literature (Gilkey, 1926). This phenomenon may also be manifested in the geopolymer case and will be further investigated and reported elsewhere by the authors. However, if the strength gain is in fact genuinely independent of the mentioned phenomenon, then it may be

concluded that geopolymer reactions can also be accelerated by reducing the water content during the curing process.

3.3 SEM Test

Scanning Electron Microscopy (SEM) testing was proposed to observe the pace of microstructural development on geopolymer networks. SEM test was immediately applied on the residual pieces of geopolymers after strength tests. Four pieces were collected from four different parts of the geopolymer samples, and the dominant type of structure seen in the SEM images was chosen to be the representative image. The images for the 7 and 14 days ambient curing samples with $W/G=0.22$ and 0.26 are therefore presented in Figure 3. For comparison, the image of 7 days 4-hour heat curing samples with $W/G=0.22$ is also presented in part (e) of the same Figure.

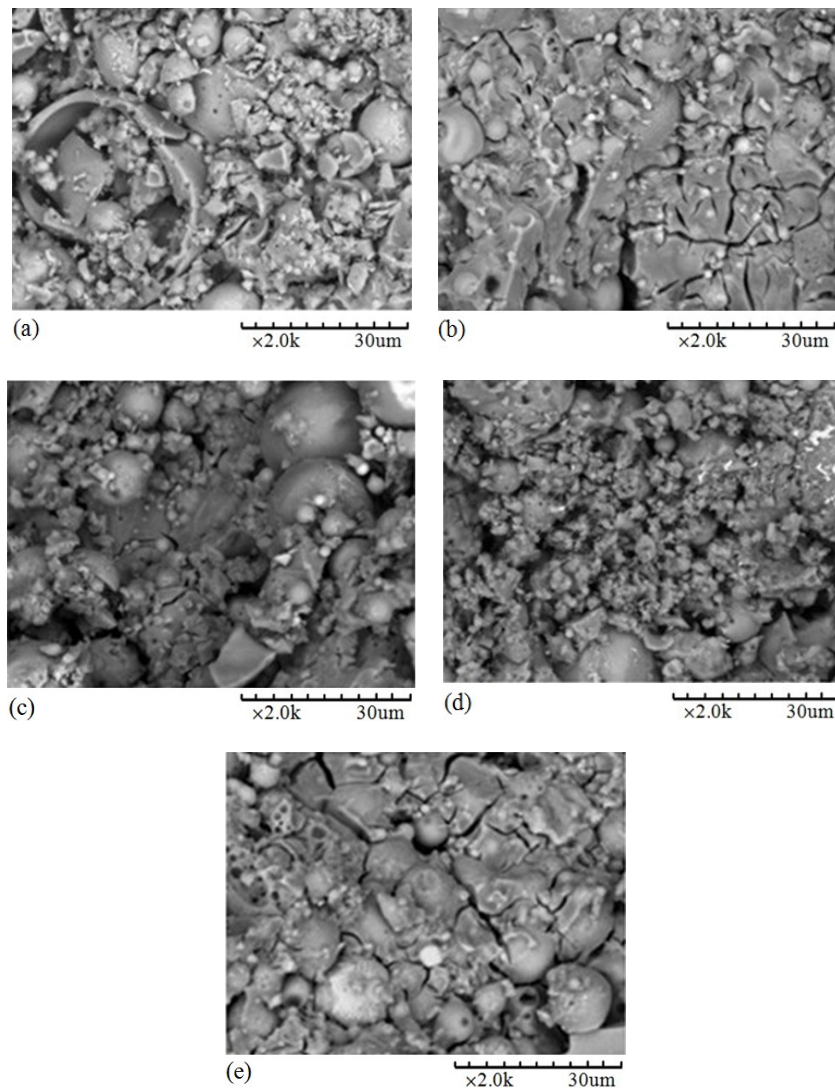


Figure 3. SEM Images of the Ambient-cured Geopolymer with $W/G=0.22$ after 7 Days (a) and 14 Days (b), and $W/G=0.26$ after 7 Days (c) and 14 Days (d), and the 4-hour $60^\circ C$ Heat-cured Geopolymer with $W/G=0.22$ after 7 Days (e)

The images in Figure 3(a) and (b) displayed a more densified mass that developed under ambient-cured condition during the period from 7 to 14 days. At the age of 7 days there is indication that fly ash particles were partially dissolved and started to form small loosely connected blocks. After 14 days such blocks became denser and more closely connected with a reduction in the intermediate pores. This clearly corresponds with the strength development results. In the image (c), a similar phase like that shown in image (a) was observed, while a higher proportion of unreacted fly ash particles existed. This may be due to the lower alkali strength caused by relatively higher water content. The loose particle connections observed in Figure 3(d) may be the cause of the observed lower strength compared to the material whose structure is depicted in image (b), as revealed in the strength test results of Figure 1(b). This may also indicate that the growth of strength in the samples with $W/G=0.22$ could be much faster than the samples with $W/G=0.26$. Hence, this observation may further support the conclusion that higher water content could decelerate the geopolymer reactions.

Despite the same mix designs for the materials, the structures shown in the image (a), (b) and (e) were quite different. In the image (a), many large voids were detected which separate the particles and blocks far from each other. This could be one reason for its low strength in Figure 1(b). In the image (b) and (e), these voids were disappeared and new structural blocks were generated to connect the loosely particles together. Besides, continuous micro cracks were detected in the image (e) that grew through both the generated blocks and the separation of original particles. Similar micro cracks were also observed in image (b) but they became shorter and narrower, and not continuous. These micro cracks could be the footmarks of the new generated materials that helped to bear the exterior compressive forces.

On the other hand, the extent of the structural development shown in image (b) was quite similar to the structure shown in image (e). This indicates that the lower water content can cause the ambient-cured geopolymers to achieve an adequate structural development comparable to that of the short-term heat-cured geopolymers.

4. CONCLUSIONS

The water content can be varied in two stages of geopolymer synthesis. These are: the initial mix design and during the curing processes. Relative strength and microstructural development tests have been performed to investigate the effects of changing the water content in one or both of the aforementioned stages, on geopolymer development. The effects of such water content variation on the ambient-cured geopolymers have also been investigated in order to explore the possibility of improving the rate of geopolymerisation without resorting to heat. The conclusions of this investigation may be summarised as follows:

- According to the results, the water content has an important impact on geopolymer strength gain. Less water content in the initial design resulted in higher strength development.
- Unlike the heat-cured samples, the lower water content in the initial design also results in a higher rate of strength gain in the ambient-cured geopolymers from 7 to 14 days compared to the rate exhibited in higher water content mixes.
- Meanwhile, reducing the water content achieved through curing processes by allowing the water to escape or by desiccation may also result in better strength growth.

- Quite importantly, it has been found that a combination of long-term curing with low water content could improve ambient-cured geopolymers and produce strength results comparable with those of geopolymers that were heat treated. This result may be quite significant as it demonstrates the potential of manufacturing geopolymers using far less energy than has been previously envisaged.

REFERENCES

- Davidovits, J. 1989. Geopolymers and geopolymeric materials. *JTAC*, 35, 429-441.
- Davidovits, J. 2008. *Geopolymer Chemistry and Application*, Saint-Quentin, Institut Géopolymère.
- Duxson, P., Fernández-Jiménez, A., Provis, J. L., Lukey, G. C., Palomo, A. & Deventer, J. S. J. 2007. Geopolymer technology: the current state of the art. *Journal of Materials Science*, 42, 2917-2933.
- Fang, Y. & Kayali, O. 2012. The fate of water in fly ash-based geopolymers. *Construction and Building Materials*.
- G. I. 2012. *What is a geopolymer? Introduction* [Online]. Geopolymer Institute. Available: <http://www.geopolymer.org/science/introduction> [Accessed].
- Khale, D. & Chaudhary, R. 2007. Mechanism of geopolymerization and factors influencing its development: a review. *Journal of Materials Science*, 42, 729-746.
- Kumar, S. & Kumar, R. Year. Tailoring Geopolymer Properties Through Mechanical Activation of Fly Ash. *In: Second International Conference on Sustainable Construction Materials and Technologies*, 2010 Italy.
- Lizcano, M., Gonzalez, A., Basu, S., Lozano, K. & Radovic, M. 2012. Effects of water content and chemical composition on structural properties of alkaline activated metakaolin-based geopolymers. *Journal of the American Ceramic Society*, 95, 2169-2177.
- Palomo, A., Grutzeck, M. W. & Blanco, M. T. 1999. Alkali-activated fly ashes A cement for the future. *Cement and Concrete Research*, 29, 1323-1329.
- Provis, J. L. & Van Deventer, J. S. J. 2007. Geopolymerisation kinetics. 2. Reaction kinetic modelling. *ChEnS*, 62, 2318-2329.
- Provis, J. L., Van Deventer, J. S. J. & Lukey, G. C. Year. A conceptual model for solid-gel transformations in partially reacted geopolymeric systems. *In: SINGH, J. P. B. N. P. K. W. M.*, ed. *Proceedings of the 106th Annual Meeting of The American Ceramic Society*, 2005 Indianapolis, USA. 49-70.
- Provis, J. L., Yong, C. Z., Duxson, P. & Van Deventer, J. S. J. 2009. Correlating mechanical and thermal properties of sodium silicate-fly ash geopolymers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 336, 57-63.
- Rangan, B. V. 2007. Low-calcium fly ash-based geopolymer concrete. *In: NAWY, E. G. (ed.) Concrete Construction Engineering Handbook*. 2 ed. New York: CRC Press.
- Rangan, B. V., Hardjito D, Wallah, S. E. & Sumajouw, D. M. J. Year. Studies on fly ash-based geopolymer concrete. *In: Geopolymer 2005 Proceedings*, 2005. 133-137.
- Rovnaník, P. 2010. Effect of curing temperature on the development of hard structure of metakaolin-based geopolymer. *Construction and Building Materials*, 24, 1176-1183.
- Zuhua, Z., Xiao, Y., Huajun, Z. & Yue, C. 2009. Role of water in the synthesis of calcined kaolin-based geopolymer. *Applied Clay Science*, 43, 218-223.