

REACTION BEHAVIOUR OF ARMORPHOUS SILICA IN ALKALI-ACTIVATED GEOPOLYMERIC CEMENTITIOUS MATERIALS

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Abstract

For exploring the behaviour of alkali-silica reactivity (ASR) of amorphous silica in geopolymeric materials and assessing the procedures for testing ASR in alkali-activated cementitious, the expansion behaviour of fly ash based geopolymer mortars with pure silica glass cured at various conditions, i.e. 23°C and 38°C with relative humidity over 95%, immersed in 1M NaOH solution at 80°C and autoclaved in 10% KOH solution at 150°C, was studied. Results show that, at four kind of curing conditions, no harmful ASR was observed with the criteria specified for OPC system. However, with the change of curing conditions, the geopolymer binder and amorphous silica may experience different reaction processes leading to quite different dimensional changes, especially with additional alkalis and elevated temperatures. It suggests that high temperature with additional alkali for accelerating AAR in traditional OPC system may not appropriate for assessing the alkali-aggregate reactivity behaviour in geopolymers designed for normal conditions.

KEYWORDS: geopolymer; amorphous silica; alkali silica reaction; deformation behaviour

1 INTRODUCTION

Geopolymers refer to a group of cementitious materials manufactured by reacting alumino-silicate materials (e.g. fly ash and metakaolin) with an alkali solution [1]. Comparing with traditional Ordinary Portland Cement (OPC), which is an extremely resource and energy intensive product, those new cementitious materials have abundant raw materials resources, low energy consumption in manufacture and superior mechanical and physical properties. Since the pioneer work by Dividovits [1], geopolymers have gained more and more interest as alternative candidates for cementitious materials in civil engineering and other applications in waste management, art decoration, etc [2,3].

Alkali has duplex effects on the synthesis of geopolymers and their durability. On one hand, alkali

cations are considered as structure-forming element balancing the negative framework charge of tetrahedral aluminum, while the OH-ions are catalyst in the dissolution of source aluminosilicates. Therefore, sufficient alkali is essential for both the geopolymerization process and the final product. The alkali content in geopolymers is about 4~6%(Na_2O_e), which is several times higher than that in OPC. On the other hand, the existence of certain amount of free alkali may have harmful effect on its long term stability. Both chemistry theory and experimental results indicate that the free alkali does exist in geopolymers [4,5]. The release of the alkali could result in efflorescence of the geopolymer binder itself and excess free alkali may also cause possible harmful aggregate reactions, especially when alkali-susceptible aggregates are available. Therefore, a study on the behavior and mechanism of the interaction of geopolymeric binder phases with aggregates, especially the alkali-susceptible aggregates in OPC binders, is of paramount importance in the development of geopolymer concretes.

Previous findings of alkali-aggregate reaction in alkali-activated slag concretes have shown that the alkali-aggregate reaction behaviour could be significantly different depend on the composition of raw materials, the types of reactive aggregates and curing conditions, etc [6-8]. Gifford and Gillott [6] found that, in alkali-activated slag cement concrete, ASR induced expansion was much lower than that in traditional OPC system, while ACR induced expansion was significantly higher than that in traditional OPC system. While Krivenko [7, 8] thought that the processes taking place during “alkali-aggregate reaction” in alkali-activated cementitious materials could be either destructive or constructive ones. However, for geopolymers, the raw materials, polymerization mechanism and products of geopolymerization are quite different from alkali-activated slag cements [9]. No systematic research has yet been carried out on the alkali-aggregate reaction behaviour and mechanisms in geopolymers. Limited research focused only on the comparative study on AAR induced expansion between geopolymers and traditional Portland cement concretes [10,11]. Most of these findings were based on results in the accelerated mortar bar method (ASTM C1260), which has been the mostly widely used test with additional alkali and elevated temperature to accelerate AAR in traditional OPC system. In order to establish suitable test procedure for assessing ASR in geopolymeric materials and explore the mechanisms of ASR in geopolymers for future performance improvement on geopolymers, the reaction behaviour of amorphous silica in geopolymers was studied by length measurement and microstructure study of geopolymer mortars with silica glass cured at different curing conditions specified in the traditional laboratory tests for ASR in OPC systems.

2 MATERIAL AND EXPERIMENTAL

2.1 Materials

A class F low calcium fly ash (FA) and a calcined superfine metakaolin (MK) were used as primary

aluminosilicate sources. Sodium water glass mixed with reagent sodium hydroxide was used as activated alkali solution. The modulus and solids content of the modulated water glass are 1.4 and 37%, respectively. High-purity recycled amorphous silica glass (QG) was used. QG was crushed and sieved into the following size fractions, 0.15~0.80 mm and 2.5~5.0 mm. The chemical compositions of FA, MK and QG are listed in table 1.

2.2 Experimental

Geopolymer binders were prepared by first dry-mixing FA and MK powders, then combining with alkali solutions with a mechanical mixer. The mass ratio of FA to MK was 65/35. Sodium silicate solution was prepared at molar $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 1.4, the water to solids mass ratio of the geopolymer binder was 0.31. For geopolymer mortars with 2.5-5.0mm QG, the geopolymer binder was mixed first, QG was then mixed into the binder by mass ratio of $\text{QG}/(\text{FA} + \text{MK}) = 1:1$.

For each of the three kinds of curing conditions, 23°C and over 95% R.H., 38°C and over 95% R.H., immersed in a 1M NaOH solution at 80°C, four bars, 20mm×20mm×80mm in size, were cast from the geopolymer binder and the geopolymer mortars, respectively. All casted molds were covered with a plastic film and cured at 23°C for 24 h, then demolded, the initial length measured then moved into different environments for further testing. For specimens cured without additional alkali, i.e., 23°C and over 95% R.H., 38°C and over 95% R.H., specimens were sealed with plastic film aging to test at specific periods. For specimens immersed in a 1M NaOH solution at 80°C, the bars were moved into the solution at room temperature after taking the initial readings, then warmed up to and maintained at 80°C. The length changes of specimens were measured regularly with a comparator. For the specimen cured at 38°C, over 95%R.H. and in 80°C 1M NaOH solution, the bars were cooling down at 23°C for 6 h before each measurement.

The autoclave test for geopolymer binder and mortars were generally the same as that in the Chinese Autoclave Test CECS48:93 [12]. Six minibars, 10mm×10mm×40mm, with 0.15~0.80mm size of QG were made at each binder/aggregate ratio of 10:1, 5:1, 1:1, respectively. The 24 h of curing in mold is the same as the 20mm×20mm×80mm bars. The minibars were steamed at 100°C for 4h, then autoclaved in a 10% KOH solution at 150°C for 6h, 12h, 18h, 24h, 30h. The length measurements were taken with a micrometer.

Microstructures of selected specimens were examined by JSM5900 SEM, combined with Thermal Noran EDS. The specimens were cut and vacuum dried at 60°C and Au coated for surface observation.

3 RESULTS AND DISCUSSIONS

3.1 Deformation behaviour of geopolymer binder and mortars

Fig. 1 shows the deformation curves of geopolymer binder and mortars cured at 23°C with a relative

humidity over 95%. Geopolymer binder without QG shrunk in the whole storing period. The process of shrinkage can be divided into two stages. The binder shrunk rapidly before 7 days, finishing almost half of the total shrinkage attained in the testing period. The shrinkage then continued to increase at a steady rate throughout the testing period. Compared with the binder, the deformation behaviour of geopolymer mortars with QG aggregate was very different. Contrary to the rapid shrinkage of the binder at early ages, a slight expansion was observed in specimens with QG aggregate at the first day. The expansion then reduced at first few days, dominated by the shrinkage of the geopolymer binder with similar trend. But the shrinkage of geopolymer mortars with glass was smaller than that of the geopolymer binder at the same age. It indicates that QG glass was involved in a very rapid expansive reaction other than geopolymerization at early age, leading to quick and slight expansion of the geopolymer mortars. However, the expansion did not last with time suggesting that the glass-induced expansive reaction and its effect was either suppressed by the following geopolymerization process or the glass continued to react but formed the non-expansive product with the inter-reaction with geopolymerization.

Fig. 2 shows the deformation curves of geopolymer binder and mortars cured at 38°C with a relative humidity over 95%. Similar to Fig.1, the geopolymer binder shrunk throughout the testing periods, and specimens with QG aggregate had a slight expansion at the first days, then shrunk with a similar trend as in the geopolymer binder. Compared with geopolymer binder cured at 23°C, the shrinkage behaviour of geopolymer binder cured at 38°C was quite different in two aspects. Besides two stages of the development of shrinkage mentioned above, rapid and slow down stages, geopolymer binder cured at 38°C seemed to reach dimensional stabilization after 60 days. It indicates that increasing the curing temperature would promote the geopolymerization reaction and shorten the time needed for the binder to reach dimensional stabilization. It is in accordance with literatures results that both the dissolution rate of Si and Al from raw aluminosilicates and the geopolymerization rate of gel products increased with increasing temperature [13, 14]. The deformation of mortars with QG was also different from those cured at 23°C. Generally, a much smaller expansion at the early age was observed in geopolymer mortars. The results from Figs 1 and 2 suggest that, the increase of curing temperature, will accelerate the geopolymerization process, while weakening the effect of glass reaction and its interaction with geopolymerization.

Fig. 3 shows the deformation curves of geopolymer binder and mortars immersed in 1M NaOH solution at 80°C. The process of shrinkage development in geopolymer binder can be divided into four stages, rapid shrinkage, continue to shrinkage slowly, stabilization and shrinkage reduction, which were obviously different from those in binders cured at relative low temperatures and without additional available alkali (Figs. 1 and 2). The binder shrunk rapidly at the first day, finishing almost of the total shrinkage attained in the testing period. The shrinkage continued to increase at a steady rate before 7 days, and then the binder arrived

at dimensional stabilization before 21 days. With the prolonging of curing time, the binder started to expand. It indicates that high alkali solution combined with high temperature accelerates the geopolymerization reaction and promotes the formation of structural stable geopolymer binder. However, with the extension of curing period, the composition and structure of binder could be modulated by external alkali intervention and further geopolymerization. Some transformations with dimensional expansion took place in the binder. Compared with specimens with QG cured at relative low temperatures and without additional available alkali, the deformation behaviour of specimens with QG was also different significantly. Contrary to a slight expansion of the mortars with QG at early ages, the deformation behaviour of mortars cured at higher temperature and with additional alkali was dominated by the shrinkage of the binder in the whole testing period, but with a smaller shrinkage than that in the binder at the same age. The expansive effect at later age was also weaker than that in binder. Since a lot of gels floating in the curing alkali solution and the obvious gap between glass particles and binder were observed, glass particles were involved in reaction, but probably formed low viscosity non-expansive products. The gap between glass particles and binder were acted as a buffer for the expansion due to the phase transformation in the binder, resulting in a lower expansion than that in binder at later age.

Fig. 4 shows the deformation curves of geopolymer binder and mortars autoclaved in 10% KOH solution at 150°C. The measurements after steam treatment at 100°C for 4h were taken as the initial length. The shrinkage of all specimens was about 0.048% after steam treatment at 100°C for 4h, and was not affected by the QG contents in the mortar. Fig 4 indicates that all the mortars shrunk slightly at first 12 hours autoclave treatment. Similarly, the binder gave a larger shrinkage than the mortars, and the effect of QG content on shrinkage was not so significantly. However, with the prolonging of autoclave time, all the mortars expanded, and the more the glass content in the mortars, the larger and faster expansion was developed. It suggests that the alkali-glass reaction has taken place and contributed to the harmful expansion under autoclave treatment with additional alkails.

3.2 Microstructure of geopolymer mortars with QG aggregate

Fig. 5 shows the SEM images of the fracture surface of specimens with QG cured for 1 year at 23°C with a relative humidity over 95% (Fig. 5 (a)) and 38°C with a relative humidity over 95% (Fig.5 (b)). There was no obvious difference in both the type and morphology of gel products and binder-glass interfaces between the mortars cured at these two conditions. Both mortars with QG developed a massive of relative dense, continuous and heterogeneous gel binder with fly ash particles. A clear interface between geopolymer binder and QG aggregates was observed in the specimens with QG and no typical ASR gel and cracks were noticed near the interface, suggesting no obvious alkali-glass reaction occurred in geopolymers even after 1

year of curing.

Fig. 6 shows the SEM images of the fracture surface of specimens with QG immersed in 1M NaOH solution at 80°C for 28 days. In addition to the massive dense gels and some loose and porous gels, which are the common products formed in geopolymers (Fig. 6 (a)). According to our previous study on microstructure and composition of geopolymers [15], the porous products was probably formed by the dissolution of MK. Additional alkali and high temperature would promote the dissolution of MK and fly ash, favoring the formation of porous gels in the binder and the transformation of gels to crystals. Clear gaps between the binder and QG aggregate could be easily observed, suggesting the mass dissolution of glass and the weakness of the interfacial transition zone (ITZ). A layer of loose coil-like deposits were formed on the surface of the gap along the binder side (Fig. 6 (c)). EDS analysis (Fig. 6 (f)) shows that the coil-like deposits were typical high Si low Al and Na products with neglectable calcium content, and the Si content of coil-like deposits is significantly higher than that in the matrix of the binder.

3.3 Discussion

Alkali in geopolymer plays a critical role in the dissolution of aluminosilicate, and the following geopolymerization reaction to form stable structure. The mechanism proposed by Dividovits involves the chemical reaction of precursors such as alumino-silicate oxides (Al^{3+} in IV-fold coordination) with alkali polysilicates resulting in polymeric Si-O-Al bonds[1]. It includes several steps. First, alumino-silicate oxides dissolve in the alkali solution, then dissolved Al and Si complexes diffuse from the particle surfaces to the inter-particle spaces. Finally, a gel phase is formed from the polymerization of added silicate solution and Al and Si complexes. Although the precise mechanism of the traditional geopolymerization process have yet to be fully understood, it is commonly believed that geopolymerization is a volume decreasing process with the release of water. Results from present paper show that the geopolymer binder cured at various conditions shrinkage unanimously, although the rate to reach dimensional stable and the total shrinkage attained were different with the curing temperature, with and without additional alkalis. High temperature favors the geopolymerization, and thus the shrinkage development. Previous work has shown that with the prolonging of curing time, the involvement of additional alkali could lead to the transformation of gels into zeolite crystals [16].

For geopolymer mortars with extremely high reactive amorphous silica, alkali in geopolymer mixes does react with glass and cause expansive alkali-silica reaction, as shown in Figs 1 and 2. And the reaction starts at the very early age, even with a faster rate and stronger effect than that with the geopolymerization. However, with the proceeding of the geopolymerization and the more involvement of aluminosilicates, expansive ASR with amorphous silica was totally suppressed. It was not surprising when considering that in

traditional OPC sufficient fly ash or MK could reduce the expansion due to ASR from most of reactive aggregates, even such extremely high reactive aggregate as opal. The mass content of FA and MK in the geopolymer binder was about 81.6%, which should be sufficient to control almost all expansion due to ASR. Considering the different behaviour of mortars shown in Figs. 1 and 2, elevated temperature seems to have more impacts on accelerating geopolymerization than on ASR.

The involvement with additional alkalis complicates the scenarios in geopolymer mortars with glass. On one hand, it may act as a constituent to intervene the geopolymerization process, and later, promote the transformation of geopolymeric alkali aluminosilicate gel into zeolite crystals, resulting in the volume increase [16]. On the other hand, additional alkalis promote the attack and dissolution of amorphous silica to release more tetrahedral $[\text{SiO}_4]^{4-}$, which is the element to form non-expansive alkali-aluminosilicate gel and low viscosity ASR gel.

Autoclave with additional alkali combined three important factors affecting the dynamics of chemical reaction, temperature, alkali and pressure, which make the scenarios more complicated. Mortars autoclaved in 10%KOH solution at 150°C have a different evolution pattern compared with 80°C in 1M NaOH solution. The transformation of geopolymer gel into crystals did occur[16], but the interactions between geopolymerization and alkali-silica reaction under autoclave condition need further study.

At four kind of curing conditions used in this paper, no harmful ASR was observed with the criteria specified for OPC system. ASR seems not an issue in fly ash based geopolymer. However, with the change of curing conditions, the geopolymer binder and mortar with glass may experience different reaction processes leading to quite different dimensional changes, especially with additional alkalis and elevated temperatures. It means that high temperature with additional alkali for accelerating AAR in traditional OPC system may not appropriate for assessing the alkali-aggregate reactivity behaviour in geopolymer designed for normal conditions.

4 CONCLUSIONS

The deformation behaviour of geopolymer binders without aggregate is strongly influenced by the curing conditions. Binders cured without additional alkali shrinkage in the whole storage period. The higher of the curing temperature, the faster of the geopolymerization process occurs, and the shorter time needed for the binders to reach dimensional stabilization.

The deformation behaviour of the geopolymer mortar with glass aggregate is significantly affected by the binder deformation behaviour and curing conditions. Geopolymer mortars with silica glass did not show harmful expansion in the four kinds of curing conditions and periods specified for OPC system.

With the change of curing conditions, the geopolymer binder and mortar with glass may experience

different reaction processes and may lead to totally different dimensional changes, especially with additional alkalis and elevated temperatures. The methodology using high alkali, high temperature to accelerate AAR in traditional OPC is not appropriate for quick evaluation of AAR in geopolymers.

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TABLE 1: Chemical Composition of fly ash, metakaolin and silica glass w/%										
	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO	Fe ₂ O ₃	MgO	SO ₃	TiO ₂	Total
FA	50.80	31.34		1.50	3.90	5.93	1.27	1.45		96.28
MK	55.03	43.33		0.46		0.82			0.36	100
QG	99.70	0.07	0.07		0.05	0.01		0.02		99.92

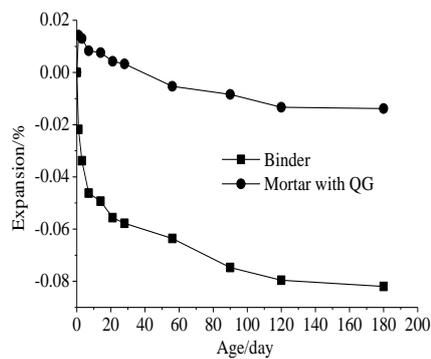


FIGURE 1: Deformation curve of geopolymer binder and mortars cured at 23°C with a relative humidity over 95%

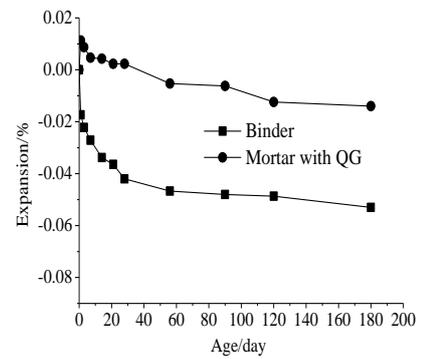


FIGURE 2: Deformation curve of geopolymer binder and mortars cured at 38°C with a relative humidity over 95%

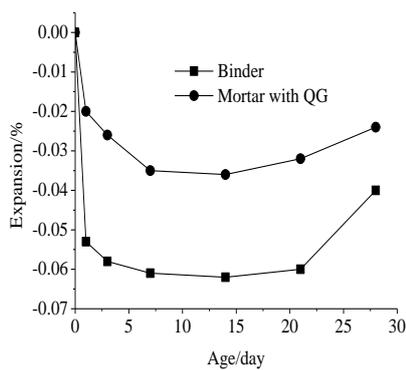


FIGURE 3: Deformation curves of geopolymer binder and mortars immersed in 1M NaOH solution at 80°C

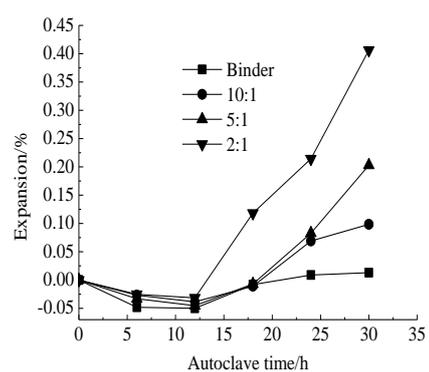


FIGURE 4: Deformation curves of geopolymer binder and mortars autoclaved in 10% KOH solution at 150°C

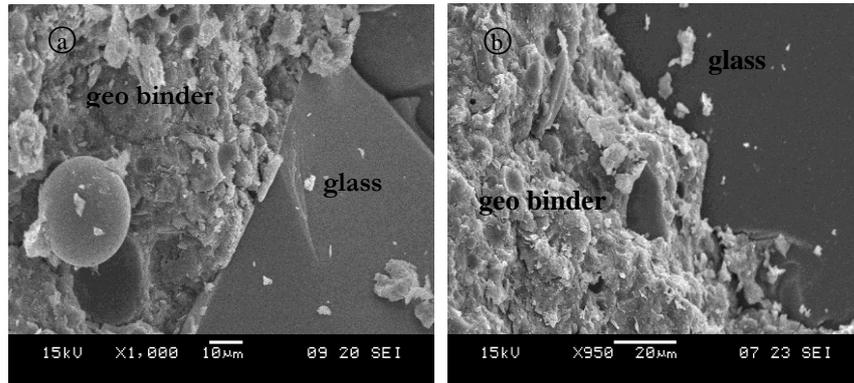


FIGURE 5: SEM images of the fracture surface of specimens with QG cured for 1 year (a) at 23°C with a relative humidity over 95%, (b) at 38°C with a relative humidity over 95%

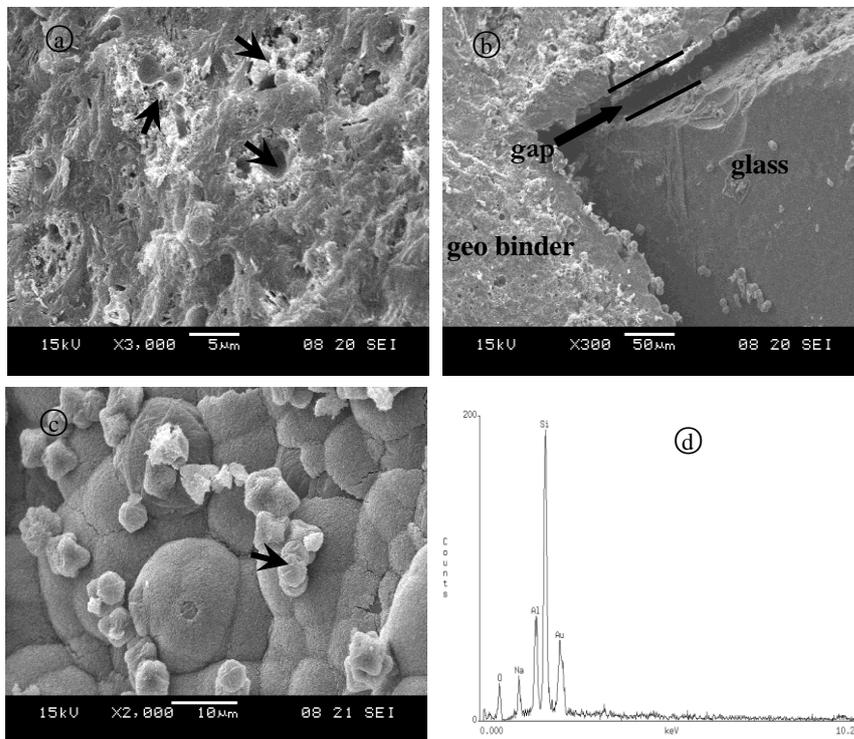


FIGURE 6: SEM/EDS images of the fracture surface of specimens with QG immersed in 1M NaOH solution at 80°C for 28 days (a) fracture surface of binder, (b) binder-glass interface, (c) coil-like deposits, (d) EDS analysis of coil-like deposits