

REACTION BEHAVIOUR OF DOLOMITIC LIMESTONE FROM KINGSTON, CANADA IN ALKALI-ACTIVATED GEOPOLYMERIC MATERIALS

Duyou Lu* Yanzeng Zheng, Yongdao Liu, Zhongzi Xu, Mingshu Tang

Nanjing University of Technology, Nanjing, 210009, China

duyoulu@njut.edu.cn

Abstract

For understanding the alkali reactivity of carbonate rocks in geopolymer and the mechanism of traditional alkali-carbonate reaction (ACR), the linear dimensional changes of geopolymer mortars with pure dolomite (YT) and dolomitic limestone from Kingston, Canada (CK) were studied by curing at different conditions, i.e. room temperature with over 95% R.H., 38°C R.H.>95% and 80°C 1mol/L NaOH. Results show that, at the three curing conditions, YT acts as a filler to dilute and constrain the shrinkage of the mortar; With differences to the unanimous shrinkage of geopolymer mortar with YT, the deformation behavior of geopolymer mortar with CK varies remarkably with the changes of the curing temperature and with or without additional alkalis. Especially, the mortar with CK expands slightly in different curing stages when cured at 38°C R.H.>95% and 80°C 1mol/L NaOH. Contrary to the harmful expansive reaction in OPC, slight expansive reaction in geopolymer may be beneficial to compensate the shrinkage of geopolymer matrix.

KEYWORDS: geopolymer; alkali-carbonate reaction; expansion; shrinkage compensation

1 INTRODUCTION

Geopolymers refer to a group of new cementitious materials manufactured by reacting aluminosilicate materials (e.g. fly ash and metakaolin) with an alkali solution [1]. They have gained more and more interest as alternative candidates for cementitious materials in civil engineering and other applications in waste management, art decoration, etc [2-4]. Similar to other alkali-activated cements, the alkali content in geopolymers is much higher than that in OPC. The binder phase in geopolymers is mainly alkali-aluminosilicate gel with alkali cations as charge balancing elements. Significant shrinkage resulting from the formation of the gel and the concerns raised on the stability of high alkaline systems are two of the main challenges for the application of these new cementitious materials [5-7]. 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 depending on the composition of raw materials, the characteristics of reactive aggregates and curing conditions, etc [8-10]. Gifford and Gillott [8] found that, in alkali-activated slag cement concrete, ASR-induced expansion was much lower than that in traditional OPC system, while ACR induced significantly higher expansion than that in traditional OPC system. Krivenko [9, 10] proposed that the processes of “alkali-aggregate reaction” in alkali-activated cementitious materials could be either destructive or constructive ones depending on the composition of raw materials, the types of reactive aggregates and curing conditions. For geopolymers, however, the type of raw materials, polymerization mechanism and products of geopolymerization are quite different from alkali-activated slag cements [5]. No systematic research has yet been carried out on the behaviour and mechanisms of alkali-aggregate reactions in geopolymers.

On the other hand, alkali carbonate reaction (ACR) is an important type of harmful alkali-aggregate reactions in Portland cement concrete. The reaction mechanism of alkali-carbonate reaction is still not well understood [11]. The focus of the controversy is on the role of dedolomitization in the expansion process.

In order to explore the reaction behaviour of carbonate rocks in geopolymer and shed some light for understanding the mechanism of traditional ACR, the reaction behaviour of argillaceous dolomite-bearing rock in geopolymers was studied by length measurement on geopolymer mortars cured at different curing conditions specified in the traditional laboratory tests in OPC systems.

2 MATERIALS 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. The chemical composition of FA and MK is listed in table 1. 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. Argillaceous dolomitic limestone from Kingston, Canada (CK) and a pure dolomite from China(YT) were used. CK and YT were crushed and sieved into the 2.5~5.0 mm size fraction. The chemical and calculated mineral compositions of CK and YT are listed in table 2.

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 CK and YT, the geopolymer binder was mixed firstly, CK or YT was then mixed into the binder by mass ratio of $(\text{CK or YT})/(\text{FA} + \text{MK}) = 1:1$.

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 furthering 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.

3 RESULTS AND DISCUSSIONS

Fig. 1 shows the linear dimensional change curves of geopolymer binder and mortars cured at 23°C with a relative humidity over 95%. All specimens shrunk with similar trend in the whole storing period. The shrinkage developed rapidly at early ages (before 7 days), then continued to increase at a slower rate then reached stable at later period. Compared with the control binder without aggregate, geopolymer mortars with CK and YT gave a smaller shrinkage and stabilized at an earlier time. There was no obvious differences in shrinkage behaviour between the mortars with CK and YT.

Fig. 2 shows the linear dimensional change curves of geopolymer binder and mortars cured at 38°C with a relative humidity over 95%. Similar to Fig.1, the control geopolymer binder and mortar with YT shrunk in similar trend. Both shrunk rapidly at early period, then continued to increase steadily and reached stable at later period. Mortar with YT gave a similar shrinkage at early period and a smaller shrinkage at later period. Mortar with CK, however, showed a very different trend from the both the control and the mortar with YT. It shrunk very slightly at the first 5 days, and then turned to slight expand after a stabilization till 56 days,

Fig. 3 shows the linear dimensional change curves of geopolymer binder and mortars immersed in 1M NaOH solution at 80°C. The control and the mortar with YT shrunk in the whole testing period and

generally gave similar trends as those in Figs.1 and 2. Mortar with YT developed a smaller shrinkage than that in the control. Mortar with CK gave a very different behaviour from the the control and the mortar with YT, as well as the same mortar but cured at 23oC and 38oC without additional alkalies. Contrary to the rapid shrinkage of the control and mortar with YT at early period, mortar with CK expanded slightly before 7 days, then shrunk slightly dominated by the shrinkage of the binder matrix.

Summaries of the results in Figs.1, 2 and 3, the control specimen cured at three conditions gave similar trend of shrinkage. After a rapid increase at early period, the shrinkage kept increasing at a steady rate and finally stable at later period. compared with the control, mortar with YT showed a similar trend but a with a relative smaller shrinkage. It suggests that the YT in the specimen mainly acted as a filler to constrain the shrinkage of the geopolymer matrix. The curing conditions do not have much impact on the behaviour of YT in the mortar. Mortar with CK showed very different behaviour with the change of curing conditions. It gave simialar behaviour with YT at room temperature, shrinkaging in the whole testing period. When cured at 38 °C, it expanded at later period after a slight skrinkage at early and medium period. When the mortar was cured at a higher temperature and with additonal alkalies, it expand at early period and almost gave no shrinkage throughout the 28 days, which is opposite to the behaviours of the control and the mortar with YT.

CK is a typical ACR rock, while YT is nonreactive in OPC. When sufficient alkalies is available in OPC, CK could develop rapid expansion and keep increasing steadily even at room temperatures. The alkali content in geopolymer is about 4% in Na₂O_e, which is much higher than that in OPC. However, CK and YT gave no obvious difference in geopolymers cured at room temperature. It suggests that the characteristic of aggregate does not have much influence on the behaviour of geopolymers cured at room temperatures. They only diluted the binding phase and acted as aggregate to constrain the shrinkage of the binder. Improving the curing temperature, in addition to accelerate the geopolymerization, it also promote the reaction of CK and change its behaviour. The reaction of CK leads to a slight expansion of the mortar at later period. High temperature combined with additional alkalies could further promote the reaction of CK and induce early expansion to compensate the shrinkage of the binder. It is hopeful, therefore, to control the dimensional change of geopolymer mortar or concrete by selecting the type of carnorate rocks and the appropriate curing conditions.

On the other hand, the expansion of CK keeps increasing in OPC cured in 1M NaOH solution at 80°C, and reached 0.15~0.22% at 28 days[12]. In geopolymer mortar cured at the same condition, however, CK developed a much smaller expansion and the dimesional change of the mortar was dominated by the matrix after a slight expansion at early days. It suggests that the reaction mechanism of CK in geopolymers is probably different from that in OPC. It will be further explored by microstructural studies.

4 CONCLUSIONS

Changes in the curing temperatures, with or without additional alkalis have little impact on the linear dimensional change behaviour of mortars with pure dolomite (YT). YT acted mainly as a filler to constrain the shrinkage of the geopolymer binder.

Curing condition has strong influence on the behaviour of CK in geopolymer. Especially, CK could induce slight beneficial expansion to compensate the shrinkage of geopolymer binder at appropriate curing condition. It is possible to make dimensional stable geopolymer mortar or concrete by changing the characteristic of aggregate and curing conditions.

5 ACKNOWLEDGEMENTS

The supports received from the Key Project of Chinese Ministry of Education (No. 210079), National Natural Science Foundation of China (No.51072080) and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) are gratefully acknowledged.

6 REFERENCES

- [1] J. Davidovits (1991): Geopolymers: Inorganic polymeric new materials [J]. *J Thermal Anal*, 37: 1633-1656.
- [2] G Habert., J.B d'Espinose de Lacaillerie., N Roussel.(2011): An environmental evaluation of geopolymer based concrete production: reviewing current research trends [J]. *Journal of Cleaner Production*, 19: 1229-1238.
- [3] Behzad Majidi, (2009): Geopolymer technology, from fundamentals to advanced applications: a review [J]. *Mater Tech*, 24(2): 79-87.
- [4] JGS Van Jaarsveld, JSJ Van Deventer, (1997): The potential use of geopolymeric materials to immobilize toxic metals: Part I. Theory and application. *Mineral Engineering* (10): 659-669.
- [5] D M Roy (1999): Alkali-activated cements: opportunities and challenges [J]. *Cem Concr Res*, 29(2): 249-254.
- [6] P Duxon , GC Lukey, , F Separovic, , J S J Van Deventer, (2005): The effect of alkali cations on aluminum incorporation in geopolymeric gels. *Industry engineering Chemistry Research* (44): 832-839.
- [7] P Duxon, , J L Provis, , G C Lukey, , JSJ Van Deventer, (2006): ³⁹K NMR of free potassium in geopolymers. *Industry engineering Chemistry Research* (45): 9208-9210.
- [8] PM Gifford, , J E Gillott, (1996): Alkali-silica reaction (ASR) and alkali-carbonate reaction (ACR) in activated blast furnace slag cement (ABFSC) concrete. *Cement and Concrete Research* (26): 21-26.

- [9] PV Krivenko, , NM Mhitaryan, , VV Chirkova, , EP Zgardan, (1997): Durability of alkaline cement concrete made with alkali-reactive aggregates. In: Malhotra, VM (Editor): Proceedings of the fourth CANMET/ACI international conference on durability of concrete, Sydney, Australia: 587-596.
- [10] P V Krivenko, , AG Gelevera, , YV Fedorenko, (2010): The effect of alkali on destructive and constructive processes during alkali-aggregate reaction. In: Caijun Shi and Xiaodong Shen (Editor): RILEM PRO 72, Advances in Chemically-Activated Materials, Jinan, China: 147-154.
- [11] V Jensen,(2012): the controversy of alkali carbonate reaction:state of art on the reaction mechanism, paper to be presented at the 14th ICAAR.
- [12] D Lu, B Fournier, P E Grattan-Bellew, Z Xu, M Tang (2008), Development of a universal accelerated test for alkali-silica and alkali-carbonate reactivity of concrete aggregates, Materials and Structures, 41 : 235-246

TABLE 1: Chemical Composition of FA and MK 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

TABLE 2: Chemical and Mineral Compositions of Aggregates wt%

	Chemical Composition						Mineral Composition	
	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	MgO	LOI	Dolomite	Calcite
YT	0.76	0.75	0.20	29.60	21.76	46.55	97.34	—
CK	3.14	10.16	0.89	40.31	5.51	37.88	25.19	58.30

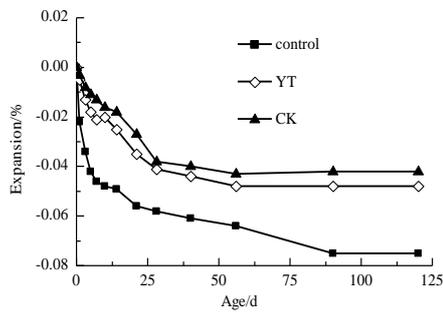


FIGURE 1: Linear dimensional change curves of geopolymer binder and mortars cured at 23°C with a relative humidity over 95%

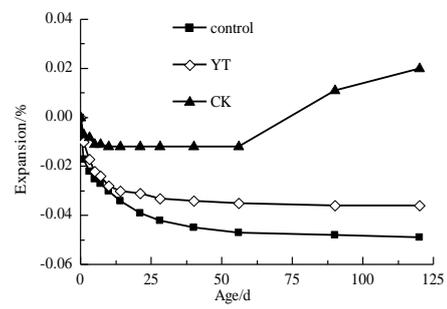


FIGURE 2: Linear dimensional change curves of geopolymer binder and mortars cured at 38°C with a relative humidity over 95%

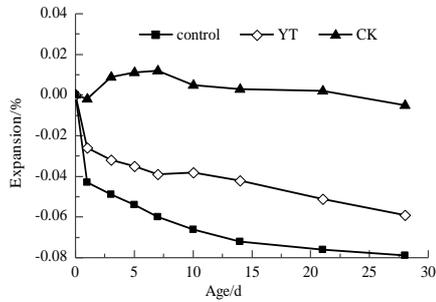


FIGURE 3: Linear dimensional change curves of geopolymer binder and mortars immersed in 1M NaOH solution at 80°C