

CHARACTERISTICS OF ALKALI-SILICA REACTION IN ALKALI-ACTIVATED SLAG CEMENT SYSTEMS

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ABSTRACT

In the paper, alkali-silica reaction (ASR) expansion of alkali-activated slag cement (AASC) Portland cement (OPC) mortars were measured using the mortar bar test. Influence of modulus of water glass on ASR expansion of AASC mortars was studied, and composition of product of ASR in AASC system and OPC system were detected by way of XPS analysis. Results show that alkali-activated slag cement system may generate dangerous ASR expansion, and the factors such as total amount of alkali and content of aggregate as well as modulus of water glass have important effects on the expansion of AASC mortars. The higher the content of active aggregate, the larger the expansion, and the more amount of alkali, the larger the expansion. The expansion of AASC mortars is much higher than that of OPC mortars due to the differences between the two systems in reaction degree and composition of ASR product.

Key words: Alkali-silica reaction, Alkali-activated slag cement, Expansion.

1 INTRODUCTION

Alkali-activated slag cement (AASC) is a super high alkali one in which alkali takes up 2%~6% of the total mass (counted as Na_2O equivalent) and grind blast furnace slag over 80%[1]. The composition and hydration mechanism of this binder is much different from that of ordinary Portland cement [2]. It has been proved that [3,4] it might generate dangerous alkali-silica reaction expansion when active aggregate exists. Up to now, researches on alkali-aggregate reaction of alkali-activated slag cement is limited, and worries on AAR of AASC system are one of the most important issues to obstacle application of the cement. Thus, research on the characteristics of AAR in AASC system is of important significance.

2 RAW MATERIALS AND EXPERIMENTS

2.1 Raw materials

Alkali: water glass was used as an alkali activator, its chemical composition and main properties were shown as Table 1. Chemical grade NaOH was used to adjust modulus of the water glass.

Slag: blast furnace slag from Chongqing Iron-Steel Corporation was used, and its composition is shown in Table 2.

Cement: ordinary Portland cement from Chongqing cement plant was used as a reference cement, its composition is shown in Table 2.

Aggregate: quartz glass (GL) with particle size in the range of 0.15~0.75mm was used as active aggregate, and standard sand meet with requirements of china's specification GB178-77 was used as non-active aggregate.

Table 1 Chemical composition and main properties of water glass

Na ₂ O content (%)	SiO ₂ content (%)	Water content (%)	Modulus (M)
12.11	31.70	42.97	2.70

Table 2 Composition of slag and ordinary Portland cement

Constitute (%)	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	SO ₃	Na ₂ Oequiv.
Slag	40.00	33.14	12.91	2.80	6.75	2.08	/	0.69
Cement	58.36	21.97	6.72	3.43	2.13	1.84	2.24	0.85

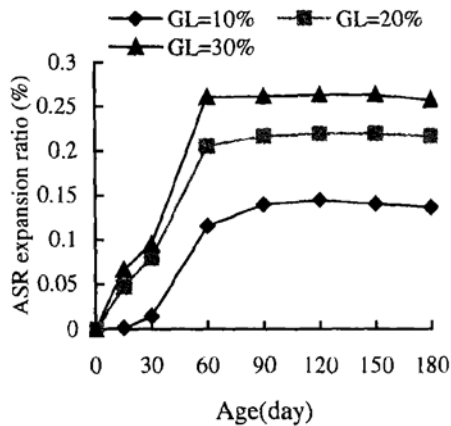
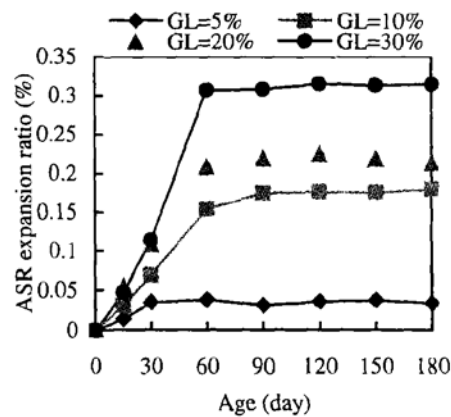
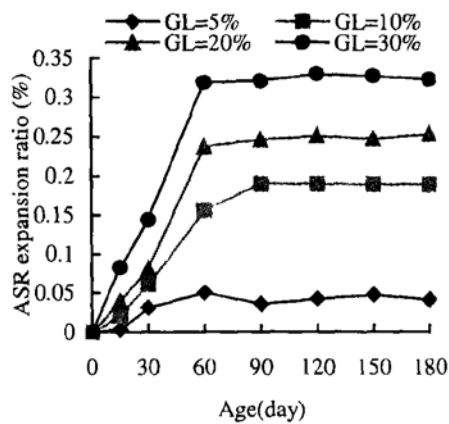
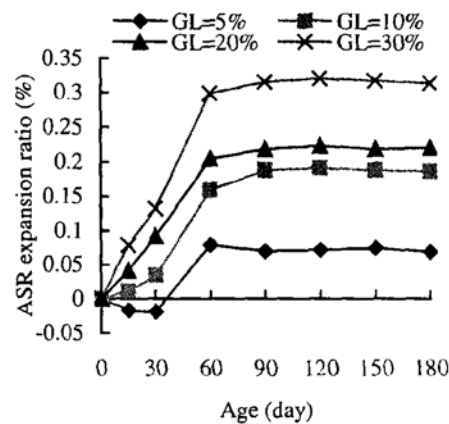
(a) Na₂O=3%(b) Na₂O=4%(c) Na₂O=5%(d) Na₂O=6%

Fig.1 ASR expansion ratio of AASC mortars
(Water glass with modulus of 2.0 is used as alkali component)

2.2 Experiments

Alkali-silica reaction (ASR) expansion was measured using the mortar bar test. Mix proportion of the mortar is that binder: aggregate: water: alkali (Na₂Oequiv.)=1:2.25:0.40:(0.03~0.06). The mortar mixtures were mixed according to the proportion and cast prisms with size of 10×10×60mm, and the

stainless steel studs were inserted in each end of the prisms. After on day of curing at room temperature, the mortars were placed in a sealed container with a controlled temperature of 38±2°C and a relative humidity of greater than 95% for curing.

3 RESULTS AND DISCUSSIONS

3.1 ASR expansion of AASC mortars

ASR expansion of AASC mortars containing different amounts of alkali and active aggregate were measured at different ages. Results are shown as Fig. 1. In order to compare the difference in ASR expansion between AASC and ordinary Portland cement, ASR expansion of ordinary Portland cement mortars were also measured, and results are given as Fig. 2.

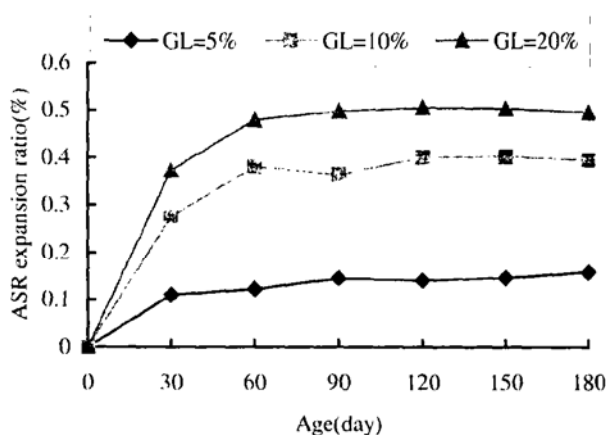


Fig.2 ASR expansion ratio of OPC mortars
($\text{Na}_2\text{O}_{\text{equiv.}}=1.5\%$)

It can be seen that the total amount of alkali and of active aggregate have important influences on the ASR expansion of AASC mortars. ASR expansion

increases as the alkali content increase in the range of 3%~6% when other factors keep constant. The 180-day ASR expansions of AASC mortars containing more than 5% active aggregate have exceeded the limit of 0.1% and were dangerous. The higher the content of active aggregate, the larger the ASR expansion of the mortars. Though the ASR expansions of AASC mortars increase as curing time increases, the expansion almost kept constant after 60 –days of curing, that the expansion of ordinary Portland cement mortars increases with age continuously. The most important reasons lie in the strong dispersal effects of high alkali solution on the active aggregate. Thus, the ASR expansions of AASC mortars are in the safe range when the content of active aggregate is lower than 5%.

Fig. 1 and Fig. 2 illustrate that total amounts of alkali in alkali-activated slag cement are much higher than that in ordinary cement, expansion of AASC mortars generated from ASR is much lower than that of OPC mortars for given age content of active aggregate. ASR expansion of OPC mortars at age of 180 days has already exceeded 0.1% even when active aggregate is only 5% of the total.

3.2 Influences of modulus of water glass on ASR expansion of AASC mortars

In order to investigate the influences of modulus of water glass on ASR expansion of AASC mortars, length changes of mortars at different ages were measured, and are shown as Fig. 2. It illustrates that ASR expansion of AASC mortars changes with modulus of water glass when content of Na_2O and active aggregate are the same. When modulus is lower than about 2.0, ASR

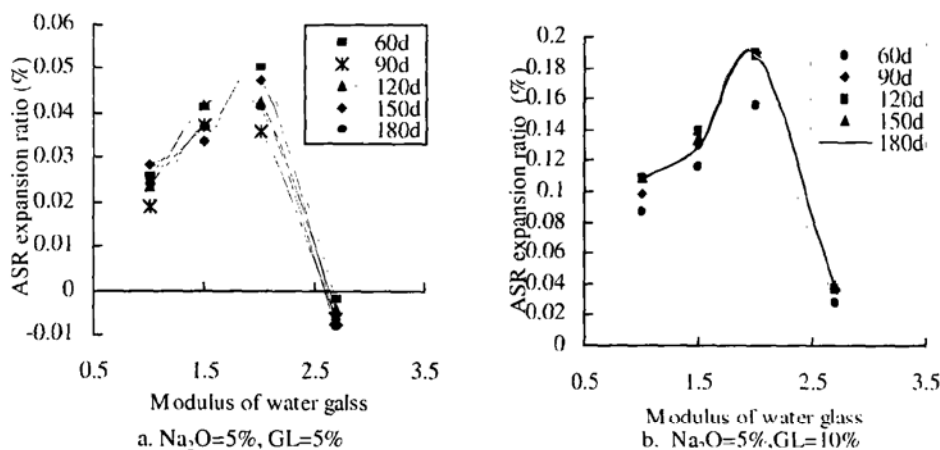


Fig. 3 Influence of modulus of water glass on ASR expansion ratio of AASC mortars

expansions of AASC mortars increase with modulus, ASR expansions of AASC mortars decrease with as the modulus of water glass increases. Water glass is most common alkali component for alkali-activated slag cement, and the lower modulus indicates the alkali solution has lower viscosity and high ratio of $\text{Na}_2\text{O}/\text{SiO}_2$, and the solution has very strong ionic force to accelerate dispersion of active aggregate and the rate of ASR, and leading to larger expansion in the end. When the modulus of water glass increases to certain degree, the amount of SiO_2 in the liquid phase increases, this might lead to the migration of dissolved Si^{4+} from active aggregate to liquid be difficult, and the movement of Ca^{2+} and alkali ions from liquid to surface of active aggregate be difficult also. The changes may slow down speed of ASR and reduce

total amount of product formed in the process of ASR. This may be the most important reasons for ASR expansion of AASC mortars decreases with modulus of water glass increases within the range of 2.0~2.7.

3.3 Composition of product of ASR in AASC system

The expansion ability of ASR products is intimately connected to its composition. Though the quantitative relationship between ability of ASR product and its composition is not clear, it is known that [5] expansive alkali-silica gel contains certain amount of Na_2O and CaO as well as Si^{4+} (SiO_2). In the experiment, atoms distribution on the surface of active aggregate in AASC mortars and ordinary Portland cement mortars were measured using XPS analyzer, as given in Table 3 and Table 4.

Table 3 Atom distributions on the surface of active aggregate in AASC system

Etching time (min.)	Na	K	Si	Ca
0	7.0	7.0	72.1	3.5
4	1.9	1.0	92.4	1.8
10	1.3	0	97.9	0.6

It can be seen from Table3 that the number of alkali atom and calcium atom decreases with etching time increase, whereas the number of silica atom increases with etching time increases. The results indicate that alkali-silica reaction in AASC mortars is developed gradually from surface of active aggregate. Results in Table3 and Table 4 show that surface of active aggregate in OPC system is richer in Ca and Si, and poor in alkali ions relatively. Surface of active aggregate is the location for alkali-silica reaction, so the distributed atoms on surface of active aggregate can stand for composition of ASR product. Alkali silica reaction is a solid-liquid one, and the composition of the reaction product is affected by

composition of liquid phase. It is known that [6] liquid phase in alkali-activated slag cement paste is rich in K^+ and Na^+ and poor in Ca^{2+} . This may be the most important reason for the ASR product in AASC system has the character mentioned above.

Corrosion time and atoms distribution indicate thickness or the degree of ASR indirectly, and results gained from XPS analysis show that the degree of ASR in OPC mortars is higher than that in AASC mortars. The fact that the expansion of AASC mortars is much higher than that of OPC mortars at the same age is just resulted from the differences between the two binder systems on reaction degree and composition of reaction product.

Table 4 Atoms distribution on the surface of active aggregate in OPC system

Etching time (min)	Na	K	Si	Ca
0	5.5	7.8	81.9	4.7
2	2.3	0	96.1	1.5
4	2.1	0	96.3	1.4
14	1.7	0	96.9	1.2

4 CONCLUSIONS

From above mentioned, it can be concluded as fellows: (1) alkali-activated slag cement mortars may generate dangerous ASR expansion, and the expansion is less than 0.1% when total amount of alkali is in the range of 3%~6% and content of active aggregate does not exceed 5%. (2) ASR expansions of AASC mortars increase as amount of alkali and active aggregate increases, and AASC mortars perform the highest ASR expansion when modulus of water glass is about

2.0. (3) ASR product formed in AASC mortars is rich in K^+ and Na^+ and poor in Ca^{2+} in comparison with that in OPC mortars.

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