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Effects of alkali dosage and silicate modulus on alkali-silica reaction in alkali-activated slag mortars

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ABSTRACT

The effects of silicate modulus and alkali dosage on alkali-silica reaction (ASR) of alkali-activated slag (AAS) mortars are investigated under accelerated mortar bar testing conditions as specified in ASTM C1260. At a given alkali dosage, an intermediate silicate modulus with respect to highest ASR expansion is observed, which increases from 1.0 to > 2.0 with increase of alkali dosage. The effect of silicate modulus on ASR expansion is found to be governed by the pore solution alkalinity. At a given higher silicate modulus such as 1.5 and 2.0 at 14 day, the ASR expansion tends to increase with increase of alkali dosage, whereas it decreases with increase of alkali dosage at a given lower silicate modulus such as 0–0.5 at 28 day. The mechanism governing the effect of alkali dosage on ASR expansion is more complicated and cannot be explained by only the pore solution alkalinity.

1. Introduction

Alkali activated cements have received considerable attentions over the past decades as a result of their low environmental impact and comparable properties to traditional hydraulic cements [1]. Although these materials can be produced by alkali activation of a variety of industrial by-products and waste (e.g. fly ash and slag) as well as a number of aluminosilicate raw materials (e.g. metakaolin and natural pozzolans), much of the development and application of alkali-activated or alkaline cements is limited to alkali-activated slags (AAS) due to its rapid strength development and more consistent raw materials. For the purpose of alkali activation, several alkalis and alkaline salts can be used as alkaline activators including alkaline metal or alkaline-earth hydroxides (MOH or $Me(OH)_2$), weak acid salts (M_2CO_3, M_2SO_3, MF), strong acid salts (Na_2SO_4, $CaSO_4{\cdot}2H_2O$) and $M_2O{\cdot}nSiO_2$-type silicates, where M is alkaline ion such as Na^+, K^+ or Li^+ [2]. Depending on the types of precursors and alkali activators, alkali-activated cements can exhibit a wide variety of properties. Among the above listed alkaline activators, the hydrated sodium silicates (waterglass) have shown optimal mechanical resistance and good durability [2]. Although alkali-activated cements have several advantages against traditional Portland cements, their high alkali concentration may raise the concern of alkali-silica reaction (ASR) [3].

Many studies [4–6] have investigated the effect of alkali dosage and silicate modulus on the hydration and strength of AAS cements. It is generally true that the higher alkali dosage used, the higher the compressive strength obtained within the practical range of 2–8% by slag weight [4–6]. Above this range, the compressive strength may decrease along with the increase of alkali dose [4]. The effect of silicate modulus on the compressive strength is more complicated. At a given alkali dosage (2–8%), the higher the silicate modulus the more the contribution from silica gel and the higher the compressive strength within a certain range (0–optimum silicate modulus). Above this modulus range, the compressive strength can decrease with the increase of silicate modulus. The optimum silicate modulus is found to be lower when the slag alkalinity is lower [4]. In addition to the changes in compressive strength, the alkali dosage and silicate modulus can also alter the pore solution chemistry. Song and Jennings [7] reported that the concentrations of Si and Al were high and the concentration of Ca was low at high pH. Liu [8] reported that the concentration of Si increased with the increase of silicate modulus, whereas the concentration of Al was decreased.

The changes in mechanical performance and pore solution chemistry as discussed above suggest that the AAS mortars with different alkali dosages and silicate modulus may exhibit different resistance against ASR. Shi et al. [3] reviewed the effect of alkali dosage and/or silicate modulus on ASR. Some studies reported that ASR expansion increased with the increase of alkali dosage [9–11], and others reported

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Table 1
Chemical compositions of the binder materials (wt%).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3
SL	33.00	13.91	0.82	39.11	10.04	1.91	–	0.16

that ASR expansion decreased with the increase of alkali dosage [12, 13]. Yang et al. [9] reported that waterglass-activated slag mortars exhibited highest ASR expansion at intermediate silicate modulus of 2.0 at a given alkali dosage of 5%. However, Al-Otaibi [11] reported that concretes with silicate modulus of 1.65 had significant lower expansion than the ones with silicate modulus of 1.0, when the alkali contents were 4 and 6%. From these studies, it can be seen that the effect of alkali dosage and silicate modulus on ASR of AAS concrete is still not conclusive.

In light of the discrepancies of the results reported in previous studies [9–13], the aim of this study is to investigate systematically the effect of alkali dosage and silicate modulus on the ASR expansion. To better understand the mechanisms, the mass gain, formation of ASR products, compressive strength, total porosity and the hydroxyl ion concentration of the extracted solution have also been investigated.

2. Experimental

2.1. Raw materials

Granulated blast-furnace slag (SL) was used in this study as the solid raw materials of alkali activated cement (AAC) manufacturing. The chemical composition of the slag was determined by X-ray florescence and is given in Table 1. Waterglass with silicate modulus (Ms = SiO_2/Na_2O by mass) of 0.5, 1.0, 1.5 and 2.0 were prepared by adding analytical grade sodium hydroxide (NaOH, purity 99% ± 1) into an industry grade waterglass with Ms of 3.3 (water content of 65.2 wt%). Sodium hydroxide was also used as an activator, which was regarded as a waterglass with silicate modulus of 0. The aggregate used for mortar preparation was natural sand from Xiangjiang River, Hunan, China. The sand was sieved and remixed to the particle size distribution requirement as per ASTM C1260 [14]: 10% (4.75–2.36 mm), 25% (2.36–1.18 mm), 25% (1.18–0.6 mm), 25% (0.6–0.3 mm), 15% (0.3–0.15 mm). The sand grains have relatively smooth surfaces and irregular shapes, which contains a significant fraction of reactive siliceous components, i.e., cryptocrystalline and microcrystalline quartz in greywacke fragments as reported in an earlier study [15, 16]. Moreover, the measured expansion of the Portland cement mortars containing the same aggregates following the ASTM C1260 method indicated that the sand used in the present study are alkali reactive [17].

2.2. Mortar preparation

Alkali-activated slag mortar specimens (25 mm × 25 mm × 285 mm) were prepared with one part of waterglass activated slag and 2.25 parts of graded sand by mass at a water-to-binder ratio of 0.47. The slag was activated using the prepared NaOH and waterglass solutions containing different alkali dosages, i.e., 4, 6 and 8 wt% Na_2O by mass of the slag. The mix proportions of the studied mortars are summarized in Table 2. The activator was pre-mixed with mixing water. The mortars were mixed and then cast in 25 mm × 25 mm × 285 mm molds. After casting, the mortar specimens with molds were stored in a standard curing room at 20 ± 2 °C with relatively humidity (RH) above 95% for 24 h. Then, the specimens were demolded and subsequently steam cured in a chamber at 80 °C for 22 h. This curing process avoids the problem of alkali leaching at the very early reaction of AAS in the water bath conditions, as pointed out in [18]. Mortars with different silicate modulus above 0 were labeled as M0.5, M1.0, M1.5 and M2.0.

Table 2
Mix proportions of the waterglass activated slag mortars (wt%).

Mortar ID	Alkali dosage	Silicate modulus (SiO_2/Na_2O)	Sand/slag	water/binder
–	4, 6 and 8% Na_2O (by weight of slag)	0	2.25	0.47
M0.5		0.5		
M1.0		1		
M1.5		1.5		
M2.0		2		

2.3. Accelerated mortar bar test

The accelerated mortar bar test was considered to investigate the ASR expansion of the studied mortars following the procedures described in ASTM C1260 [14]. Three mortar specimens for each mixture were submerged in 1 mol/L NaOH solution in a sealed plastic container then stored in a chamber at 80 °C following the curing procedure described in the previous section. After 2 h of exposure in the NaOH solution, the initial length of the mortar specimen was measured using a digital length comparator. Subsequent lengths of the specimens were measured after 1, 3, 5, 7, 10, 14, 21 and 28 days of exposure. Each reported expansion value was an average of measurements from the three specimens. The mass change of the mortar specimen was determined by weighing the specimen immediately after the length measurement. This method is used in the present study since it is especially useful for aggregates which reacts slowly or produces expansion late in the reaction [14], whereas alternative methods such as ASTM C227 [19] are not suitable for such aggregates (e.g. greywacke) according to previous study [20].

2.4. SEM/EDX examinations

Scanning electron microscopy and energy-dispersive X-ray analysis (SEM/EDX) were performed on selected mortar samples after 28 days of exposure in 1 mol/L NaOH solution using an environmental scanning electron microscope (FEI Quanta-200). The samples were cut into slices with a thickness of 10 mm and submerged in isopropanol for 3 days, followed by a drying process in a vacuumed incubator at 60 °C for 2 days prior to analysis. Thus, SEM/EDX was performed on flat but non-polished surface in order to see the full morphology of the ASR products. It should be mentioned that the morphology and chemical composition of the ASR products are independent of the locations because the cut surface of the samples does not always allow the distinction between pastes and aggregates. Therefore, five to ten points of each interesting area were analyzed to obtain the average chemical composition of the ASR products.

2.5. Alkalinity of the extracted solution

The concentration of hydroxyl ion (OH^-) in the extracted solution was determined after 0, 1, 7, 14 and 28 days of exposure following the procedure described in ref. [21]. Mortars were firstly surface dried using wet cloth, then ground and passed through 0.30 mm sieve as fast as possible to minimize the potential risk of carbonation. Powered sample of 50 g was collected and mixed with 50 g distilled water in sealed plastic bottles. The bottles were rotated for 3 days at 20 °C and