



Effect of the inherent alkalis of alkali activated slag on the risk of alkali silica reaction



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ABSTRACT

Alkali silica reaction (ASR) occurred in the alkali activated slag (AAS) concrete was evaluated by a revised mortar prism method. The mortars were made of blast furnace slags activated by alkali silicate solution possessing different modulus (0.5, 0.75, 1 and 2) as well as cations (sodium and potassium) and standard sand with a volume replacement of 25 vol% by borosilicate glass beads. Their changes in length and dynamic elastic modulus were monitored up to 7 months. The results showed that ASR has taken place among some mortars, which were evident under both light microscopy and electron microscopy with EDX analysis. The results also revealed that high alkali content did promote the risk of ASR but the degradation due to ASR was affected in a much more complex way.

1. Introduction

Alkali-silica reaction (ASR) occurs when the amorphous or poorly crystallized silica phase in an aggregate is attacked by the OH⁻ of alkali hydroxide in the pore solution of concrete [1]. The subsequent degradation arises as a result of physicochemical responses due to ASR reaction, but not necessarily as a result of the reaction itself [2]. The alkali originated from cement together with sufficient moisture and alkali-reactive aggregate are essential for the initiation and progression of ASR in concrete, inducing micro cracks generated by swelling alkali-silica gel [3]. Therefore, cement with low Na₂O_{eq} (where the K₂O content is included on a molar equivalent basis) is recommended to inhibit ASR in concrete [4,5].

Recently, alkali activated materials have drawn great attention since they manifest their potential for low CO₂ emission [6] and reusing of a high proportion of supplementary cementitious materials (SCM), like fly ashes, ground granulated blast furnace slags or silica fume. The typical alkali content in alkali activated slag binders reaches 2–5% by weight of slag [7,8]. Thus the alkali content employed in these materials is much higher than a typical restriction of 0.6 wt% Na₂O_{eq} for OPC [9]. On the one hand, the high alkali content may arise the risk of ASR; on the other hand, it has long been proved that SCM such as blast furnace slag and fly ash etc. can mitigate the deterioration of ASR in Portland cement concrete (PCC) [10,11]. It was also found that SCM with high calcium content was less effective, i.e. higher replacement of such materials was required to achieve the desired effect. Indeed, the

role of calcium in the destructive ASR has been explored [2,12–14], while its presence has a significant influence on the expansion of ASR gel. Thus, alkali-activated slag (AAS) concrete containing alkali-reactive aggregate should be used with caution particularly with respect to the degradation due to ASR, since ground granulated blast furnace slag (GGBFS) contains a relative large proportion of calcium.

In terms of expansion due to ASR in AAS concrete, a few studies have been carried out [8,15–19]. Gifford and Gillott [15] found that AAS based concrete (6% Na₂O_{eq} by weight of slag from sodium silicate or sodium carbonate) with reactive siliceous aggregate exhibited much lower expansion after one year than that of PCC according to CSA A23.2-14A-94 (38 °C, 100% R.H.). In contrast, Bakharev et al. [16] conducted the investigation under a similar condition according to ASTM C 1293 but observed an opposite result. They found that AAS based concrete (5.4% Na₂O_{eq} by weight of slag from sodium silicate and sodium hydroxide) was more likely to be deteriorated due to ASR than PCC. Chen et al. [8] further conducted a systematic experiment under 38 °C and 95% R.H. by varying alkali activators (type, dosage) and slag (basic, neutral, acidic) in AAS concrete. They concluded that the expansion induced by AAS mortar is influenced by the slag chemistry (more expansion with basic slag than with acidic slag), but were systematically lower than that by PCC. Al-Otaibi [18] received a neutral result when the AAS concrete (4–6% Na₂O_{eq} by weight of slag from sodium silicate and sodium metasilicate) made of reactive aggregates was stored under higher temperature (60 °C, 100% R.H.) according to BSI DD218. While more critical test condition was applied

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(immersed in 1 M NaOH solution at 80 °C), Fernández-Jiménez and Puertas [17] found that AAS concrete (4% Na₂O_{eq} by weight of slag from sodium hydroxide) exceeded the criteria according to ASTM 1260-94 after 80 days of immersion but was still lower than that of PCC. Wang et al. [19] also confirmed that trend while varied parameters (e.g. alkali content and type of activator) in the mix design of AAS were applied.

In general, most of the publications agree on the conclusion that the potential of the degradation due to ASR in AAS concrete is less than that in PCC at equivalent conditions. Though low alkali content in PCC is not sufficient to inhibit the deterioration due to ASR [9], high alkali content in AAS concrete seems to be a risk with respect to ASR. The reaction, however, does not necessarily lead to the deterioration if certain prerequisites are fulfilled [20]. Therefore, this paper aims to differentiate ASR and the deleterious expansion in the presence of high inherent alkalis within AAS. A basic slag was activated by alkali silicate solution by varying parameters to prepare AAS. Mortar prisms (4 · 4 · 16 cm³) made of AAS and CEN reference sand (EN 196-1) out of which 25 vol% were replacement by borosilicate glass beads, were casted. The mortar prisms were stored in a climate chamber revised from the German Alkali-Guideline [21] (40 °C and 100% R.H.). Their length changes and dynamic E-moduli were monitored up to 7 months. Besides, selected samples were analyzed by optical microscopy and SEM to link the reaction and the expansion.

2. Materials and methods

2.1. Materials

GGBFS with a glass content of 99 wt% was used in this study. The Blaine test showed a specific surface area of 4150 cm²/g. Its chemical composition is shown in Table 1. Several sodium and potassium silicate solutions (Woellner GmbH & Co. KG, Ludwigshafen, Germany) were used as alkaline activators, which differ in their moduli (SiO₂/M₂O with M = Na, K) but the alkali concentrations were kept constant (2 or 4 mol/kg alkali in the silicate solution) for all the samples. Table 2 shows the activators used in the study. As can be seen, the SiO₂ content rises with higher modules for a constant alkali concentration. The abbreviations for the activators in the text and graphs were composed of the alkali water glass, its silicate module and alkali concentration (e.g. K-WG-1.0 (2): potassium water glass with module of 1.0 and alkali concentration of 2 mol/kg).

Borosilicate glass beads with a mean diameter of 3.5 mm and a density of 2.23 g/cm³ were employed as the reactive aggregates in this study, its chemical composition is shown in Table 3.

2.2. Methods

Alkali activated slag binders were prepared by mixing the slag with the same amount of different alkali silicate solutions (Table 2) and additional water to get a water-to-slag-ratio of 0.4. The slag/aggregate ratio is set as 1/3, where 25 vol% of CEN reference sand (according to EN 196-1) is replaced by borosilicate glass beads. This aggregate combination has been proved by Ott and Wolter [22] to be effective to demonstrate the alkali reactivity in Portland cement mortar and concrete. As a reference, some samples with pure CEN reference sand were prepared. Sample preparation was in compliance with EN 196-1 and the storage of the specimens was according to the concrete test (storing in a climate chamber at 40 °C and 100% R.H.) of the German

Table 1
Chemical composition of the slag [wt%].

SiO ₂	Al ₂ O ₃	FeO	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	S ²⁻
36.9	10.9	0.3	0.7	37.3	11.2	0.3	0.7	0.8

Alkali Guideline issued by the DAfStb (German Committee for Reinforced Concrete) [21]. The prisms were casted with a dimension of 4 · 4 · 16 cm³, while measuring pins were embedded on both face sides. They were stored at 20 °C and 65 R.H. for 23 ± 1 h. After demolding, initial length and resonance frequency of the specimen were recorded. Resonance frequency (f_R) was determined by laser vibrometry. The setting and operating mode are described in literatures [22,23]. The dynamic elastic modulus was calculated from the measured resonance frequency by employing following equation:

$$E_{\text{dyn}} = 4 \cdot f_{\text{R}}^2 \cdot l^2 \cdot \rho$$

where,

E_{dyn} is the dynamic elastic modulus;

l is the length of the prism;

ρ is the density of the prism.

The specimens were then transferred into the climate chamber and taken out at specific ages for the measurements.

At the end of storing in the climate chamber, some selected samples were prepared as polished sections and thin sections for the investigation under optical microscopy (Zeiss Stereomicroscope Stemi SV 11) as well as SEM (Hitachi S-4000) by employing backscattered electron detector. The chemical composition of the interfacial zone between borosilicate glass beads and paste matrix was also analyzed by EDX.

3. Results and discussion

3.1. Length change of the mortar prisms

As described before the focus of these investigations was the potential of alkali silica reaction of alkali activated slag mortars with borosilicate glass beads as a reactive aggregate. Nevertheless, the influence of reactive and non-reactive aggregates on the properties should be randomly monitored. Therefore, selected mortars with potassium silicates were chosen and measured additionally with non-reactive aggregates. So far, only the influence of sodium silicate solutions with variable alkali concentration has been studied on the drying and autogenous shrinkage [24]. High alkali silicate solution resulted in extremely high drying shrinkage but moderate autogenous shrinkage. Several authors found that drying shrinkage of AAS mortar increased with the increase of silicate modulus (M_s = SiO₂/M₂O) [24–27]. Fig. 1 presents the length change of the mortar prisms with reactive and non-reactive aggregates. For samples with non-reactive aggregates, the AAS mortar prisms shrank as expected. Apparently, autogenous shrinkage dominates the process in our study because the measurements were done under moist conditions, which favors ASR (40 °C and 100% R.H.). An increase in alkali concentration was insignificant with respect to AAS mortar shrinkage. For our measurements it seems that the modulus and consequently the SiO₂ content play a similar role on autogenous shrinkage as described above for drying shrinkage. Nevertheless, AAS mortar with non-reactive aggregates behaves as normal. For samples with reactive borosilicate glass beads, the samples with K-WG-0.75 (2) and K-WG-2.0 (2) shrank, while only the sample K-WG-2.0 (4) expanded. In particular, when comparing the samples K-WG-2.0 with and without reactive aggregates the influence of the ASR potential can be seen. The lower shrinkage for K-WG-2.0 (2) and the expansion for K-WG-2.0 (4) is an effect of a reaction between the alkalis of the activator with the borosilicate glass beads. That resulted in an expansion which compensated the shrinkage. The height of shrinkage and expansion depends on the modulus of the activator. As a rule of thumb, RILEM TCC 224-AAM stated that there is some evidence that expansions increase with the alkali content (M₂O) of the mix and decrease with increasing silicate modulus (M_s = SiO₂/M₂O) [7].

However, the results presented in Fig. 2a) and b) make the rule

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