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The alkali–silica reaction in alkali-activated granulated slag mortars with reactive aggregate

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Abstract

The expansion of alkali-activated granulated blast furnace slag (AAS) cement mortars with reactive aggregate due to alkali–silica reaction (ASR) was investigated. The alkaline activator used was NaOH solution with 4% Na_2O (by mass of slag). These results were compared to those of ordinary portland cement (OPC) mortars. The ASTM C1260-94 Standard Test Method based on the NBRI Accelerated Test Method was followed. The nature of the ASR products was also studied by SEM/EDX. The results obtained show that the AAS cement mortars experienced expansion due to the ASR, but expansion occurs at slower rate than with OPC mortars under similar conditions. The cause of the expansion in AAS cement mortars is the formation of sodium and calcium silicate hydrate reaction products with rosette-type morphology. Finally, in order to determine potential expansion due to ASR, the Accelerated Test Method is not suitable for AAS mortars because the reaction rate is initially slow and a longer period of testing is required. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Alkali–silica reaction; Alkali activated cement; Granulated blast furnace slag

1. Introduction

In ordinary portland cement (OPC) mortar and concrete, the alkali–silica reaction (ASR) takes place between potentially reactive aggregates and the alkalis present in cements ($Na_2O + K_2O$), $Ca(OH)_2$ under favourable humidity conditions. The absence of one of these factors reduces or can even inhibit reaction and, consequently, expansion. Some authors [1,2] point out that the ASR is not merely a reaction between the alkalis present in the porous solution and the reactive aggregate, but sufficient Ca^{2+} ions are also required (which are supplied by the portlandite ($Ca(OH)_2$) in the OPC paste). The general outline of this process, which was established by Plum and Poulsen in 1958 [3] is:

$$Ca(OH)_2 + SiO_2 + NaOH + H_2O$$
$$\rightarrow n_1Na_2O \cdot n_2CaO \cdot n_3SiO_2 \cdot n_4H_2O$$

Regarding the above reaction, NaOH stands for the equivalent M_2O (M = Na and K). The resulting gel will have an expansive nature depending on the content of CaO [1,2].

The presence of granulated blast furnace slag in OPC concrete either minimises or slows down the destructive process of ASR, because the slag is able both to fix the cement alkalis and also to reduce the concentration of portlandite. According to some authors [1–5], the absence of $Ca(OH)_2$ may be considered as a positive factor to reduce the possibility of ASR.

Although alkali-activated slag (AAS) cements are characterised by the absence of $Ca(OH)_2$ (positive factor), the concentration of alkalis is high, over 3% in many cases (OPC usually contains less than 0.8%). The high alkali content can promote ASR together with reactive aggregates.

Some authors point out that [6–8] it is not possible for ASR to take place in the activated slag mortar, because all or almost all the alkalis (more than 80%) are combined in the different hydration products. Others [5,9] indicate that in activated slag mortars with opaline aggregates, the expansion can take place.

According to the former paragraphs, we think that it is necessary to study the behaviour of these alkaline materials in the presence of potentially reactive aggregates. In this way, the objective of the present work was to determine the

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Table 1
Chemical composition of slag, reactive aggregate and portland cement (%)

	SiO_2	CaO	Al_2O_3	MgO	Na_2O	K_2O	Fe_2O_3	SO_3	LOI[a]	IR[b]	CO_2
Aggregate	44.8	27.7	–	1.57	–	–	0.16	–	24.7	24.9	22.9
Slag	35.5	41.4	12.2	8.3	0.58	0.64	1.01	–	–	0.2	–
Cement	18.2	62.8	5.96	1.43	0.2	0.54	2.17	3.50	3.48	1.65	–

[a] Loss on ignition.

[b] Insoluble residue.

degree of expansion and the nature of the reaction products formed as a consequence of the ASR in AAS mortars if alkali aggregate (opaline) is used.

2. Methods

2.1. Materials

A Spanish granulated blast furnace slag with a specific surface of 460 m^2/kg was used. Its chemical composition is shown in Table 1. A potentially reactive aggregate (opal) with a reactive silica content of 21% was also used. Its chemical composition is presented in Table 1. The granulometry distribution of the opal aggregate used is shown in Table 2.

2.2. Tests

The test used to evaluate the ASR was ASTM C1260-94 [10,11]. It is designed to determine the potential deterioration caused by the ASR in cement mortars in a short time (16 days). In this work, the test lasted 140 days.

Mortar specimens (2.5 × 2.5 × 23 cm) were prepared, with a slag/aggregate ratio of 1/2.25. The aggregate had a fixed grain size according to the ASTM conditions (see Table 2). As activator, NaOH solution 4% of Na_2O (by mass of slag) was used with a solution/slag ratio 0.57. The mortar specimens were cured in the mould for 24 h at 25 °C and 99% of relative humidity (RH). After this time, they were demoulded, and the initial reading was taken. The specimens were stored in containers with deionized water (reference mortar) and also in a solution of 1 N NaOH. After the containers were sealed, they were maintained in an oven at 80 °C. The specimens were measured periodically during 140 days. These samples were also analysed by SEM/EDX at the end of the test (140 days).

Table 2
The granulometry distribution of the opal aggregate used

Sieve size		
Passing	Retained on	Mass, %
4.75 mm (No. 4)	2.36 mm (No. 8)	10
2.36 mm (No. 8)	1.18 mm (No. 16)	25
1.18 mm (No. 16)	600 μm (No. 30)	25
600 μm (No. 30)	300 μm (No. 50)	25
300 μm (No. 50)	150 μm (No. 100)	15

In order to compare the results obtained in the AAS mortars with those of OPC mortars, such OPC mortars were submitted to the same conditions. An EN CEM I 42.5 cement (OPC) was used, whose chemical composition is shown in Table 1.

3. Results

3.1. Alkali–silica reaction

Fig. 1 shows the values of both shrinkage and expansion obtained for AAS and OPC mortars. The slag mortars activated with 4% Na_2O and stored in 1 N NaOH solution initially shrink before expanding. AAS mortars stored in deionized water do not expand except for a small initial expansion. The cement mortars stored in deionized water and those ones stored in 1 N NaOH solution have a higher expansion than the respective AAS mortars (see Fig. 1).

Fig. 2 shows the variation of weight obtained for the AAS and OPC mortars with time. AAS mortars stored in 1 N NaOH solution initially decreased in weight coinciding with the mentioned shrinkage before (see Fig. 1). Later, the specimens increased in weight in all cases.

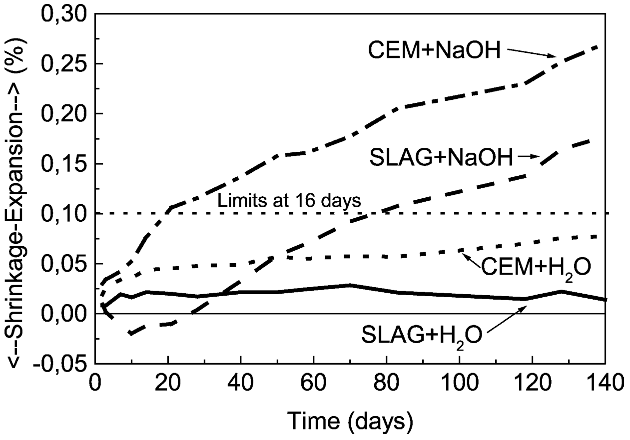

Fig. 1. Expansion curves. (SLAG + NaOH = AAS mortars stored in 1 N NaOH solution; SLAG + H_2O = AAS mortars stored in deionized water; CEM + NaOH = OPC mortars stored in 1 N NaOH solution; CEM + H_2O = OPC mortars stored in deionized water.)

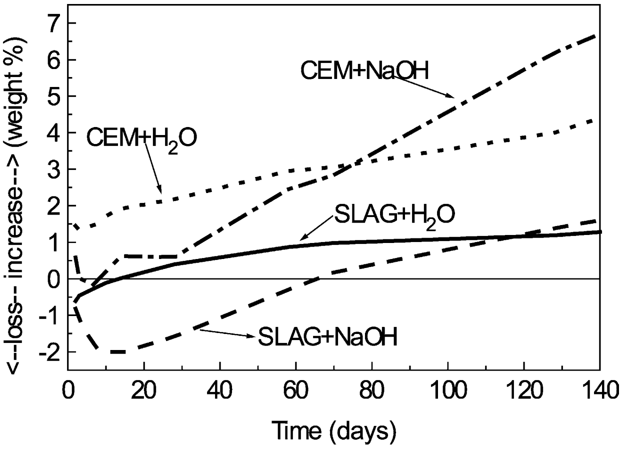

Fig. 2. Change in weight of AAS and OPC mortars with the time.

3.2. Characterization of the reaction products.

This characterization was done by SEM/EDX. Fig. 3(a) shows the surface of the reactive aggregate. The aggregate particles are characterized by the absence of Na, low content of Al and Mg and C/S = 0.36 (see Table 3).

Fig. 3(b) shows AAS mortar stored in deionized water for 140 days at 80°C. The sample has few microcracks and a small amount of pores. Little attack was seen on the surface of aggregate by the formation of a gel without Al and low Mg content. Fig. 3(b) shows also the morphology of the main reaction products of AAS, this is a calcium silicate hydrate with C/S = 0.71, A/S = 0.26 and N/S = 0.07 (see Table 3). This product, according to Davidovits [12], can be named as NCASH.

Fig. 4 shows features of the AAS mortars stored in 1 N NaOH solution at 80°C for 140 days. These mortars display a good interfacial aggregate–paste zone. However, they have more cracks, both in the paste and in the aggregate than those stored in water. The main products formed in AAS was a calcium silicate hydrate with low Al and Na content (C/S = 0.82 and A/S = 0.16; see Table 3). As second products, a bar-type reaction product was observed on the surface of the aggregate (Fig. 4(a)). This phase is associated with the formation of an initial sodium and calcium silicate hydrate gel with a high Na ($Na_2O \cong 30\%$) content. This phase is formed in the first stages of ASR. This gel is characterized by C/S = 0.18 and N/S = 0.59 (analysis P1, Table 3). In addition, rosette-type crystals (Fig. 4(b)) corresponding to a sodium and calcium silicate hydrate at a more advanced stage of ASR were observed in pores in the aggregate. This phase has a composition rich in Si ($SiO_2 = 68\%$), Ca (CaO = 14.3) and Na ($Na_2O = 17.1$) (analysis P2, Table 3).

The OPC mortars stored in 1 N NaOH solution at 80 °C for 140 days show a high degree of cracking both in the paste and in the aggregate (see Fig. 5(a)). In this case, the main products formed was a calcium silica hydrate (C-S-H) type gel with C/S = 1.09 (see Table 3). As second reaction products, a massive gel-type characterized by the absence of Al, high Na content and a low C/S ratio (C/S = 0.24 and N/S = 0.38, analysis P3, Table 3) was observed in this mortar. In addition, crystals with a sword-type morphology (Fig. 5(b)), which are associated with a more advanced stage of ASR (C/S = 0.18 and N/S = 0.23, analysis P4, Table 3), are present in the pores.

4. Discussion

In this investigation, ASR in AAS mortars, activated with 4% of Na_2O using an opaline aggregate (with 21% reactive silica), was studied and compared with OPC mortars under similar conditions.

The Accelerated Test Method [10,11] was employed to enhance the rate of reaction. According to ASTM C1260, expansion at 16 days, less than 0.10% is indicative of innocuous behaviour, but more than 0.20%, is considered as a potentially deleterious expansion.

4.1. Absence of external alkalis

Cement (OPC) mortars stored in deionized water gave an expansion of about 0.05%. With OPC mortars, the presence

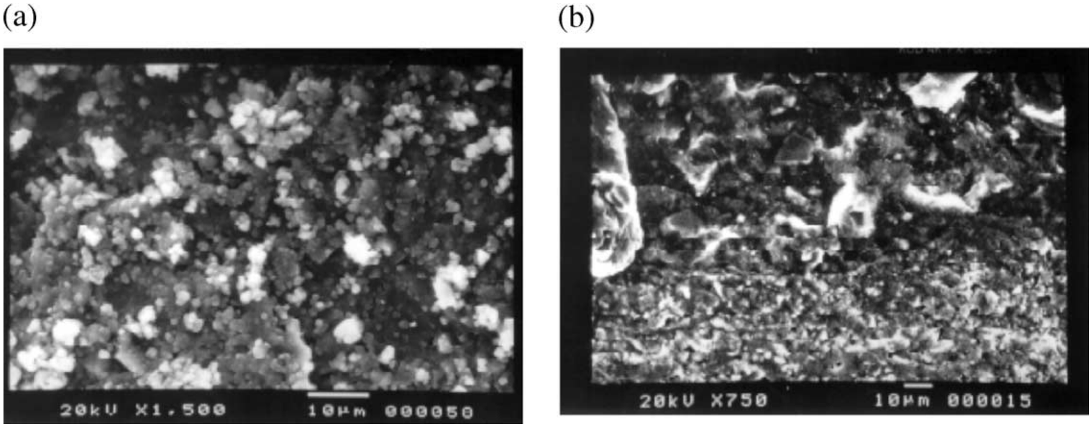

Fig. 3. (a) Surface of the reactive aggregate (opal); (b) AAS mortar stored in deionized water at 80 °C for 140 days.

Table 3
Elemental composition determined by EDX

		NaO (%)	MgO (%)	CaO (%)	Al_2O_3 (%)	SiO_2 (%)	SO_3 (%)	C/S	A/S	N/S
Aggregate (opal)		–	2.01	26.02	–	71.97	–	0.36	–	–
AAS (water)	Aggregate	0.65	1.87	31.42	–	65.18	0.25	0.48	–	–
	Pastes	3.11	8.31	30.45	10.92	42.58	2.46	0.71	0.26	0.07
AAS (1 N NaOH)	Aggregate	12.17	2.53	35.62	–	49.67	–	0.72	–	0.24
	Paste	4.95	5.10	36.34	6.99	44.21	2.40	0.82	0.16	0.11
	P1	31.25	6.67	9.33	–	52.75	–	0.18	–	0.59
	P2	17.07	0.59	14.27	–	68.07	–	0.21	–	0.25
OPC (1 N NaOH)	Aggregate	5.48	0.24	29.40	1.1	62.59	1.20	0.47	–	0.09
	Paste	1.86	2.28	47.3	3.2	43.34	1.56	1.09	0.07	0.04
	P3	23.09	–	14.76	–	61.1	0.67	0.24	–	0.38
	P4	15.96	–	12.46	1.6	70.17	–	0.18	0.02	0.23

P1 = bar type (Fig. 4(a)); P2 = rosette type (Fig. 4(b)); P3 = massive gel; P4 = sword type (Fig. 5(b)).

of portlandite favours ASR because it provides Ca^{2+} ions in solution. However, ASR is limited by the relative low concentration of available alkalis (0.76%), and, consequently, nondeleterious expansion occurs.

AAS mortars stored in deionized water expand less (0.02%) than OPC mortars under the same conditions (see Fig. 1). Microstructural analysis by SEM/EDX shows that ASR products are absent (see Fig. 3(b)). This is because in AAS mortars, most of the alkalis are fixed in the different reaction products as the calcium silica hydrate formed with low Na and Al content. This gel is characterised by a lower C/S ratio (C/S = 0.7–0.8) than those formed in cement paste (C/S = 1.1) (see Table 3). Gels with a low C/S ratio and high Al content have more Na^{+} ions in their structure [4]. Therefore, a competition between the slag and ASR is established. This factor, together with the absence of free Ca^{2+} ions, justifies the low expansion of the AAS mortars stored in water compared to OPC mortars, despite the higher alkali content. This agrees with Krivenko's [13] results.

4.2. In the presence of external alkalis

When the alkali content is high, mortars stored in 1 N NaOH solution at 85°C, both AAS and OPC mortars expand.

The OPC mortars have a low concentration of alkalis, which limits the expansion when stored in water. However, when they are stored in 1 N NaOH solution, there are sufficient alkalis and Ca^{2+} ions in the solution for the formation of expansive products from reaction with the reactive aggregate. For this reason, ASR takes place from the first moment, reaching a 0.08% of expansion in a period of 16 days (see Fig. 1), very close to the deleterious limit (0.10%), which was exceeded after 20 days. The SEM/EDX studies clearly showed that sodium and calcium silicate reaction products (C/S = 0.24–0.18 and N/S = 0.38–0.23; see Table 3) with massive- and sword-type gel morphologies were formed. In these samples (Fig. 5), the presence of portlandite crystals was not observed.

The AAS mortars stored in 1 N NaOH solution expanded less than OPC mortars under similar conditions in spite of their higher alkali content. The reason is that, in the AAS mortars, there is competition between the slag and the aggregate for the alkalis and also the small amount of Ca^{2+} ions in the pore solution. In this case, the main product of AAS mortars was a calcium silicate hydrate with low Al and Na content (C/S = 0.82, A/S = 0.16 and N/S = 0.11) similar to that formed in AAS mortars stored in water (see Table 3). Later, when the reaction time increased, at a

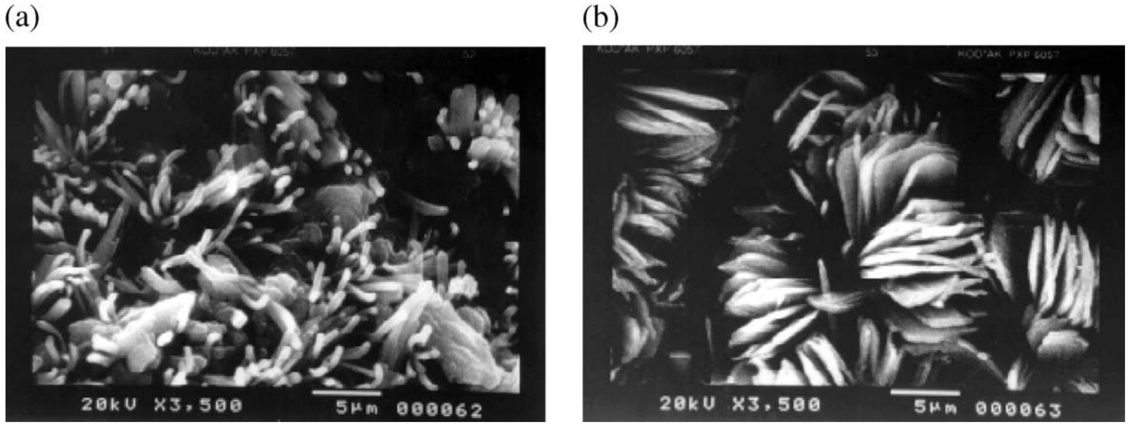

Fig. 4. AAS mortar stored in 1 N NaOH solution at 80 °C for 140 days (a) reaction product on the surface of aggregate; (b) rosette-type reaction product in pores.

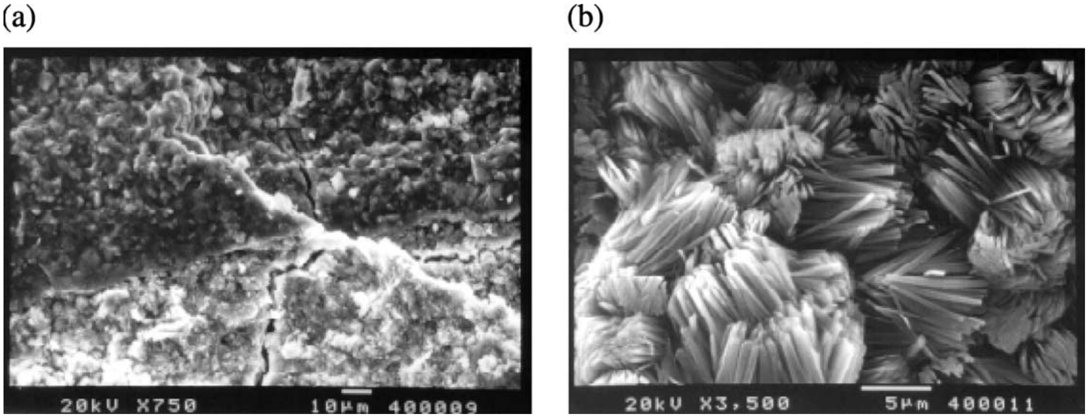

Fig. 5. OPC mortar stored in 1 N NaOH solution at 80 °C for 140 days (a) area of aggregate–paste interphase; (b) sword-type gel in pores.

high alkali content, a second reaction product formed to produce expansion. This is a sodium and calcium silicate hydrate gel ($C/S = 0.18–0.21$ and $N/S = 0.59–0.25$) with bar- and rosette-type morphology (see Fig. 4).

On the other hand, a densification of the 1 N NaOH solution, whose OPC and AAS mortar specimens were stored, was observed. This densification was more in AAS mortars than in OPC mortars. In the first days of reaction, a greater loss of weight of AAS mortars stored in 1 N NaOH solution than in those of OPC mortars was observed. These losses in the OPC mortars were about 0.17% in 7 days, whereas in the AAS mortars, it was about 2.02% in 14 days. Later on, the weight of the specimens increased (see Fig. 2). A possible explanation for this loss of initial weight would be the one given by Davies and Oberholster [11] who observed that OPC mortars submerged in a solution of NaOH showed a slight exudation of tobermorite-type gel.

Finally, the initially slow rate of expansion in AAS mortars shows that the Accelerated Test Method [10,11] is not the most suitable test to determine possible expansion due to ASR in the AAS mortars. The Accelerated Test Methods [10,11] permit detection within 16 days of the potential for deleterious ASR of aggregate in OPC mortar bars. In AAS mortars, this time is insufficient. If the test is limited to 16 days, deleterious ASR may not be observed for the AAS mortars, giving a misleading result (see Fig. 1). Some authors point out that the test should continue for at least 6 months [1,2,4]. We agree with it regarding AAS mortars.

5. Conclusions

In the absence of external alkalis, AAS mortars expand ($< 0.02\%$) less than OPC mortar under similar conditions. In the presence of external alkalis, AAS mortars, with reactive silica containing opaline aggregate, expand due to ASR. However, the expansion rate is less than that of OPC mortars under similar conditions, in spite of the higher alkali content. The rate of ASR in AAS mortars is initially less than that of OPC mortars because of competition between the slag and the aggregate for the alkalis.

For determining the potential expansion due to ASR in AAS mortars, the Accelerated Test Method (16 days) is not suitable. The rate of reaction is initially slower than that of OPC mortars, and it requires a longer period of testing.

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