



Comparison of alkali–silica reaction products of fly-ash- or lithium-salt-bearing mortar under long-term accelerated curing

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Abstract

The alkali–silica expansion of mortar specimens bearing fly ash (FA), lithium carbonate, and lithium fluoride under long-term accelerated curing was investigated. ASTM C1260 standard test method was applied and expansions were recorded up to 56 days. The composition of alkali–silica reaction (ASR) products was also studied by environmental scanning electron microscopy (ESEM). It was observed that in Li-bearing mixtures, the expansions ceased beyond 28 days. However, in fly-ash-bearing mixtures, the reactions were continued and expansions were increased steadily throughout the test. No clear correlation was found between the composition of massive reaction products and expansion values. However, except for lithium-fluoride-bearing samples, good correlation was observed between the composition of crystallized reaction products and expansion values.

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1. Introduction

The interaction between alkali and reactive silica in the presence of moisture leads to alkali–silica gel, which swells upon moisture absorption. The composition of the gel varies widely, depending on the temperature and age of the reaction, concentration and nature of the reactants (alkalies and reactive silica), admixtures and/or additions used. Alkali–silica gel may be regarded as a mixture of alkali–silicate hydrate and calcium silicate hydrate phases [1,2].

Morphologically, alkali–silica reaction (ASR) products may be divided into two distinct types, gels and crystals. Gels should be either massive or textured (grainy, spongy, or foliated). Crystalline products are described as lamellar or rosettelike, needle or rodlike, and bladlike crystals. Massive gel may partially transform into textured gel with time [3]. The rosettelike crystals are observed at more advanced stages of ASR [4].

Thaulow et al. [5] examined 4- to 9-day-old steam cured, prestressed concrete railroad ties by SEM-EDX analysis. It was stated that, generally, gel in close contact with cement

paste was more Ca rich in older than in younger concretes and that the content of Ca in gel in cracks increased away from aggregate particles. Therefore, they implied that the Ca content of gel is a result of a reaction between gel and paste, and calcium richness of gel is time dependent irrespective of the position of the gel.

Moranville-Regourd [2] made semiquantitative analyses (by mass) of ASR products of mortar bars made with quartz-bearing metasediment from tests at 80 °C in 1 N NaOH or KOH. The average chemical composition of massive gel was found to be SiO₂ = 61.7%, CaO = 16.3%, Na₂O = 17.7%, and K₂O = 1.2%; corresponding values for a rosettelike ASR product were reported to be SiO₂ = 71.7%, CaO = 12.4%, Na₂O = 14.8%, and K₂O = 0.4%. Calculated SiO₂/CaO (S/C) ratios for massive gel and rosettelike product were 3.57 and 5.55, respectively.

Wigum and French [6] examined gel compositions in voids of 14-day-old mortar bars produced with different types of aggregate cured according to ASTM C1260. Calculated S/C ratio values of gels of mortar bars produced with three reactive aggregates (% expansion >0.1) varied between 2.5 and 2.7, where the same value for gels of mortar bars produced with an innocuous aggregate (% expansion <0.05) was 4.6.

Fernandez-Jimenez and Puertas [4] studied both ordinary portland cement (OPC) + reactive aggregate and alkali-acti-

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Table 1
Chemical composition of cement and FA

Material	Composition (%)											
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Free CaO	Na ₂ O	K ₂ O	Na ₂ O _{eqv}	IR	LOI
Cement	20.18	5.70	3.27	62.64	2.05	2.11	0.89	0.36	1.11	1.09	0.51	1.23
Fly ash	52.34	18.91	9.30	7.47	5.75	2.25	0.20	0.88	2.05	2.24	–	0.92

vated slag (AAS)+reactive aggregate mortar bar samples that were under long-term (140 days) ASTM C1260 curing. At the end of 140 days curing, both of the samples showed high expansion (>0.1%) in 1 N NaOH solution, and their gel compositions were identified. The OPC sample showed higher expansion than the AAS sample. The AAS sample had S/C ratios of 5.65 and 4.76 in bar-type and in rosette-type reaction products, respectively. The OPC sample had S/C ratios of 4.14 and 5.63 in massive gel and in sword-type reaction products, respectively.

The effects of lithium hydroxide or several lithium salts on the ASR have been investigated by many researchers. It is known that some Li-bearing compounds including LiF and Li₂CO₃ are able to suppress the expansion caused by the ASR [7–9]. However, the mechanism of this behavior is not yet well understood [10].

Since the early 1990s, ASR has been a significant problem throughout the Aegean region. Some deleterious expansion caused by ASR has occurred in many highway bridges built in this region. Research showed that volcanic aggregates of the Gediz and Nif riverbed and terraces were the primary cause of the reaction. An extensive study is still going on in the Materials of Construction Laboratory of the Civil Engineering Department at Ege University to minimize the deleterious expansion by using mineral and chemical admixtures. The present study, as a part of this research, was done to investigate the chemistry and morphology of reaction products of some selected mortar bars, which were under long-term curing (56 days) in ASTM C1260 con-

ditions (80 °C, 1 N NaOH), by using environmental scanning electron microscopy (ESEM).

2. Materials and methods

2.1. Materials

Mortar bars meeting ASTM C1260 specifications were prepared with one type of cement and one type of reactive aggregate. Fly ash, lithium fluoride, and lithium carbonate were used as admixtures. Selected mixtures, showing different expansions, were chosen for microstructural investigation. Cement used was a high-alkali (Na₂O_{eqv} = 1.09%) Type I portland cement conforming to the relevant Turkish Standard. The aggregate was a highly reactive one, which previously showed unsatisfactory field performance in many ASR-affected bridges. The major minerals of fly ash (FA) detected by X-ray diffraction (XRD) were quartz, feldspar, dolomite, and illite. The specific surface area of FA was 425 m²/kg and its 28-day pozzolanic activity index with cement was 79.7%. Chemical compositions of cement and FA are given in Table 1. Lithium fluoride and lithium carbonate were commercial products of around 99% purity.

2.2. Mixture characteristics of mortar bars

Various mixtures of the reactive and nonreactive aggregates were prepared to obtain the pessimum percentage causing maximum ASR expansion. The maximum 14-day expansion was obtained in a mixture containing 75% reactive aggregate and 25% nonreactive aggregate. This mixture, called the control mixture, is designated as AT in

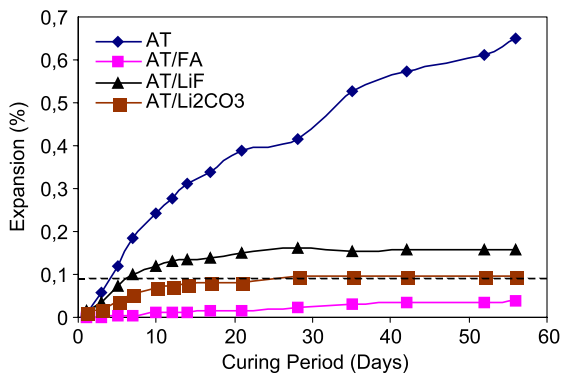


Fig. 1. Expansion curves of mortar specimens.

Table 2
Average chemical compositions of gel products

Item	AT		AT/FA		AT/LiF		AT/Li ₂ CO ₃	
	M	C	M	C	M	C	M	C
SiO ₂	45.62	52.05	44.22	38.72	25.46	21.94	52.71	46.13
CaO	19.36	12.95	9.58	25.28	33.46	23.59	9.20	19.95
MgO	0.73	0.60	0.87	0.57	0.25	1.08	1.35	0.85
Na ₂ O	14.23	18.71	14.77	9.68	0.86	2.99	2.86	8.11
K ₂ O	1.88	0.53	1.54	0.46	0.34	0.58	5.18	1.47
Na ₂ O _{eqv}	15.47	19.10	15.79	9.98	1.08	3.37	6.28	9.08
CaO/SiO ₂	0.42	0.25	0.22	0.65	1.32	1.08	0.17	0.43
E _{BIV}	0.55	0.41	0.39	0.72	0.96	0.87	0.57	0.68
56-day expansion (%)	0.651		0.039		0.159		0.098	

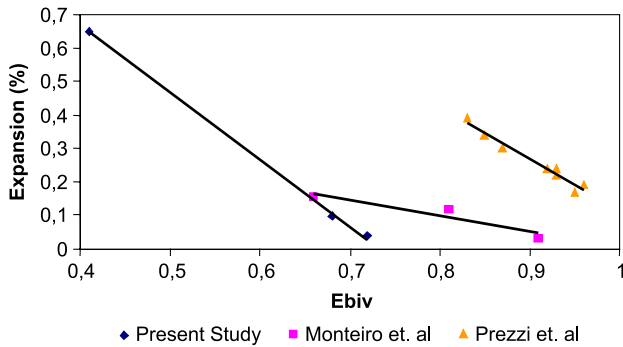


Fig. 2. Plot of E_{BIV} and expansion values of the crystallized reaction products.

this study. AT/FA denotes the mixture in which 40% (by mass) of cement was substituted with FA. AT/LiF was produced by adding 0.75% lithium fluoride (by mass of cement) to the mixing water. AT/Li₂CO₃ was produced by adding 2% lithium carbonate (by weight of cement) to the mixing water. Both Li salts were added in an initial molar concentration of about 0.12 in the mixing water. All three mixtures had the same amount of aggregate as the control mixture. W/C ratios of the mixtures were equal to 0.47 as specified in ASTM C1260. Expansion measurements were performed on at least three mortar bars. Average values are reported.

2.3. ESEM

A Philips XL30 environmental scanning electron microscope equipped with energy dispersive X-ray analyzer (EDAX) was used for microstructural studies. A gaseous secondary electron detector was used in ESEM (wet mode). Samples did not undergo a coating process.

3. Results and discussion

The expansion values of various mixtures up to the age of 56 days are given in Fig. 1. Fourteen-day expansion

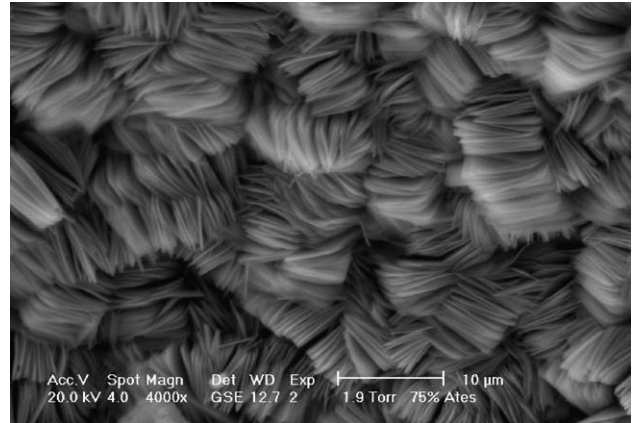


Fig. 4. Micrograph of crystallized reaction product of AT sample.

values of AT and AT/LiF samples are above the standard limit (>0.1%), whereas FA and LiCO₃ additions caused significant decrease in expansion. Compared to 14-day expansions, the control mixture (AT) and the sample AT/FA showed significant increase in expansion after 28 days, whereas the length of samples containing chemical admixtures (AT/LiF and AT/Li₂CO₃) remained almost constant beyond 28 days. The same trend of expansion after 28 days' curing was also observed in 0.5% and 1.0% LiF-bearing as well as 3% and 4% Li₂CO₃-bearing mixtures, details of which were reported elsewhere [11]. Note that the gel-aging hypothesis is consistent with expansion test results of Li-bearing samples. However, it seems that the reaction products in fly-ash-bearing samples are being produced steadily throughout the test without any drop in the rate.

Massive, textured, and crystallized reaction products were observed in all of the samples. Crystalline and textured reaction products were generally observed on the surface of massive gel layers. Average chemical compositions of reaction products taken from at least six locations of each sample and their 56-day expansions are shown in Table 2, where M denotes clear massive gel and C denotes textured gel or crystalline product. Fifty-six-day expansions are taken into consideration because ESEM observation of all

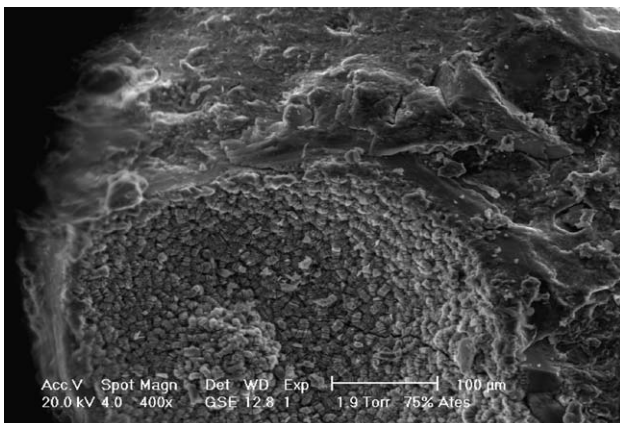


Fig. 3. Micrograph of reaction product of AT sample.

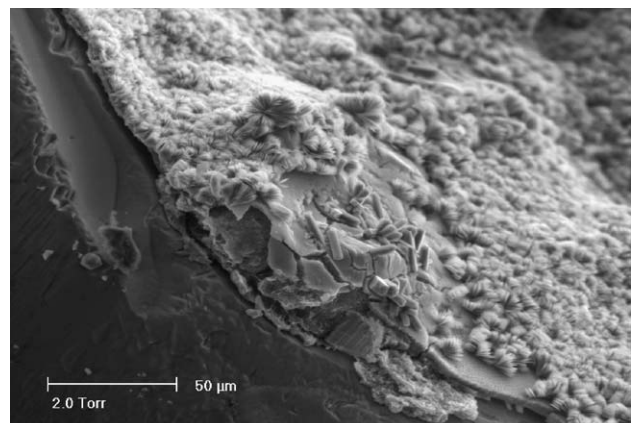


Fig. 5. Micrograph of reaction product of AT/FA40 sample.

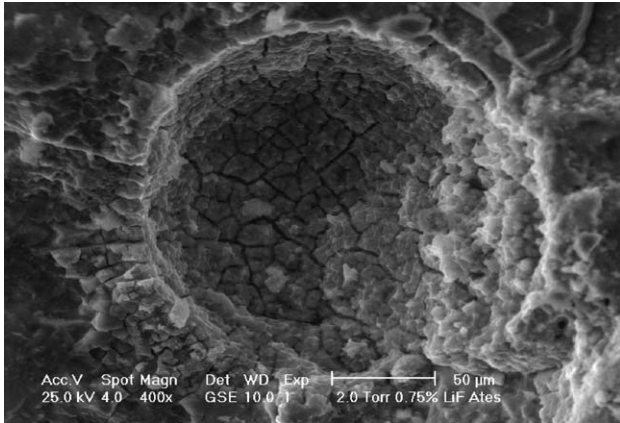


Fig. 6. Micrograph of reaction product of AT/LiF sample.

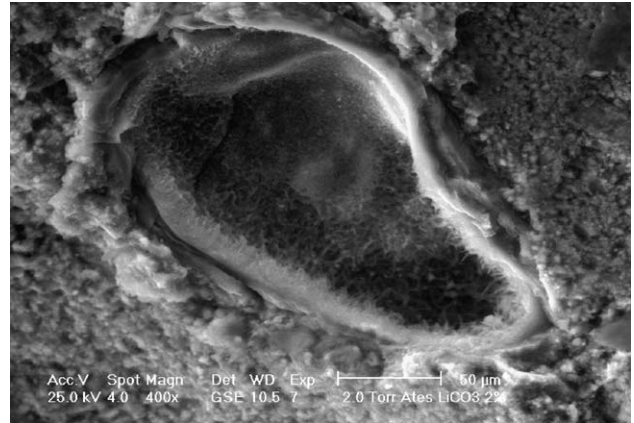


Fig. 8. Micrograph of reaction sample product of AT/Li₂CO₃.

samples was carried out on 56-day-old specimens. The ratio of bivalent cations (E_{BIV}), is calculated by the formula given by Prezzi et al. [10] and Monteiro et al. [12]:

$$E_{BIV} = \frac{(\text{mol CaO} + \text{mol MgO})}{(\text{mol CaO} + \text{mol MgO} + \text{mol Na}_2\text{O} + \text{mol K}_2\text{O})} \quad (1)$$

No clear correlation was found between the composition of massive gels and corresponding expansion values. These products were mainly located in the vicinity of the aggregate; thus the probability of some calcium or silica contamination in the reaction product is high. Besides, if the thickness of the gel layer was small, the ESEM analysis may have picked up calcium from the paste underneath.

Except for the LiF-bearing mixture, the C/S ratios of the crystallized gel formed in mortar bars varied between 0.25 and 0.65. Similar ranges are reported in the literature for gels examined using EDX techniques [10]. The C/S ratio of crystallized reaction products increased from the control sample that expanded the most, to the FA sample that expanded the least.

Except for the LiF-bearing sample, experimental results show strong negative correlation between expansion and E_{BIV} values of the crystallized reaction products as shown in Fig. 2. In the same figure, a similar relationship proposed by other investigators is also presented. There is good agreement between the results obtained in these studies. Moreover, the gel compositions reported by other investigators were obtained on a larger number of locations than considered in this study. The slight differences between the results of the present and previous studies may have arisen from the differences between the reactivity of the aggregates used, the duration of curing of the specimens in NaOH solution, and the number of locations considered for gel composition evaluation. In this study, the specimens were cured in NaOH solution for 56 days, whereas in the other two investigations the curing period was 30 days only.

It should be noted that Li cannot be detected by ESEM analysis; therefore, the actual values of E_{BIV} in Li-salt-bearing samples are expected to be lower than that given in Table 2.

AT and AT/LiF samples, which show deleterious expansion (>0.1%) and visual cracking at 56 days have higher S/C

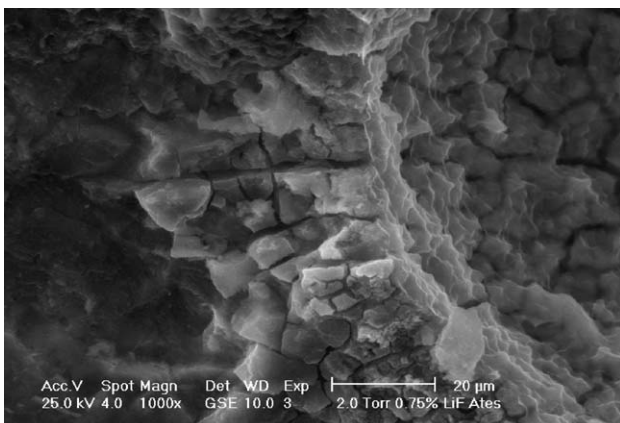


Fig. 7. Micrograph of reaction product of AT/LiF sample.

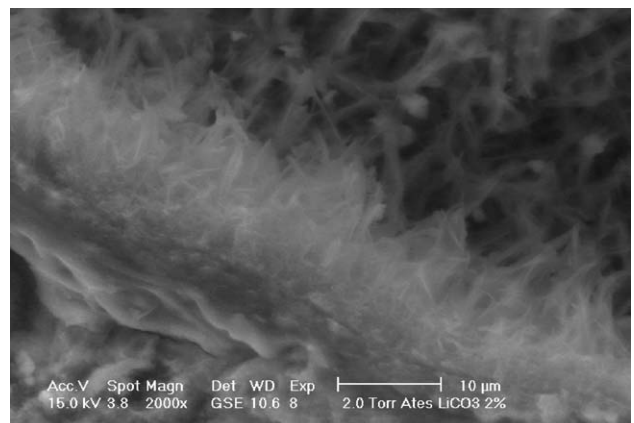


Fig. 9. Micrograph of reaction sample product of AT/Li₂CO₃.

values in crystallized or textured gels than in massive gels. In contrast, the other two samples that show innocuous behavior ($<0.1\%$) have higher S/C values in massive gels than in crystallized or textured ones. It seems that at early stages of reaction, massive gels form, which transform partially into textured or crystallized type over time. During this transformation, when some Ca ions are taken into the gel structure, a considerable reduction occurs in its expansion. However, interestingly, the increase in CaO content of the crystallized gel as compared to its massive counterpart is not necessarily accompanied by a reduction in its $\text{Na}_2\text{O}_{\text{eqv}}$. It means that Ca ions are not necessarily exchanged for alkali ions during gel transformation.

ESEM micrographs of the selected samples are shown in Figs. 3–9. Fig. 3 is taken from inside a void of AT sample. Textured gel and crystalline products are located on cracked massive layers. Fig. 4 is a $10\times$ magnified view of crystallized (rosettelike) reaction product.

Fig. 5 is taken from the sample AT/FA where some crystalline products are observed on cracked massive gel.

Fig. 6 is taken from a void of AT/LiF sample; Fig. 7 is a $2.5\times$ magnified view of the same micrograph. A different textured gel is observed where cracks are clearer.

Figs. 8 and 9 are taken from a void of AT/ Li_2CO_3 sample where a clear foliated structure is observed.

The morphology of the gel products seems to be independent of the expansion values, but rather changes with the admixture used. Fly ash does not have a prominent effect on morphology of crystalline gel; the product (rosettelike) is quite similar to the control sample. The morphology of the crystalline gel product is changed due to the addition of two different lithium salts. Textured and foliated structures as well as some platelike structures are observed instead of rosettelike gel product.

4. Conclusions

From the materials used and test methods applied in this study, the following conclusions may be drawn:

1. Gel aging hypothesis is consistent with expansion test results of Li-bearing samples beyond 28 days. However, in FA-bearing mixtures the reactions were continued and expansions were increased steadily throughout the test.
2. Massive reaction products formed in the vicinity of aggregate or in thick layers over the paste may be contaminated by aggregate, or ESEM analysis may pick up some elements from the paste underneath. Thus, no clear correlation was found between the composition of massive reaction products and expansion values.
3. The composition of crystallized reaction products, formed on the massive gel, on the other hand, showed good correlation with expansion values. Except for LiF-bearing samples, the expansion is larger for lower E_{BIV} values or lower CaO/SiO₂ ratios.
4. The increase in CaO content of the crystallized gel as compared to its massive counterpart is not necessarily accompanied by a reduction in its $\text{Na}_2\text{O}_{\text{eqv}}$ content. Thus, Ca ions are not necessarily exchanged for alkali ions during the transformation of massive gel into crystallized one.

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