Effect of Alkali-silica Reaction on Delayed Ettringite Formation in Concrete

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We investigated the effects of alkali-silica reaction (ASR) on delayed ettringite formation (DEF) using mortar test pieces comprising ASR reactive aggregates with added potassium sulfate under various environmental conditions. As a result, it was observed that ASR not only promotes expansion caused by DEF, it causes the expansion to occur prematurely, even under conditions where the amount of sulfate and water supply are not significantly large. The increased DEF expansion could be attributed to microcracks accompanying the progress of ASR at high temperatures, and the decrease in the cured product's pH owing to the consumption of an alkaline component during ASR. However, the final expansion caused by DEF tended to be less in mortars where ASR had occurred.

Keywords: ettringite, alkali-silica reaction, expansion, complex deterioration

1. Introduction

Delayed ettringite formation (hereafter, “DEF”) is known as a cause for the deterioration of concrete structures. DEF is a gradual reformation of ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$, Fig. 1), following their original formation in concrete and subsequent decomposition in high temperatures. Ettringite is a normal product of early cement hydration and has in itself no influence on concrete deterioration. On the other hand, DEF, a reformation of ettringite in hardened concrete, causes the concrete to expand and possibly crack over the years. Incidences of DEF-induced expansion and cracking have been reported typically in steam cured precast concrete structures in Japan and abroad and in cast-in-place concrete structures abroad that have been subjected to extreme heat of hydration [1][2].

It is said that DEF-induced expansion is likely to occur in concrete structures that have been subjected to high temperatures, have a high sulfate ratio and are in contact with large amounts of water after hardening [3]. A study on DEF reported numerous events of extreme expansion of concrete pieces with an excessive sulfate ratio when they were dipped in water, a DEF promoting environment. In addition, cases have been reported in which concrete structures that neither have a high sulfate ratio nor are in contact with a large amount of water, i.e. in an ordinary environment, deteriorated due apparently to DEF or a combination of DEF and alkali-silica reaction (hereafter, “ASR”) [4]. In the cast-in-place concrete structure shown in Fig. 2, observation of the concrete core using an electron microscope revealed needle-shaped ettringite and crabmeat like products (Fig. 3) in the cement paste. It has been reported that these crabmeat like products are similar to ettringite in that they have an approximate Al to S ratio of 2:3 although they have a slightly higher ratio of Ca than ettringite [4]. In addition, SEM observations revealed small amounts of ASR gel and the suggestion of having been subject to a heat of hydration, which together points to the possibility that the crabmeat like products may have been formed due to a combination of ASR and DEF. Although the above possibilities have been proposed, no methods are available today for determining whether cracks in concrete structures are caused by the influence of DEF. It is therefore extremely difficult to ascertain whether the deterioration of concrete structures in an ordinary environment is due to DEF or a combination of DEF and ASR. This would make it difficult to protect concrete structures from further deterioration through appropriate maintenance based on an analysis of causal factors.

Given the above, we examined the possibility of DEF-induced expansion in an ordinary environment and that of deterioration due to a combination of DEF and ASR while focusing on how ASR would affect DEF.

![Fig. 1 SEM observation photo of ettringite in concrete](image1)

![Fig. 2 Concrete structure with apparent attributes of combined DEF/ASR deterioration](image2)

![Chemical composition of the crabmeat like products](image3)
2. DEF/ASR-induced deterioration test and test piece

ASR is a phenomenon in which alkaline components in concrete produce a high pH pore solution, which causes ASR reactive aggregate to turn into ASR gel, which absorbs water and expands, cracking the concrete. Studies have shown that the formation of ASR gel consumes alkaline components in the pore solution, reducing pH, and that the reduced pH facilitates the formation of ettringite [5] [6]. It is known that ettringite can form within ASR-induced cracks in concrete. Ettringite formed in that way is thought not to influence expansion [7]. However, with concrete that has been subjected to high temperatures, the formation of ASR gel and the resultant reduction in pH of pore solution can induce DEF-induced expansion. It appears important, therefore, to clarify what effects DEF can have on expansion to provide appropriate maintenance. Given the above, mortar test pieces with some containing ASR reactive aggregate and some not, were prepared. Using those test pieces, the influence of ASR on DEF was studied by comparing DEF-induced expansion in various environments, pH of pore solutions and reaction products.

2.1 Test pieces

Table 1 Composition of mortar test pieces

| Composition | Fine aggregate | AR reactivity (Total SO₃ ratio) |
|-------------|----------------|---------------------------------|
| A-2%        | A: ASR reactive aggregate + Standard sand | Yes | 2% (4.6%) |
| S-2%        | S: Standard sand | No  |  |
| A-0.5%      | A: ASR reactive aggregate + Standard sand | Yes | 0.5% (3.1%) |
| S-0.5%      | S: Standard sand | No  |  |

Table 2 Environments for mortar test pieces

| Environment | Environment from Day 7 onward | Remarks |
|-------------|--------------------------------|---------|
| 1 20W       | Dipped in 20°C water (Overflow water tank) | DEF promoting environment |
| 2 20M       | 20°C moist atmosphere (R.H. > 90%) | Ordinary environment (DEF-inviting high humidity) |
| 3 40M20W    | 40°C moist atmosphere for 21 days → 20°C water | ASR promoting environment followed by DEF promoting environment |
| 4 40M20M    | 40°C moist atmosphere for 21 days → 20°C moist atmosphere | ASR promoting environment followed by ordinary environment |

Test pieces measuring 4 × 4 × 16 cm were used for the measurements of expansion and mass increase rates. For other analyses, test pieces measuring 4 × 4 × 8 cm were used. The 4 × 4 cm sides on both the long and short test pieces were covered with epoxy resin to offer the same uncovered-surface-area to volume ratio.

2.2 Test content

Table 2 Environments for mortar test pieces

On the test pieces for measuring expansion and mass increase rates, those rates were measured with the mass and length of the test pieces on Day 7 as the reference values. The length of the test pieces was measured using a contact-type strain gauge in accordance with JIS A1129-2:2010 "Methods of measurement for length change of mortar and concrete - Part 2: Method with contact-type strain gauge."

On the test pieces used in the other analyses, a 1 cm-thick samples was cut around the middle of the test piece on a specified day for analysis. Each test sample was pulverized into particles measuring 300 μm or less and the particles were mixed with water of the same mass and agitated for two minutes. The mixture was then filtered and the filtrate was measured for pH at 25°C. Using ion chromatography, sulfate ions (SO₃⁻) in the filtrate were
measured as soluble SO$_4^{2-}$. In addition, the products were investigated using powder X-ray diffraction (XRD) and scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS) capabilities.

3. Results and Discussion

3.1 Products, chemical composition, and pH

SEM observation found that a gelatinous substance (Fig. 4) was found in the A-2% test pieces containing ASR reactive aggregate before they were put in Environments 1 to 4. EDS analysis for gel composition suggested that the gelatinous substance might be alkali silica gel possibly produced during ASR in a high temperature phase. Figure 5 shows pH of the test pieces on Day 7 (before being dipped in water and/or exposed to a moist atmosphere). For both the K$_2$SO$_4$ additive ratios of 2% and 0.5%, the test pieces containing ASR reactive aggregate had a lower pH than those containing standard sand. This appears attributable to alkali components having been consumed during the formation of ASR gel.

Figure 6 shows X-ray diffraction patterns of the test pieces on Day 7 (before being dipped in water and/or exposed to a moist atmosphere) and those of the test pieces 70 days after having been dipped in water or exposed to a moist atmosphere. Focusing on the peak intensity of ettringite at 2$\theta$ = 9.1° (CuK$_{\alpha}$), the peaks were no longer visible on Day 7 on the test pieces, which appears attributable to high temperatures having decomposed the ettringite. In the case of the test pieces with a K$_2$SO$_4$ additive ratio of 2%, on the 70th day ettringite reformed on the A-2% test piece, which contained ASR reactive aggregate, in all environments. With the S-2% test piece, which contained standard sand, ettringite reformation was observed only when it was dipped in water (S-2%-20W), but in smaller amounts than on the corresponding test piece containing ASR reactive aggregate in a similar environment (A-2%-20W). With the test pieces containing a K$_2$SO$_4$ additive ratio of 0.5%, ettringite reformation was observed on the 180th day in all environments, with the A-0.5% test piece containing ASR reactive aggregate showing greater amounts of reforma-

It has been shown in a study that when XRD-detected amounts of crystalline ettringite reformation are greater, DEF-induced expansion is not necessarily also greater [8]. However, the above results at least confirm that ASR is the likely cause of ettringite reformation. While the peaks marked with a circle at 2$\theta$ = 8.8° (CuK$_{\alpha}$) in Fig. 6 have not been identified, those peaks may be K-type AFm phases (K$_4$Ca$_4$Al$_2$O$_{16}$(SO$_4$)$_2$・15H$_2$O). This will be studied further including in relation to DEF. Figure 7 to 9 shows changes in the amount of soluble SO$_4^{2-}$ in the test pieces. Comparison of the test pieces with a K$_2$SO$_4$ additive ratio of 2% or 0.5% in the test environments shows that the amount of soluble SO$_4^{2-}$ tends to decrease earlier in the test pieces containing ASR reactive aggregate than in those containing standard sand. While the decrease in the amount of soluble SO$_4^{2-}$ on

| Compound | [norm. wt%] |
|----------|-------------|
| Na$_2$O  | 0.59        |
| MgO      | 0.39        |
| Al$_2$O$_3$ | 1.89       |
| SiO$_2$  | 41.31       |
| SO$_3$   | 1.46        |
| K$_2$O   | 9.66        |
| CaO      | 43.42       |
| Fe$_2$O$_3$ | 1.56       |
| Total    | 100         |

Fig. 4 SEM observation photo and chemical composition of gel in the A-2% test piece

Fig. 5 Test piece pH on Day 7 (before dipping in water and/or exposure to moist atmosphere)

Fig. 6 X-ray diffraction diagrams of pulverized mortar test pieces on specific days
the test pieces dipped in water includes the amount that dissolved into the water, the test pieces that were left in a moist atmosphere also showed decreased soluble SO$_4^{2-}$ amounts. This suggests that in the test pieces containing ASR reactive aggregate, ettringite or other amorphous substances may have formed early, immobilizing soluble SO$_4^{2-}$.

The A-0.5% test piece, which contains ASR reactive aggregate and has a K$_2$SO$_4$ additive ratio of 0.5%, was left in a moist atmosphere at 40°C for 21 days and then dipped in water (Environment 3: A-2%-40M20W), and on the 98th day underwent SEM observation and EDS analysis for element mapping. The results are shown in Fig. 10. It is known that ettringite can form within ASR-induced cracks in concrete. Ettringite formed in that way is thought not to influence expansion. However, the test revealed concentrations of S and Al, which are similar in composition and shape to the crabmeat like products in the concrete core (Fig. 3), in cement paste and cracks outside the areas where ASR gel had formed. These substances similar to ettringite could have an influence on expansion.

### 3.2 Expansion rate

Figure 11 and 12 show changes in the expansion rate of the test pieces with a K$_2$SO$_4$ additive ratio of 2% in Environments 1 and 3. The A-2% test piece containing ASR reactive aggregate shows expansion commencing earlier than in the S-2% test piece containing standard sand. Figure 12 shows that initial expansion in the A-2% test piece was greater when left in a moist atmosphere at 40°C for 21 days (Environment 3: A-2%-40M20W), an ASR promoting environment. The greater initial expansion is thought to have occurred under the influence of ASR. The final expansion rate of the A-2% test piece was about 2.8% in both Environments 1 and 3, which suggests no apparent subsequent influence of the initial exposure to a moist 40°C atmosphere. The expansion rate of 2.8% is much higher than the rates found in an ASR-induced expansion test conducted using similar aggregate and higher alkalinity [9], indicating that the much higher expansion rate is attributable to DEF. The earlier and greater expansion of the A-2% test piece compared with the S-2% test piece containing standard sand appears attributable to the ASR reactive aggregate in the A-2% test piece promoting DEF-induced expansion. The decrease in test piece pH due to the ASR reaction (Fig. 5) and the permeation of water from microcracks due to the initial expansion of 0.1% or more due to ASR (Fig. 12) are presumed to be factors that promote DEF expansion. The X mark in Fig. 11 means the end of expansion rate measurement using a contact-type strain gauge, beyond which the expansion was so rapid that the measurement was made difficult and had to be terminated. The S-2% test piece containing standard sand continued to expand after the expansion rate measurement was terminated, with the cracks showing a growing tendency during the further expansion.

Figure 13 shows the open-side surfaces of the test pieces on the 327th day. On the S-2% test piece, cracks measuring several millimeters had appeared, presumably since the test piece had warped as it expanded. The test pieces had warped in such a way that the mold-side surface forms a convex surface. It is presumed that water had penetrated into the open-side and mold-side surfaces in different manners, which may have played a part in the dis-
tinct type of expansion. On the A-2% test piece containing ASR reactive aggregate, expansion tended to converge at around 2.8% and cracks developed in hexagonal patterns all over the surface. It has not been clarified why the expansion converged on the A-2% test piece containing ASR reactive aggregate, nor has the reason for the A-2% test piece showing a different cracking pattern from that of the S-2% test piece containing standard sand been ascertained. The cracking of the A-2% test piece resembles more the one on the concrete structure in Fig. 2 that appears to have occurred under the influence of DEF.

Figure 14 shows changes in the expansion rate of the test pieces with a K₂SO₄ additive ratio of 2% in moist atmosphere Environments 2 and 4. The A-2% test piece containing ASR reactive aggregate arrived at a final DEF-induced expansion rate of about 2.5% although the expansion occurred less rapidly than in the DEF promoting dipped-in-water environment in Fig. 11.

Figure 15 shows changes in the expansion rate of the test pieces with a K₂SO₄ additive ratio of 0.5% in Environments 3 and 4. Similar to the test pieces with a K₂SO₄ additive ratio of 2%, the A-0.5% test piece containing ASR reactive aggregate arrived at an expansion rate of about 1.6% early, which at that stage was much higher than the S-0.5% test piece containing standard sand. While the A-0.5% test piece rapidly expanded at an early stage in the dipped-in-water Environment 3 (40M20W), it eventually reached roughly the same expansion rate in the moist atmosphere Environment 4 (40M20M) as well. This is thought to have occurred, helped by DEF-induced expansion, on the test piece containing ASR reactive aggregate, even in an ordinary environment without a high sulfate ratio or contact with a large amount of water. It is presumed, therefore, that concrete structures in which ASR has occurred, are likely to develop DEF. Accordingly, concrete structures that have been subjected to high temperatures and house plenty of ettringite would require review given the increased possibility of DEF. On the S-0.5%-40M20M test piece, cracking on the ends of the test piece made it difficult to continue the expansion rate measurement with a contact-type strain gauge, and the measurement had to be terminated on the 470th day, which is indicated with an
X in Fig. 12. The cracking, however, still continued after the measurement. Figure 16 shows the open-side surfaces on the 616th day of the test pieces with a K₂SO₄ additive ratio of 0.5%. It was found that DEF-induced expansion occurred even on the test pieces containing non-ASR-reactive standard sand in an environment without a high sulfate ratio or contact with a large amount of water. The cracks are in a hexagonal pattern and look similar to those observed in concrete structures with apparent DEF attributes (Fig. 2).

![Fig. 16 Open-side surfaces of test pieces with K₂SO₄ additive ratio of 0.5% on the 327th day in Environments 3 and 4](image)

4. Conclusions

We investigated the effects of alkali-silica reaction (ASR) on delayed ettringite formation (DEF) using mortar test pieces comprising ASR reactive aggregates with added potassium sulfate under various environmental conditions.

1. With each SO₃ additive ratio and environmental condition, the DEF expansion occurred earlier in the specimens using ASR-reactive aggregate than in the specimens using only standard sand, which is harmless for ASR.

2. The initial pH was lower in the specimens using ASR-reactive aggregate than in the specimens using only standard sand. This is probably due to the progress of ASR in the high temperature process. It is speculated that the penetration of water from the microcracks caused by ASR and the decrease in the pH of the specimens affected the promotion of DEF.

3. The final expansion caused by DEF tended to be less significant in mortars containing ASR reactive aggregate.

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