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Reproduction of delayed ettringite formation (DEF) in concrete and relationship between DEF and alkali silica reaction

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ABSTRACT: Delayed ettringite formation (DEF) is a phenomenon in which ettringite is generated and accumulates in the concrete after hardening, eventually leading to expansion and destruction of the concrete. In this study, DEF expansion was reproduced in laboratory using a variety of cements, sulfate additions, steam curing conditions and storing conditions. DEF was found to take place only when the three conditions of excessive sulfate, high-temperature steam curing and ample water supply are met simultaneously. The influence of the kind of calcium sulfate (gypsum, hemihydrate or anhydrite $CaSO_4$) and the heating rate of steam curing was studied. As it is reported that both the alkali silica reaction (ASR) and DEF are sometimes observed in the same deteriorated concrete, the relationship between the alkali silica reaction and DEF is also discussed.

1 INTRODUCTION

Delayed ettringite formation (DEF) is a phenomenon in which ettringite is generated and accumulates in concrete after hardening, eventually leading to expansion and destruction of the concrete. The deterioration of concrete due to this phenomenon was reported in 1990 and later in the United States and Europe (Taylor et al. 2001, Shimada 2005). It is reported that this phenomenon is liable to appear in concretes with a high sulfate content and subjected to steam curing (Hanehara 2003, Shimada 2005). Moreover, DEF takes place only when the three conditions of excessive sulfate, high-temperature steam curing and ample water supply coincide. In their previous reports (Hanehara et al. 2006a, 2006b, 2008a, 2008b), the authors confirmed that a steam curing temperature of not less than 70°C is required for the occurrence of sulfate expansion due to DEF, and that water curing at not less than 20°C is necessary after the steam curing.

This paper examines in greater detail the material conditions affecting expansion by DEF, further clarifies the conditions for occurrence of DEF, and explains the mechanism of occurrence thereof with respect to the influences of cement type and aggregate type. The results of curing in the DEF acceleration test and mortar bar test method using alkali reactive aggregates were observed and the relationships between the two compared. The relationship between the alkali silica reaction and DEF is also discussed.

2 DEF REPRODUCTION CONDITIONS

A schematic chart summarizing the authors' previous works (Hanehara et al. 2006a, 2006b, 2008a 2008b) is shown in Figure 1. It can be seen that DEF takes place only when the three conditions of presence of excessive sulfate in the cement, high-temperature steam curing at 70°C or over, and ample water supply at normal temperature coexist. Conversely, DEF does not take place if any of these conditions is missing. Based on the conditions for occurrence of DEF, we proceed to a detailed study of material conditions below.

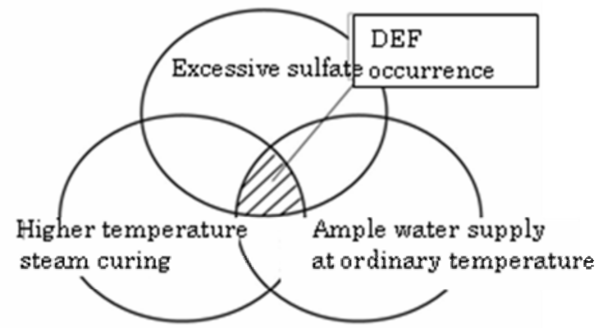

Figure 1. Occurrence condition (DEF).

2.1 *Influence of temperature of steam curing*

To identify the influences of the steam curing conditions, we added 2% potassium sulfate as SO3, maintained the pre-curing duration of 4 hours, used various steam curing temperatures in the range of 50°C to 90°C, and prepared the mortar samples using high-early-strength cement. Figure 2 indicates the changes in length of the mortar prisms.

When steam curing is done at a temperature no less than 70°C, expansion due to DEF occurs from around the curing age of 30 days to about 110 days. The higher the curing temperature, the earlier the expansion takes place, but the ultimate expansion amount is comparable, at about 2.5%. On the other hand, with steam curing at a temperature below 60°C, there is minimal expansion due to DEF as is the case when curing takes place at normal temperatures without steam curing. The boundary temperature conditions for occurrence of DEF are between 60°C and 70°C.

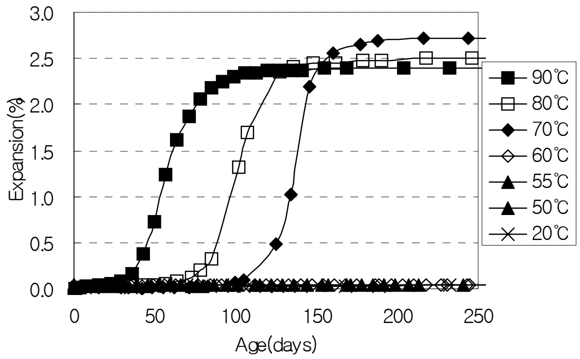

Figure 2. Influence of steam curing temperature on DEF expansion.

2.2 *Influence of sulfate content*

Potassium sulfate was added in the range of 0% to 4.0% and calcium sulfate in the range of 0% to 3.0%. The changes in length of the mortar prisms are given in Figure 3 and Figure 4, respectively.

Although the cement does not show any expansion when no sulfate is added, the greater the added quantity, the earlier the onset of expansion during curing and the larger the amount of expansion are. This is true for any addition of sulfate, regardless of its type. In the case where potassium sulfate is added, expansion in excess of 0.1%, which is the criterion of the alkali-silica reaction after 6 months curing was observed at a curing age of around 100 days, even with the minimum sulfate addition of 0.5%. The final quantity of expansion was greater than 1.0%. With potassium sulfate additions of 1.5% or over, expansion starts at a curing age of around 30 days. With potassium sulfate addition of 4%, an expansion of 6% was observed at the curing age of 150 days and the mortar was fractured. Thus DEF may occur even with a small quantity of sulfate.

In the case of calcium sulfate addition of 1.5% or more, the mortar shows a large expansion of no less than 1.5% at the curing age of 300 days. Even with a calcium sulfate addition of 1%, expansion was 0.4% at the curing age of 350 days. With a calcium sulfate addition of 0.5%, the quantity of expansion diminishes to 0.04% at the curing age of 350 days.

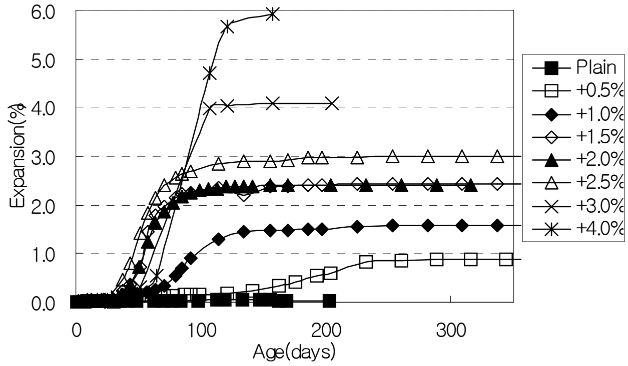

Figure 3. Influence of amount of potassium sulfate on DEF expansion.

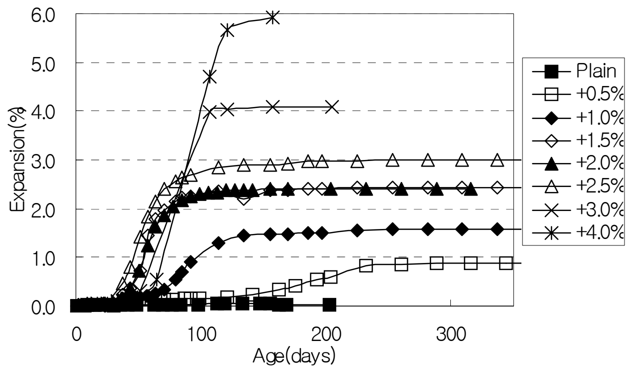

Figure 4. Influence of amount of calcium sulfate (anhydrite) on DEF expansion.

The larger the added quantity of sulfate, the greater the expansion volume. Moreover, even with similar added quantities of sulfate, the onset of expansion occurs at a later curing age in the case of the calcium sulfate addition compared to that of the potassium sulfate addition, and the final amount of expansion is also smaller. This is probably because the alkali ions of the alkaline sulfate decrease the stability of ettringite at the time of steam curing, decomposing a larger quantity of ettringite and, for that reason, subsequent regeneration of a large quantity of ettringite (DEF) results in a large expansion at an early time. The heating rate was very steep from room temperature to maximum steam curing.

2.3 *Influence of environmental and storing conditions of concrete*

To investigate the effects of storing conditions after steam curing, mortar samples were prepared using high-early-strength cement with 2% of potassium sulfate as SO_3 and then steam cured at 90°C. After steam curing, the samples were stored in water at 20°C, 40°C and 60°C and in humid air at 40°C. Figure 5 shows the changes in length of the mortar samples. In the case of storage in water at 20°C , expansion started from around the curing age of 30 days and reached 2.5%. No expansion took place during water storage at 40°C or 60°C, or in humid air at 40°C. For the production of ettringite, a temperature of around 20°C, which is a low temperature, is suitable. Furthermore, mortar cured in humid air at 20°C shows rather little expansion even after 100 days. In the production of ettringite, which is a dissolution-precipitation reaction, the reaction may be considered as progressing through a liquid phase.

An attempt will be made in this paper to put the conditions for occurrence of DEF in order, based on our previous reports.

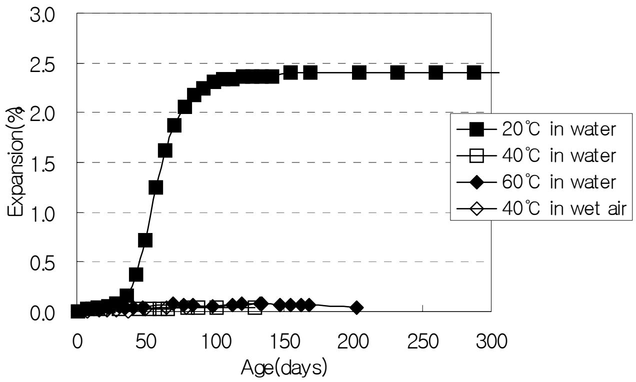

Figure 5. Influence of storing condition of haredened cement mortar after steam curing on DEF expansion.

2.4 *Influence of other factors and conditions on DEF*

The type of cement has a great influence on DEF. In the case of Portland cement, the curing age at which expansion starts is earliest, and the expansion ratio for high-early-strength Portland cement (HPC) is largest, followed by white Portland cement (WPC) and ordinary Portland cement (OPC). A larger expansion ratio is shown by cements with a large volume of C_3A and a high level of ettringite generation before steam curing, while blended cements with a small volume of C_3A, such as moderate heat cement, fly-ash cement, and blast-furnace cement, have a small expansion ratio due to DEF.

Expansion due to DEF is affected by the type of aggregate. Expansion starts earlier and the expansion volume is greater when quartzite aggregate is used, compared to when reactive aggregates are used. Limestone aggregate starts expanding at a still later curing age and its expansion volume is small.

3 EXPERIMENTS

3.1 *Materials*

High-early-strength Portland cement (HPC) obtained on the Japanese market was used. It has a density of 3.14 g/cm^3 and Blaine specific surface area of 4450 cm^2/g. As sulfate, potassium sulfate, gypsum, hemihydrates or anhydrite (calcium sulfate) were added. The sulfate content was further boosted by adding 2% of SO_3 to the SO_3 in the cement (2.8% in the case of high-early-strength cement). As fine aggregate, we used three different types, i.e. quartzite aggregate, alkali reactive aggregate, and limestone, and the particle size of all the types was 2.5 mm or less. The Rc and Sc values of the alkali reactive aggregate, as evaluated per JIS A1145 Method of test for alkali-silica reactivity of aggregates by chemical method, are 45 mmol/L and 109 mmol/L, respectively. Thus Sc is larger than Rc. Therefore this alkali reactive aggregate is categorized as reactive and not inert JIS A1145.

3.2 *Preparation of mortar*

Mortar with a water-cement ratio of 0.5 and a sand-cement ratio of 1.5 was mixed according to JIS R 5201, and formed into 4x4x16cm prisms using a mould in which a plug for measuring the length can be set according to JIS A1146 (Method of test for alkali-silica reactivity of aggregates by mortar-bar method). Steam curing (heat curing) was performed as 4 hours of pre-curing at 20°C, steam curing at 90°C for 12 hours and gradual cooling for 8 hours. Two heating methods were used for curing. One method was quick heating by placing specimens directly in an oven at 90°C after 4 hours of pre-curing, and the other was gradual heating at 20°C/hour up to 90°C after 4 hours of pre-curing. After measuring their length, the mortar specimens were stored in water at 20°C or also stored in a vessel at 40°C according to JIS A1146. Three prisms of each mortar were prepared and their lengths measured over 400 days. The changes in length were measured by means of a dial gauge and slide calipers. Table 1 lists the materials and heating method for curing.

Table 1. Material and heating Method for curing.

Cement	High-early-strength cement (HPC)	
Aggregates	Quartzite, ASR reactive aggregates	
Heating method	Quick heating in 90°C oven or gradual heating at 20°C/hr.	
Sulfate type	(K_2SO_4), gypsum, hemihydrates , anhydrite $CaSO_4$	
Addition of sulfate to cement	K_2SO_4	2.0%
	$CaSO_4$	2.0%

4 RESULTS AND DISCUSSIONS

4.1 *Influence of sulfate and heating condition*

In this study, the influence of the kind of sulfate added was studied as shown in Figure 6. The heating rate of steam curing was 20°C/hr up to 90°C after 4 hours of pre-curing. Other conditions were the same as shown in Table 1. The expansion due to DEF occurred from around the curing age of 70 days in the case of the addition of 2% of K_2SO_4. The other mortars prepared with calcium sulfate had less expansion. The mortar to which 2% of anhydrite $CaSO_4$ and hemihydrate were added exhibited no DEF expansion at all.

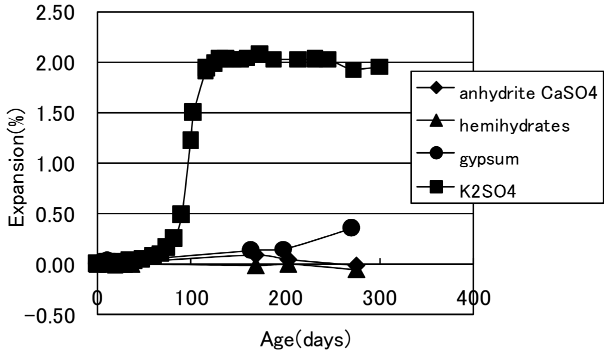

Figure 6. Influence of kind of sulfate added heating to 90°C at rate of 20°C/hr.

The mortar with the addition of 2% gypsum expanded after 200 days up to 0.3%. Figure 7 shows the influences of the kind of sulfate in mortar prepared by quick heating directly in an oven at 90°C after 4 hours of pre-curing. Mortar to which K_2SO_4 was added and quick-heated in an oven at 90°C showed the same expansion as the same type of mortar gradually heated at the rate of 20°C/hr to 90°C. Mortar to which 2% of anhydrite $CaSO_4$ was added also expanded, to 1.4%. Gypsum mortar showed expansion of 0.3% after 280 days. Hemihydrate mortar did not expand at all. Expansion by DEF was affected by the heating rate of the mortar to the maximum temperature. The heating rate influences the hydration of cement and the formation and deformation of ettringite at an early age with calcium sulfate added. Since K_2SO_4 resolves quickly to water, the influence of K_2SO_4 on the heating rate of mortar diminishes.

The addition of anhydrite $CaSO_4$ to a concrete subjected to high-temperature steam curing increases the risk of occurrence of expansion due to DEF. It is necessary in more research to explain due to DEF affected by heating rate in case of calcium sulfate.

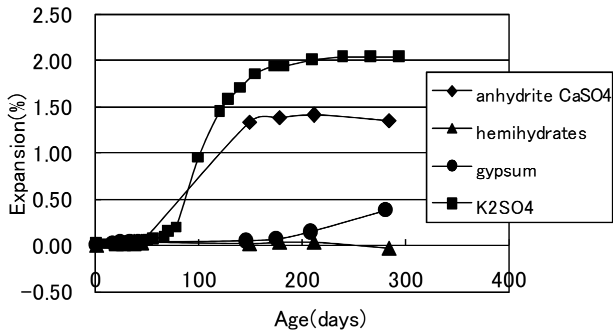

Figure 7. Influence of kind of sulfate added quick heating in 90°C oven.

4.2 *Alkali-silica reaction (ASR) and DEF*

Test specimens were prepared with alkali reactive aggregate or quartzite aggregate using high-early-strength cement with a 2% addition of potassium sulfate as SO3 and cured under the same steam condition. Figure 8 shows changes in length in the case where the storage conditions after steam curing were set for humid air curing at 40°C, identical to those of the mortar bar test method for the alkali-silica reaction, while Figure 9 indicates changes in length in the case of water curing at 20°C.

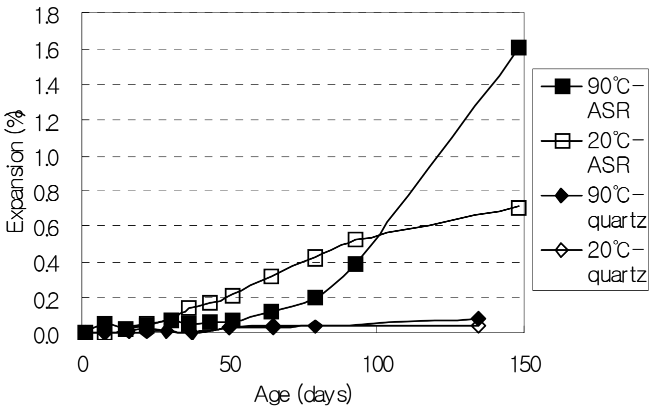

Figure 8. Influence of steam curing and aggregates (ASR aggregate, quartz) in wet air at 40℃.

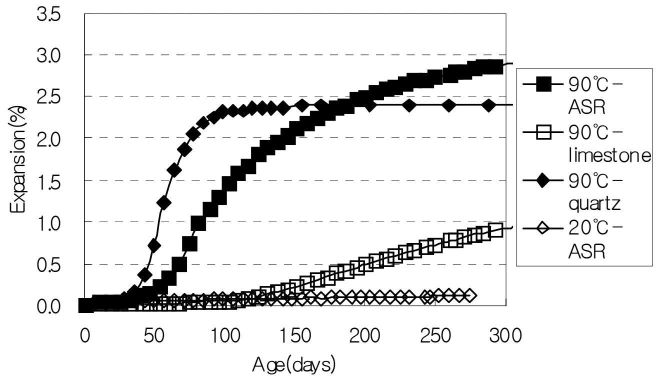

Figure 9. Influence of steam curing and aggregates (ASR aggregate, quartz) in water at 20℃.

With humid air curing at 40°C, expansion occurs in the case of reactive aggregate, regardless of whether steam curing was applied, but the quantity of expansion is smaller compared with the case of DEF expansion. No expansion due to DEF is observed even if steam curing is performed when a quartzite aggregate is used. From this fact, it is understood that with humid air curing at 40°C, the alkali-silica reaction takes place but DEF does not occur.

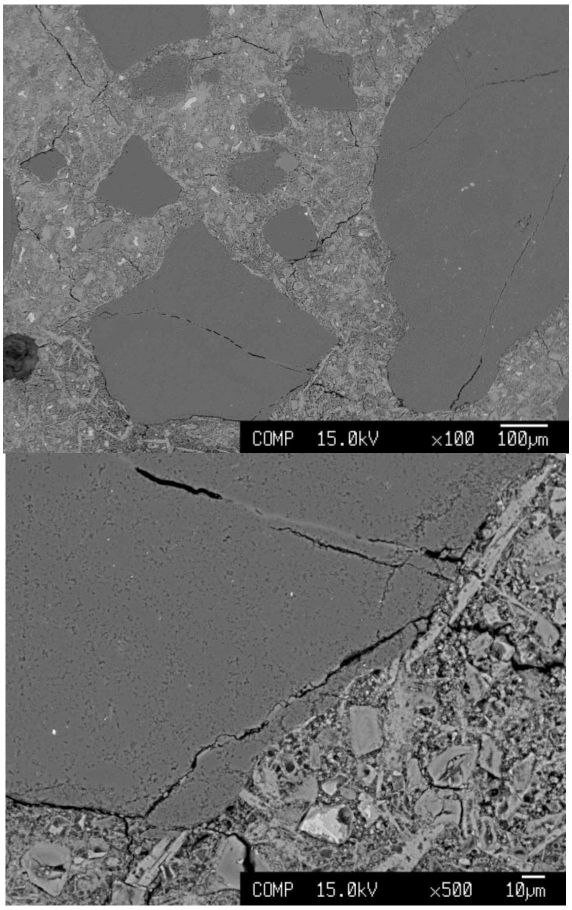

Figure 10. BEI of ASR damaged hardened mortar (ASR gel formed in the crack of ASR aggregate).

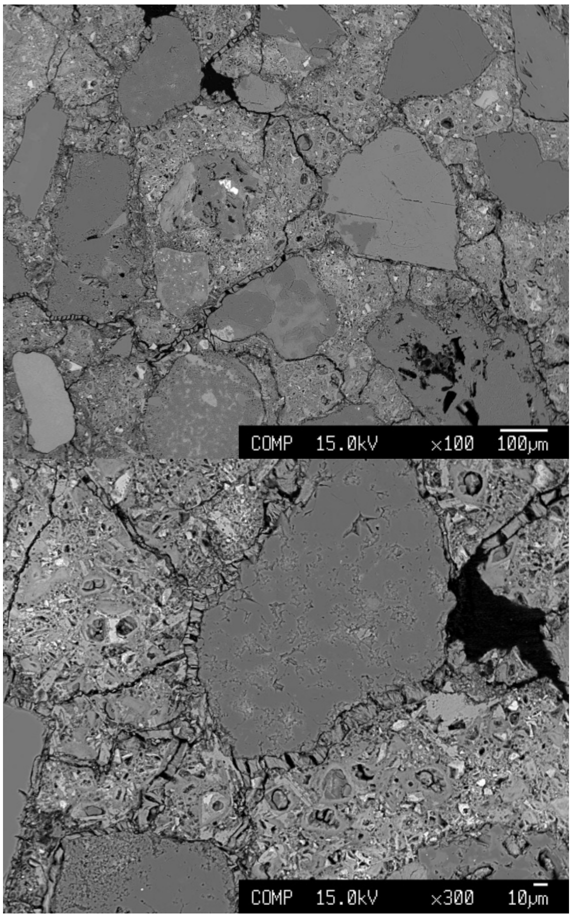

Figure 11. BEI of DEF damaged hardened mortar (AFm participated in the crack around the aggregate).

With water curing at 20°C, the expansion in the case without steam curing was small regardless of the type of aggregate, and expansion due to DEF was produced when steam curing was applied. The quantity of expansion was as large as 2.0% with both reactive aggregate and quartzite aggregate. Under such storing conditions, expansion due to DEF can be confirmed, but no expansion by alkali-silica reaction is observed. Although the alkali-silica reaction appears at an early age at the temperature of 40°C, the reaction slows down at 20°C and a longer curing age is required to cause expansion.

Figures 10 and 11 show the BEI of the alkali-silica reaction damaged mortar and the BEI of DEF damaged mortar, respectively. Through naked eye observation, both ASR and DEF damaged hardened specimens could be seen to have similar textures with cracks covering the whole specimen, producing a map-like appearance. However it is easy to distinguish DEF damaged mortar from ASR damaged mortar by the observation of BEI images of polished sections. The phase in cracks around the aggregate is determined as ettringite (AFt) by EMPA. The AFt phase is also determined by XRD. In ASR damaged mortar, aggregate reacted at the surface and the center of the aggregate and alkali-silica gel formed in the cracks and in the space of air voids, and cracks formed across the reacted aggregate. The distribution of cracks was limited as revealed by BEI images. In DEF damaged mortar, cracks were distributed uniformly as seen in BEI images, and the thickness of the cracks caused by DEF is the same thickness at 10 microns. Ettringite formed in the cracks. Crack appeared in the paste parts and around the aggregate and did not form across the aggregate. These observations coincide with the findings of a previous paper (Thomas 2008).

The alkali-silica reaction and DEF are phenomena of expansion due to the swelling and expansion of alkali silica gel and secondarily generated ettringite, produced in the presence of alkali or sulfate as the causal substance. The alkali-silica reaction and DEF have so far been discussed as phenomena similar to each other. Table 2 summarizes the relating factors of alkali-silica reaction and DEF. Although there is no factor common to both, they are produced equally when an alkali is contained in the cement in the form of alkaline sulfate. As conditions for the simultaneous occurrence of ASR and DEF, there is some deviation in the conditions common to both phenomena. In DEF, ettringite decomposes at the time of steam curing and the sulfate ion content in the pore water of hardened specimens remain high even thereafter, causing secondary production of ettringite. During the time when the sulfate ion content in the pore water is high, the hydroxide ion content in the pore water is kept low, and the pH of the pore water does not go up while DEF is taking place. For that reason, if there is any case where the alkali-silica reaction and DEF are produced simultaneously, it should be considered that an alkali-silica reaction took place after occurrence of DEF.

Table 2. Impact factors and characteristics for alkali-silica reaction (ASR) and DEF.

	ASR	DEF
ASR aggregate	○	×
Quantity of alkali	○	△
Sulfate	×	○
Steam curing	×	○
Reaction temperature	40°C	20°C
Water supply	△	○
Expansion	0.1%	1.0%

○：More effective, △: Effective,
×：Less effective

5 CONCLUSIONS

The results obtained by this research are as follows.
- DEF expansion was affected by the heating rate of mortar to maximum temperature. The heating rate influences the hydration of cement and the formation and deformation of ettringite at an early age when calcium sulfate is added. The addition of anhydrite $CaSO_4$ to a concrete subjected to quick heating through high-temperature steam curing increases the risk of occurrence of expansion due to DEF.
- Expansion due to DEF is affected by the type of aggregate. Both DEF and ASR damaged hardened specimens had the same texture with cracks covered the whole specimen, producing a map-like appearance as seen with the naked eye. However, it is easy to distinguish DEF damaged mortar from ASR damaged mortar by the observation by BEI images of polished sections. In ASR damaged mortar, cracks formed across the reacted aggregate. In DEF damaged mortar, cracks were distributed uniformly as seen in BEI images, and the thickness of the cracks caused by DEF is the same thickness at 10 microns. Ettringite formed in the cracks. Crack appeared in the paste parts and around the aggregate and did not form across the aggregate.
- With regard to the conditions for the simultaneous occurrence of the alkali aggregate reaction and DEF, there is some deviation in common points. Considering the behavior of sulfate ions and hydroxide ions in pore water, it seems reasonable to consider that the alkali aggregate reaction takes place after the occurrence of DEF.

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