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Diagnosis on Expansion of Heat-Cured Precast Concrete Blocks Due to Delayed Ettringite Formation in Japan

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ABSTRACT

Delayed ettringite formation (DEF) in concrete causes internal swelling, which reduces the mechanical properties of concrete and can lead to issues with concrete structures due to potentially large expansive deformation. In order to address the issues of DEF-affected structures, proper assessment of the structures affected is important. However, petrographic diagnosis of concrete affected by DEF remains a controversial issue. In this paper, as case studies, diagnosis on precast concrete blocks suspected of experiencing DEF was carried out. The concrete blocks were made of white Portland cement, limestone gravel, and limestone sand mixed with copper slag. The blocks were excessively heat-cured above 80 °C. The results from polarized microscope and accelerated core expansion tests strongly indicated that DEF was the cause of the expansion. Following the analysis, the long-term laboratory tests were carried out. The results obtained through the laboratory were in agreement with the experiences in actual structures. Multi-spot analysis using SEM-EDS strongly indicated the existence of invisible ettringite, which was finely intermixed with calcium-silicate hydrate gel, which supports the paste expansion theory.

Keywords: Delayed ettringite formation (DEF), diagnosis, limestone, thermodynamic modeling
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1.0 INTRODUCTION

Delayed ettringite formation (DEF) in concrete causes expansion leading to cracking, and it is a cause of concrete degradation leading to concerns about unexpected deformation and/or decrease in the integrity of structures. Although the alkali-silica reaction (ASR) is also known to cause internal swelling of concrete, DEF expansion is more serious than ASR expansion. The maximum ASR expansion under realistic conditions is approximately 0.5%, depending on the reactivity of the aggregate. DEF shows much higher expansion, which can exceed 1.0%.

Many cases of DEF-affected structure have been reported throughout the world. However, it is generally believed that DEF damage would be limited in Japan, since Japanese cement contains lower SO_3. A case of a DEF-affected massive concrete structure has not been reported so far in Japan. However, several cases of DEF in precast concrete blocks have been observed since the initial report from Matsushita and Kawabata (2005). Therefore, the Japan Concrete Institute (JCI) published the "Guidelines for Control of Cracking of Mass Concrete" in 2016. In the guidelines, DEF is one of several issues to be considered in the design process. Following publication of the guidelines, JCI launched a technical committee on delayed ettringite formation (chairman: Prof. Shunsuke Hanehara, Iwate University) in 2017, which was dedicated to establishing preventive measures against DEF in massive concrete structures, as well as petrographic/engineering diagnosis on DEF.

Petrographic/engineering diagnosis on DEF in concrete is an important issue, since abundant ettringite can be observed in voids and cracks of damaged/undamaged concrete, regardless of the existence of DEF. When analyzing ASR-affected concrete, ASR gel often coexists with ettringite. Therefore, the primary cause of damage has been discussed for decades by many researchers. Most past studies concluded that visible ettringite is the result of expansion/damage and not the primary cause of the expansion. Ettringite can be deposited in cracks and voids easily, since ettringite is stable at lower pH. ASR reduces alkalinity in the pore solution and cracking makes water penetration easier. Consequently, the pore solution pH is reduced and ettringite can be easily deposited in cracks and voids. Regarding engineering test, Thomas *et al.* (2008) reported the validity of laboratory tests using different concentrations of alkaline solution. They used 1 mol/l NaOH solution at 80 °C to accelerate ASR expansion, while limewater at normal temperature was used to promote DEF expansion. These engineering tests are also useful to support petrographic diagnosis on ASR/DEF-affected structures.

This paper presents some cases diagnosed as DEF in Japan as reported by Kawabata and Matsushita (2011). The sample was extracted from actual concrete blocks showing an unexpected large expansion and was diagnosed as DEF based on laboratory tests. Laboratory experiments using mortar and concrete were also carried out to simulate DEF expansion of concrete.

2.0 FIELD EXPERIENCES IN JAPAN

2.1 Real case of DEF in Japan

A concrete block that suffered an unusually large expansion can be seen in Fig. 1. Based on some simple assumptions, the concrete block shown in Fig. 1 was estimated to have expanded by approximately 2.5%. There have been approximately 15 similar cases reported (Matsushita and Kawabata, 2005). The concrete had been subjected to expansion and cracking after several years of service in environments, which included wet conditions. Most of the blocks affected by expansion had contact with soils directly, but the sulfate salt was not supplied from the environment according to the soil investigation. The concrete was manufactured at elevated temperatures for early shipment of the products.

Fig. 1. DEF expansion of PCa concrete block (Matsushita and Kawabata, 2005)

The concrete mixture composition is shown in Table 1. The concrete consists of white Portland cement, limestone, and copper slag. Limestone aggregate, consisting of only coarse calcite grain, is non-reactive for alkali-silica reaction. Copper slag is also non-reactive. The typical chemical composition of white Portland cement is shown in Table 2. Note that the cement shown in Table 2 is not from the same batch as the deteriorated concrete. The cement has low SO_3 and alkali contents, less than 3.0% and 0.09%, respectively. The SO_3/Al_2O_3 molar ratio of this cement was 0.70, which is slightly lower than the 0.80 threshold value reported in previous studies (Zhang *et al.*, 2002). The mineral composition of the cement calculated with the Bogue equation is also shown in Table 2, and it suggests a high C_3A content. The DEF index of the cement was only 0.3, which is significantly lower than the threshold value (1.1) proposed by Zhang *et al.* (2002). Although some researchers have pointed out that expansion can occur below the threshold value. For example, Ramlochan (2003) found a threshold value of 0.5, which was higher than the value in this study. The Blaine specific surface area of this cement was 3580 cm^2/g, which is a typical fineness.

Regarding heat curing, the temperature of the curing room was measured twice (Fig. 2): the first measurement was carried out in the middle of July and the second at the end of September. The maximum temperature during the first measurement was 82 °C, higher than 75 °C. Depending on the cement composition, one of the threshold temperatures for DEF expansion was thought to be above 65 °C (Laboratoire Central des Ponts et Chaussees, 2009). For the second measurement, the maximum temperature was 68 °C, slightly higher than the threshold temperature. The measurement was of the atmospheric temperature in the chamber, so the concrete temperature would be expected to be higher. In fact, in the second measurement, the maximum temperature of the concrete was close to 70 °C. These results indicate a possibility that the variations of atmospheric temperature in the steam chamber might affect DEF in the field.

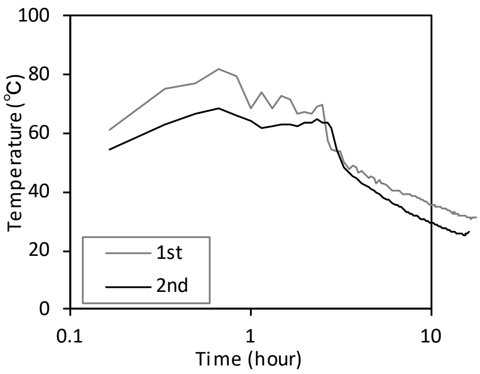


Fig. 2. Temperature history inside steam chamber (Kawabata and Matsushita, 2011)

Table 1. Mixture proportion

W/C (%)	Content per unit (kg/m^3)				
	Water	Cement	Fine aggregate		Coarse aggregate
			Limestone	Copper slag	Limestone
49	180	367	1201	272	422

Table 2. Chemical and mineral compositions (unit: wt.%)

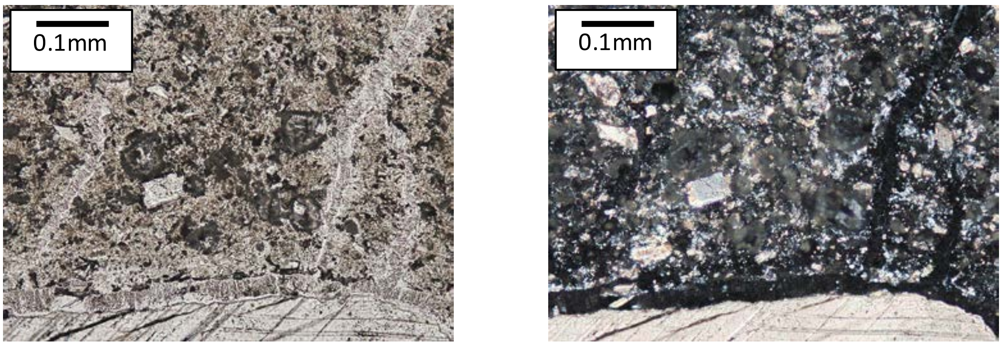
LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl	C_3S	C_2S	C_3A	C_4AF
2.83	22.88	4.60	0.19	65.13	1.35	2.52	0.05	0.06	0.003	51.3	25.1	11.53	0.56

2.2 Petrographic observation

The polished thin section prepared from the affected concrete core was observed using a polarizing microscope. The interface between cement paste and limestone aggregate is shown in Fig. 3. A gap around the limestone aggregate and radial cracks extending into the mortar can be seen, and the voids are filled with ettringite. The width of the gap is approximately 20 µm. The observation result is common in DEF-affected concrete. Elemental map analysis (not shown in this paper) revealed that S was concentrated around the limestone aggregate (Matsushita and Kawabata, 2005). It should be noted that no ASR gel or any other expansion indicators were found in the concrete, In addition, no gap was found around the copper slab. Figure 4 shows the backscattered electron image and mapping image of sulfur at the interface between limestone aggregate and cement paste observed by an electron probe micro analyzer (EPMA). An S-rich substance even fills the cracks throughout the limestone aggregate. Elemental spot analysis points to the substance being ettringite. X-ray diffraction (XRD) equipped with an optical microscope also detected ettringite precipitated in the gap and cracks. It should be noted that ettringite also fills the cracks within the limestone aggregate, suggesting ettringite precipitation subsequent to cracking. This macroscopically-visible ettringite is thought to be non-expansive and forms as a result of expansion. Formation of sub-micron scale ettringite in the outer products causes further expansion (Famy, 1999).

2.3 Core expansion tests

Cores were extracted from two different damaged concrete blocks (No. 1 and No. 13) and immersed in three types of solutions using the approach described by Thomas *et al.* (2008); the three solutions were saturated lime solution at 20 °C, distilled water at 20 °C, and hot alkaline solution at 80 °C (1 mol/l NaOH). Length change was measured during immersion to quantify the ASR and/or DEF expansions and the results are shown in Fig. 5. The concrete cores immersed in saturated limewater showed linear expansion with time up to about 0.2%, after which the expansion seemed to reach a plateau. This indicates that residual DEF swelling potential remained. The expansion of concretes immersed in distilled water also exceeded 0.1%, but was less than that in saturated limewater. However, the concrete cores immersed in hot alkali solution (which accelerates the alkali-silica reaction) showed no expansion. The concrete's expansion was less than 0.04% at 21 days, below the threshold value (0.1% at 21 days) proposed by Katayama (2004); this indicates that ASR was not occurring in the affected concrete. The DEF expansion was promoted in the saturated limewater and distilled water because of alkali leaching, but leaching was inhibited by hot alkali solution.



(a) Open nicol (b) Crossed nicol

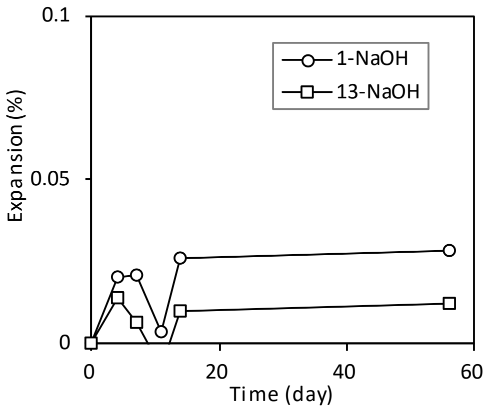
Fig. 3. Polarized microscope (Kawabata and Matsushita, 2011)

(a) Backscattered electron image (b) Mapping image of sulfur

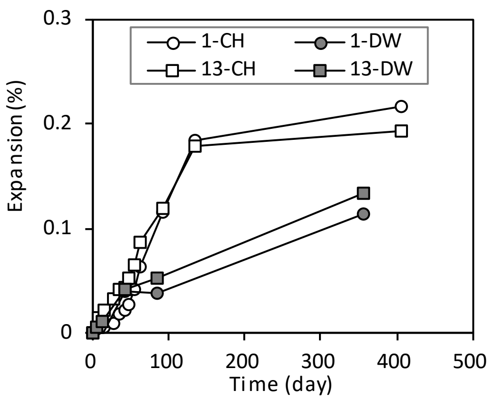
Fig. 4. Interface between limestone and mortar (Kawabata and Matsushita, 2011)

Table 3. Mixture proportions for concrete expansion test

Case	W/C (%)	Content per unit (kg/m³)				
		Water	Cement	Fine aggregate		Coarse aggregate
				Limestone	Copper slag	Limestone
N	49	180	367	1201	272	422
L				1414	0	422
C				0	1809	422



(a) Saturated lime solution (CH) or distilled water (DW) at 20 °C



(b) 1 mol/l NaOH solution at 80 °C

Fig. 5. Expansions of concrete cores immersed in different type of solution (Kawabata and Matsushita, 2011)

2.4 Primary cause of expansion of concrete block

From the diagnostic investigations, the primary cause of expansion in the concrete blocks was theorized to be DEF. The SO_3/Al_2O_3 molar ratio and the DEF index of the cement were lower than those reported in previous studies (Zhang *et al.*, 2002), but DEF might occur even for cement with this composition.

In order to investigate the mechanism in more detail, laboratory tests were carried out. The details are described in the following section.

3.0 LABORATORY EXPERIMENTS

3.1 Concrete expansion tests

Experimental Details

First, in order to replicate the DEF expansion of field concrete, a concrete expansion test was carried out. Three types of concrete were cast for the test. The mixture proportions of concrete are summarized in Table 3. The mixture "N" is the normal concrete, which is the same mixture proportion as the one showing deleterious expansion. In the mixture "L", copper slag aggregate was excluded from the mixture so that the fine aggregate was all limestone. The mixture "C", on the other hand, uses only copper slag as fine aggregate. The dimensions of the concrete specimen were 100 × 100 × 400 mm.

The casted concretes were heat cured (S) and air-cured without heating (A) to evaluate the effect of heat-curing. However, due to instrumentation issues, the temperature during heat curing could not be measured.

After curing, the concretes were immersed in water for 12 months and then exposed to drying-wetting conditions at ambient temperature. Length change was measured using a slide gauge, leading to the measured values having large variations.

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After 31 months, a 100 × 100 × 100 mm section was removed from the sample and used for polarizing microscopy and SEM-EDS analysis. Then the residual concrete specimens (100 × 100 × 300 mm) were again exposed to wetting-drying condition. The expansion test was carried out for 62 months.

Experimental Results
The expansion behaviors of the concretes are shown in Fig. 6. The legend in the Figure is expressed as “concrete mixture - curing”. It can be seen that significant expansion only occurred in concretes “N-S” and “L-S”, which were subjected to heat curing. These concretes showed especially rapid expansion after 15 months. When the concrete was subjected to wetting-drying conditions, the latency time of DEF expansion was decreased. Expansion of L-S is larger than that of N-S, though there are large variations in the measured values. It is interesting that “C-S” did not show expansion. It has been confirmed that copper slag has nothing to do with DEF expansion.

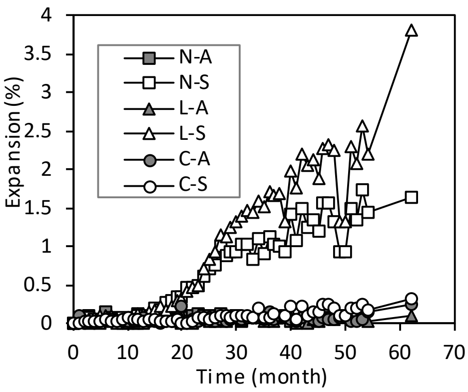


Fig.6. Expansion of concrete with different mix proportions

Figure 7 shows the concrete specimen at 31 months. Many fine cracks are observed in specimens N-S and L-S, whereas no cracks are seen in C-S. The crack patterns were very similar to real concrete blocks affected by DEF.

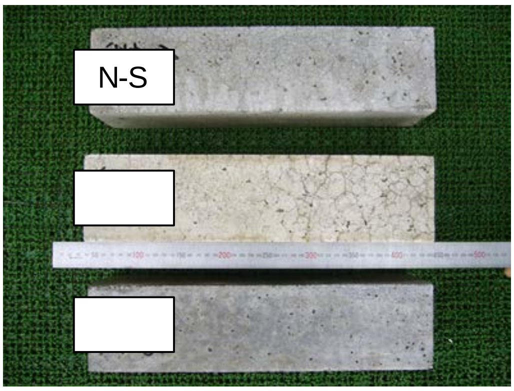


Fig. 7. Concrete surface after 31 months

The interfaces between paste and aggregate were observed with a polarized microscope (pictures are shown in Figs. 8-10). In the L-S specimen, the gaps were formed around limestone aggregates; this is commonly observed in DEF-affected concrete (Fig. 8). In the N-S specimen, however, the gap was formed not around copper slag but limestone (Fig. 9). This observation demonstrates the effect of aggregate properties on DEF expansion. There was no gap formation in the N-A specimen, where no expansion was observed (Fig. 10).

The outer products in L-S and N-S specimens after 31 months were analyzed using SEM-EDS. The analytical data of Al/Ca and S/Ca atom ratios are plotted in Fig. 11. The S/Ca atom ratio in the L-S specimen was slightly higher than that in N-S, suggesting that L-S contains a greater amount of fine scale ettringite intermixed with the outer products than N-S. This result is in agreement with the expansion behavior of concrete after 31 months. After 31 months, expansion of N-S tended to cease, whereas L-S showed constant expansion. This result strongly supports the paste expansion theory (Famy, 1999).

DEF expansion can be confirmed by the concrete expansion test, and further proved based on the polarized microscope and SEM-EDS analysis. From these results, the cause of deleterious expansion of the concrete blocks has been diagnosed as DEF. This result also supports that ASR is not necessary for DEF.

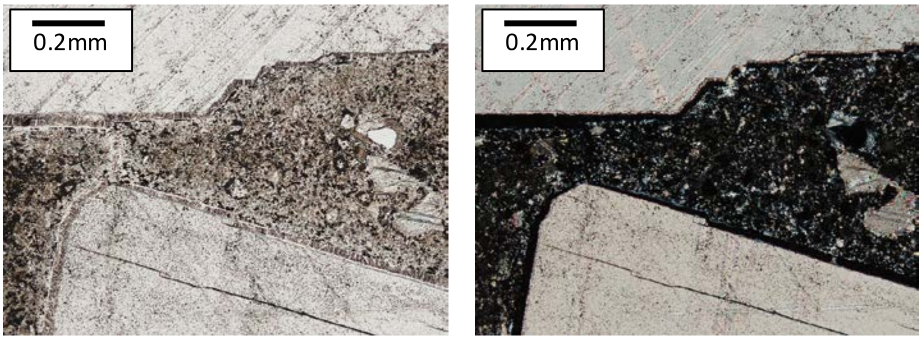
It has been observed that N-S and L-S using limestone sand showed DEF, whereas C-S without limestone sand showed no expansion. This result raises an additional question: does the negative effect of limestone sand or beneficial effect of copper slag have a greater influence on DEF expansion. Previous studies found that the use of limestone can reduce DEF expansion significantly (Lawrence, 1993; Grattan-Bellew *et al.*, 1998). It was also reported that limestone has a beneficial effect in delaying the onset of expansion (Lawrence, 1993; Grattan-Bellew *et al.*, 1998). These beneficial effects are thought to be attributable to the strongly bonded interface between the cement paste and aggregate.

3.2 Mortar expansion tests

Experimental Details
Mortars with different types of aggregate were casted to compare the effect of aggregate type on DEF expansion. Two types of aggregate were used as sand: siliceous sand (SS) and limestone (LS). In order to promote DEF expansion, K_2SO_4 was added to the mixture so that the additional SO_3 was 0, 2, or 4%. The water-to-cement ratio and sand-to-cement ratio were set as 0.50 and 1.5, respectively.

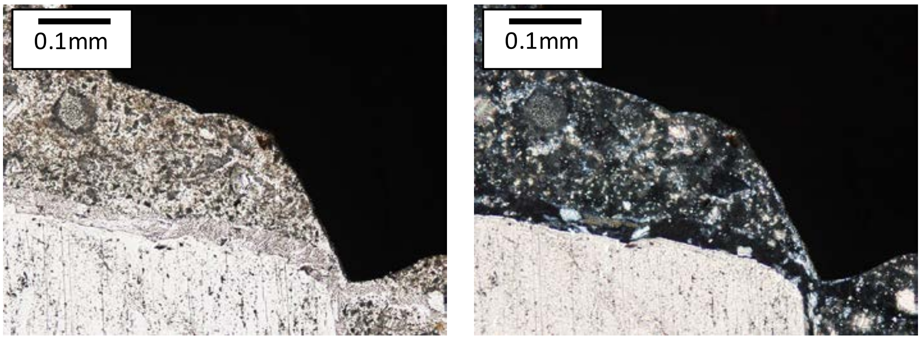
The mortar was heat-cured at 90 °C for 10 hours after 4 hours of mixing. Then, the specimens were immersed in water and length change was monitored for approximately 8 years.

Experimental Results
The mortar expansion behaviors are shown in Fig. 12. In cases of high SO_3 addition, expansion of mortar using SS was faster than when LS was used. In the case of no additional SO_3, however, onset of expansion was faster for mortar using LS. The results



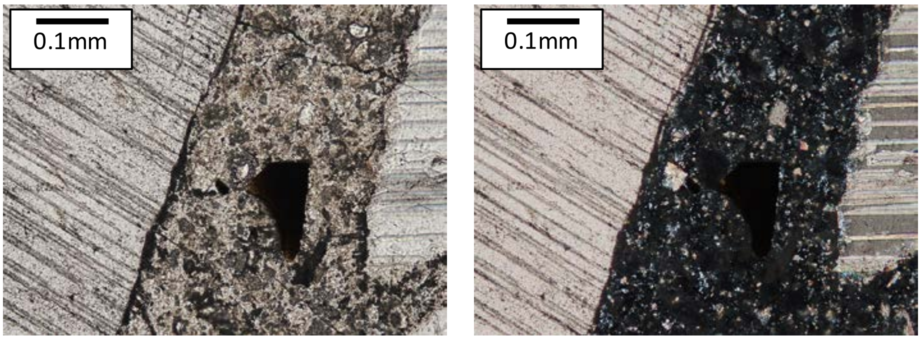
(a) Open nicol (b) Crossed nicol

Fig. 8. Polarized microscope (L-S) (Kawabata and Matsushita, 2011)



(a) Open nicol (b) Crossed nicol

Fig. 9. Polarized microscope (N-S) (Kawabata and Matsushita, 2011)



(a) Open nicol (b) Crossed nicol

Fig. 10. Polarized microscope (N-A) (Kawabata and Matsushita, 2011)

showed that the influence of aggregate type on expansion behavior varied depending on the SO_3 content. It should be noted that XRD identified monocarboaluminate as well as ettringite in mortar using limestone (LS-0, Fig. 13). This indicated that carbonate ions were supplied from limestone.

3.3 Thermodynamic calculations

In order to check the phase assemblage in the system, thermodynamic calculations were performed using GEMS (Kulik *et al.*, 2013). The specific database cemdata14 was also used (Dilnesa *et al.*, 2014). The methodology was originally proposed by Matschei *et al.* (2007). We calculated the equilibrium phase assemblage at different temperatures (25 and 90 °C) for 100 g of cement with calcite added. The cement mass was constant while the amount of calcite was increased to simulate the supply of carbonate ions from limestone, and the amount of water was 50 g. The model was simplified such that it does not take into account ion transport or space.

The calculated results are summarized in Fig. 14. The data for C-S-H, portlandite, and water are not shown for simplification. At 90 °C, the dominant phase was monosulfoaluminate (MS), and MS decreases with increasing calcite (CC) up to about 1.5 wt%. Above 1.5 wt% CC, the MS concentration plateaus. At such high temperature, ettringite (Ett) is not stable. At 25 °C, however, many phases exist in the system. Large amounts of Ett, hemicarboaluminate (HC), or MC are precipitated. In the presence of calcite, due to the formation of carboaluminate phases, Ett is more stable than MS.

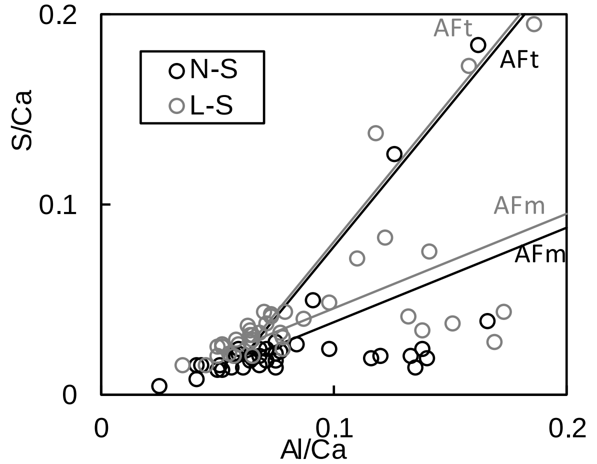


Fig. 11. S/Ca versus Al/Ca atom ratios of the outer product (Lines are intended as eye-guides only)

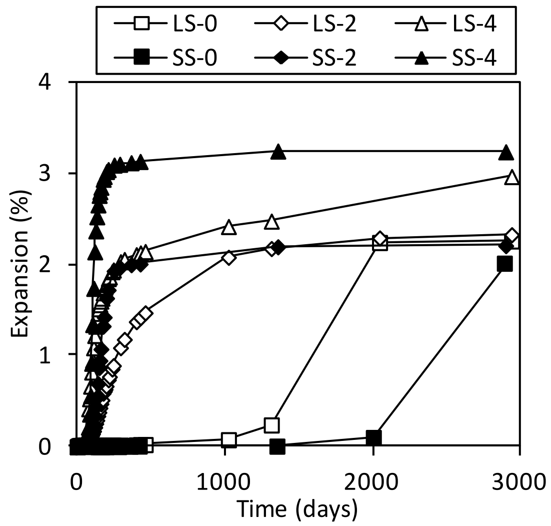


Fig. 12. Expansion behaviors of mortar using different type of aggregate (SS: Siliceous sand, LS: Limestone, Legend indicates "Aggregate type" - "SO_3 dosage") (Kawabata *et al.*, 2015)

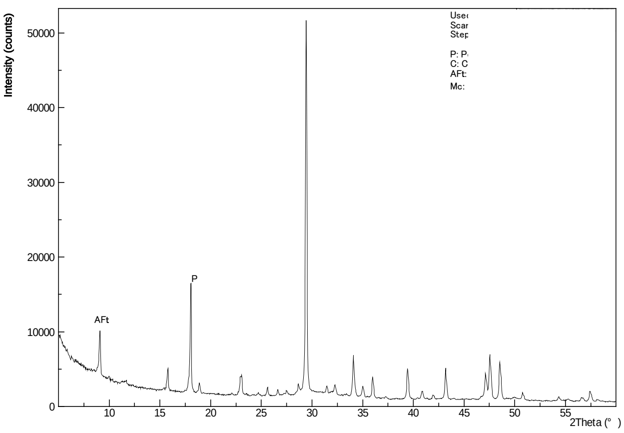
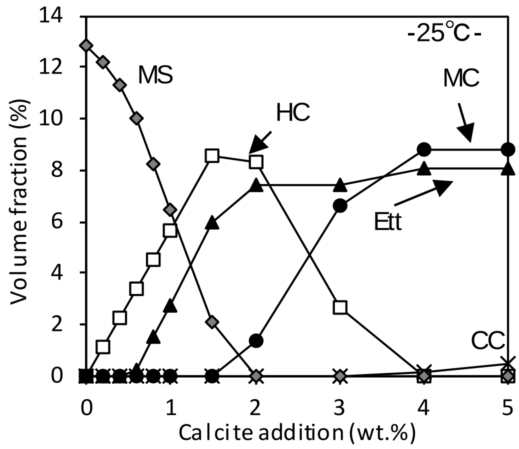
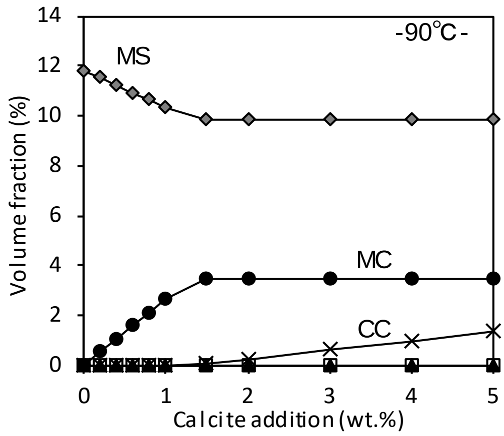


Fig. 13. XRD spectra of LS-0



(a) 25 °C



(b) 90 °C

Fig. 14. Change in phase assemblage with increasing amount of calcite added in the system (W/C=0.50,
CC: Calcite, MS: Monosulfoaluminate, MC: Monocarboaluminate, HC: Hemicarboaluminate, Ett: Ettringite)

The results confirm that Ett can be precipitated during exposure to the environment following heat curing. The presence of calcite has an especially strong influence on ettringite formation. Indeed, according to XRD analysis on DEF-expanded mortar, MC was identified (as shown in Fig. 13). This means that carbonate ions supplied from calcite accelerate ettringite formation.

3.4 Discussions

The effect of limestone has been thought to be beneficial due to strong bonding and a lower thermal expansion coefficient (Lawrence, 1993; Grattan-Bellew *et al.*, 1998). However, the diagnostic results and laboratory tests in this study showed contradicting results, especially in cements with a lower SO_3 content. The influence of aggregate type, especially in cases using limestone, on expansive behaviors changed based on the concentration of SO_3. This might be attributed to the balance between sulfate and carbonate ions.

From the results shown in this study, there is a possibility that the onset of expansion is accelerated in the presence of calcite for cases of lower SO_3 content cements. Due to the reaction between MS and calcite, available Al_2O_3 content is reduced. Consequently, the apparent SO_3/Al_2O_3 ratio is increased, which is favored for ettringite formation. Si-substitution of C-S-H by Al is also important to be considered since Al content is crucial for equilibrium phase assemblage. Previous studies reported contradicting results that limestone has a beneficial effect by reducing DEF expansion. However, this conclusion was obtained from cement with a higher SO_3/Al_2O_3 ratio than this study. In the case of cement with a higher SO_3/Al_2O_3 ratio, sulfate ions are abundant in the system so the reaction between MS and calcite is less pronounced. Therefore, the effect of calcite (or limestone) might be reduced in the past studies. From the viewpoint of surface area, the contribution of limestone aggregate has not been clarified in this study. However, the presence of MC suggests a reaction between limestone aggregate and cement paste. According to Fig. 14(a), MC is present above 2.0% calcite addition at 25 °C. Under these conditions, Ett is also present, indicating that Ett can precipitate in the system. The experimental results in this paper are consistent with these modelling results.

It should be noted that addition of calcite also contributes to reduced porosity due to the reaction of AFm phase at ambient temperatures (Matschei et al, 2007). However, special care should be taken when concrete using limestone filler/aggregate is exposed to high temperature, even in cases where cement with low SO_3/Al_2O_3 molar ratio is used.

4.0 CONCLUSIONS

This paper presented cases of concrete suspected to have experienced DEF in Japan. The core expansion tests and some analyses indicated that the primary cause of concrete expansion was suspected to be DEF. Subsequent concrete expansion tests showed significant DEF expansion, especially in the case using limestone fine aggregate; this was consistent with cement used in the actual structures. Multi-spot analysis using SEM-EDS strongly indicated the existence of invisible ettringite, which was intermixed with calcium-silicate hydrate gel, which supports the paste expansion theory.

Laboratory tests using mortar specimens indicated that limestone accelerates the onset of DEF expansion, which was caused by the reaction of calcite and AFm phase. This effect was thought to be larger when cement with a lower SO_3/Al_2O_3 molar ratio was used. The mechanism of calcite accelerating DEF expansion was discussed, with simple thermodynamic calculations. From the results, it is thought that special care should be taken when concrete using limestone filler/aggregate is exposed to high temperature.

Acknowledgement

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