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DEF Expansion Behavior of Hardened Cement Using Fine Aggregate generated by Blast Furnace Air Cooling Slag

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Abstract: In recent years, the effective use of resources in concrete materials has been considered, and blast furnace slag has been reused as a construction material. Blast furnace slag is classified into two types according to the cooling method. Blast furnace water-cooled slag is used as concrete fine aggregate and powder admixture. On the other hand, blast furnace air cooling slag has been stabilized, but the sulfur is still present as SO_3 due to oxidation. In addition, there is a concern that a rich water supply or excessive SO_3 may cause abnormal expansion. As a result, its widespread use as a concrete fine aggregate has been delayed. The probability of this expansion occurring is unclear and the mechanism has not been clarified. The extension of the use to fine aggregate will determine the reduction of environmental impact in the aggregate. In this study, air cooling slag was used as concrete fine aggregate in the preparation of mortar. In order to understand the Delayed Ettringite Formation (DEF) induced expansion behavior, the specimens were steam-cured and the quantitative evaluation of ettringite when subjected to temperature history was conducted. In addition, the type of fine aggregate, the addition of potassium sulfate, and the replacement ratio of blast furnace slag fine powder were investigated. As a result, the use of blast furnace slag powder suppressed the expansion even at high temperature curing. Also, it was found that DEF may not expand depending on the shape and timing of ettringite generation.

Keywords: Air cooling slag; DEF; DEF expansion; Cured at high temperature; Blast furnace slag powder

1. Introduction

In recent years, the construction industry has been working toward a recycling-oriented society, and the effective use of resources is being considered for concrete materials. Blast furnace slag, which is generated in the iron manufacturing process, is highly regarded as a recyclable material that reduces the burden on the environment, and is often reused for construction materials. Blast furnace slag is classified into two categories according to the cooling method: blast furnace air cooling slag and blast furnace water cooling slag. Blast furnace water-cooled slag is produced by rapid cooling of the slag by high water pressure jets, and is used as fine aggregate for concrete. It is also used as blast furnace cement due to its strong potential for hydraulic hardening in fine grinding. On the other hand, air-cooled blast furnace slag is mainly used as a coarse aggregate for concrete and as a filling material for caissons. However, since it is produced by cooling naturally and moderate water sprinkling, sulfur is oxidized and exists as SO_3. Previous studies have shown that a large amount of SO_3 is generated when air cooling slag is used, which may react with cement to cause abnormal expansion and destroy the concrete. In this study, an experimental investigation was carried out on DEF, which is concerned about the effect of SO_3, for the purpose of using air cooling slag sand as fine aggregate for concrete.

2 Outline of Experimental

2.1 Using Material and Specification

The physical properties and amount of SO_3 are shown in Table 1. The cement used was Ordinary Portland Cement (OPC), the fine aggregate was Aggregate of Air Cold Slag (ACS), and Standard Sand (SS) was used for comparison. Standard Sand (SS) was used for comparison. The ACS fine aggregate has a higher water absorption rate and contains more sulfur than standard sand.

Table 1 The physical properties and chemical composition of the materials

		Density at absolute drying(g/cm³)	Water absorption rate(%)	Chemical analysis value	
				SO_3	S
Fine Aggregate	SS (Standard sand)	2.64	0.42	-	-
	ACS (Air cooling slag)	2.79	2.79	0.5	1
Cement	OPC	3.16	-	2.07	-
Admixture	GGBFS	2.91	-	2.02	-

Table 2 shows the mix proportion of the mortar. The water-cement ratio was 50%, the mass ratio of binder and fine aggregate was kept constant at 1:3, and the fine aggregate was used in an absolutely dry state. The replacement ratio of blast furnace slag powder was 0%, 45%, and 70%, and K_2SO_4 was added to the binder at 2% and 4% of the SO_3 content for accelerate the process.

Table 2 Mix proportion of mortar

	K_2SO_4	mass weight ratio		Fine agrigate
	(SO_3 %)	OPC	BFS	
B0-SS-K2%	2	100	0	SS
B0-SS-K4%	4			
B0-ACS-K2%	2			ACS
B0-ACS-K4%	4			
B45-SS-K2%	2	55	45	SS
B45-SS-K4%	4			
B45-ACS-K2%	2			ACS
B45-ACS-K4%	4			
B70-SS-K2%	2	30	70	SS
B70-SS-K4%	4			
B70-ACS-K2%	2			ACS
B70-ACS-K4%	4			

The specimen size of the made mortar was 40×40×160mm. Figure 1 shows the high temperature curing process. After casting, the mortar was left in the formwork for 4 hours, the temperature was raised at 20℃/hr, held at 90℃ for 12 hours, and lowered at 10℃/hr for high temperature curing. After demolding, curing was carried out in water at 20°C as shown in Fig. 2.

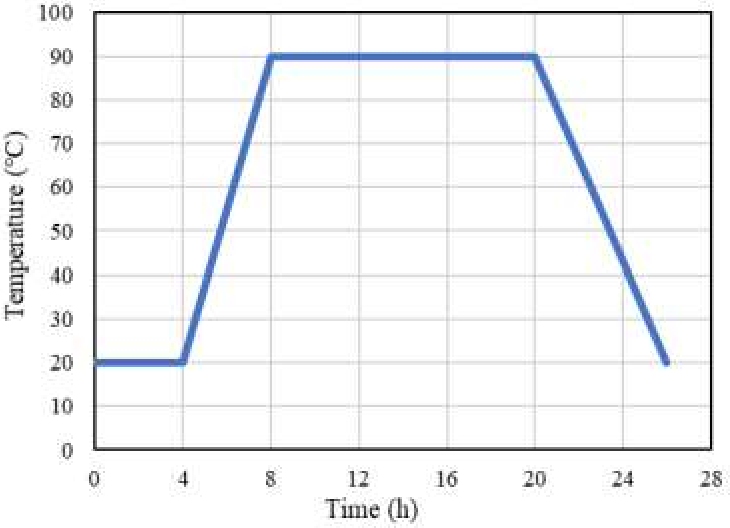


Figure 1 The high temperature curing process

Figure 2 Underwater curing

2.2 Compressive and Bending Strength Test

In order to understand the physical properties of the mortar specimens, bending and compressive strength tests were conducted in accordance with JIS R 5201 at curing 28 days in water.

2.3 Length change Test

The length change test was conducted using the dial gauge method in accordance with JIS A 1129-3. The initial value was taken at the time of demolding, and measurements were taken every week. The formula for calculating the rate of length change is shown below.

$$\varepsilon = \frac{(X01 - X02) - (Xi1 - Xi2)}{L0}$$

ε：Length change rate (%)
L0：base length
X01,X02：Measured values of the standard, standard scale, and specimen at the time of reference, respectively
Xi1,Xi2：Measured values of the standard scale and specimen at each time point i

2.4 Mass weight change Test

Since the chemical formula of ettringite is $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$, we thought that water would be absorbed inside the specimen to produce ettringite, and the amount of ettringite produced would fluctuate depending on the amount of water absorbed, contributing to the expansion. The initial value was taken at the time of demolding, and the mass was measured every week.

$$M" = \frac{Mi - M0}{M0} \times 100$$

M”： Mass weight change rate (%)
Mi：Mass at time “i”, respectively
M0：Mass immediately after demolding

3. Results and discussion of physical properties Tests

3.1 Results of Compressive and Bending Strength

The bending strength and compressive strength are shown in Fig 3 and Fig 4. It was found that the strength of the specimen using the ACS fine aggregate was greater than that of the specimen using the standard sand. This may be due to the fact that the water absorption rate of the ACS fine aggregate was greater than that of the standard sand, and the fine aggregate in its absolutely dry state absorbed the mixing water, resulting in a smaller real water-cement ratio. In the case of B70, the bending strength of the slow-cooled slag fine aggregate was smaller than that of the standard sand. This may be due to the vitrification of the slag by high replacement, and the flexural strength did not increase as much as the compressive strength.

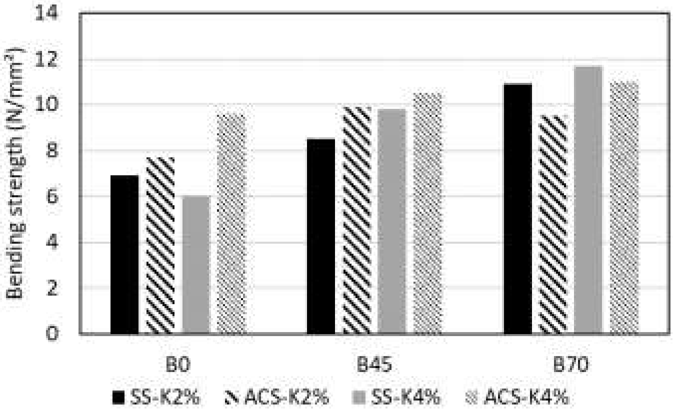


Figure 3 Results of Bending strength

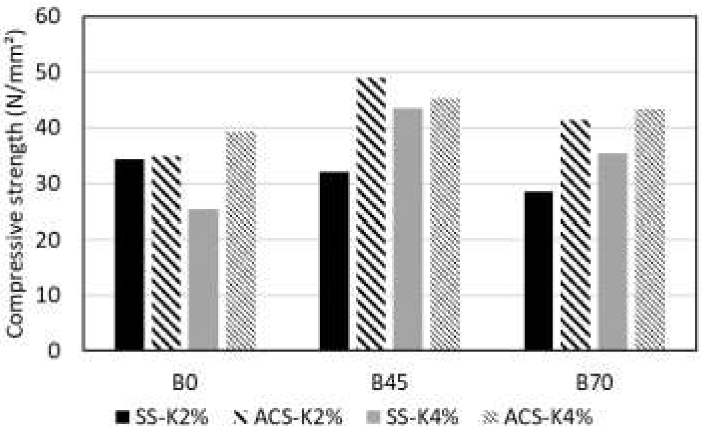


Figure 4 Results of Compressive strength

3.2 Result of length change

Fig 5 shows the change in the expansion rate of mortar specimens with time for the replacement rate of blast furnace slag powder, B0, B45, and B70.

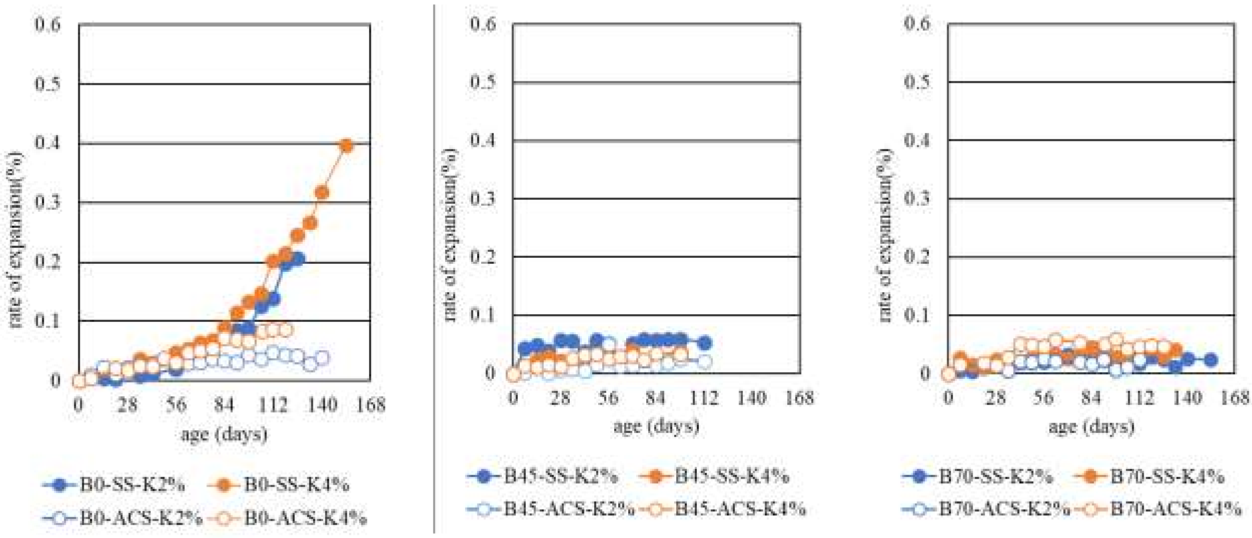


Figure 5 change in the expansion rate of mortar specimens with time

In the case of B0, a very large expansion was observed in the specimen using standard sand, and the expansion gradually started from about 84 days and rapidly increased from about 112 days. In the case of the air cooling slag fine aggregate, a slight expansion was observed in the specimen with 4% SO_3 content. However, the expansion was limited to about 0.1% in 140 days. As shown in Figs 6, B45 and B70 showed almost no expansion, and the expansion was less than 0.05% in all the replaced specimens at 84 days. The expansion was less than 0.05% in all the replaced specimens. The specimens with 70% replacement of blast furnace slag powder did not show any expansion even at 140 days. It is clear that the use of blast furnace slag powder significantly suppresses the DEF expansion. As for the air cooling slag fine aggregate, the expansion did not occur for about 100 days as feared.

3.3 Results of Mass weight change Test

The figure 6 shows the change in the rate of mass reduse over time for each replacement rate of blast furnace slag powder. In the case of SS-K2% and SS-K4%, which showed a large expansion at B0 in the figure 6, the rate of mass gain gradually increased and showed a significant increase from about 84 days when the expansion behavior was observed. In the case of the slow-cooled slag fine aggregate, the initial rate of mass reduse is large for all the replacement rates of blast furnace slag fine powder, even though it does not have a significant expansion behavior. This is thought to be due to the large water absorption rate of the air cooling slag fine aggregate and the initial water absorption.

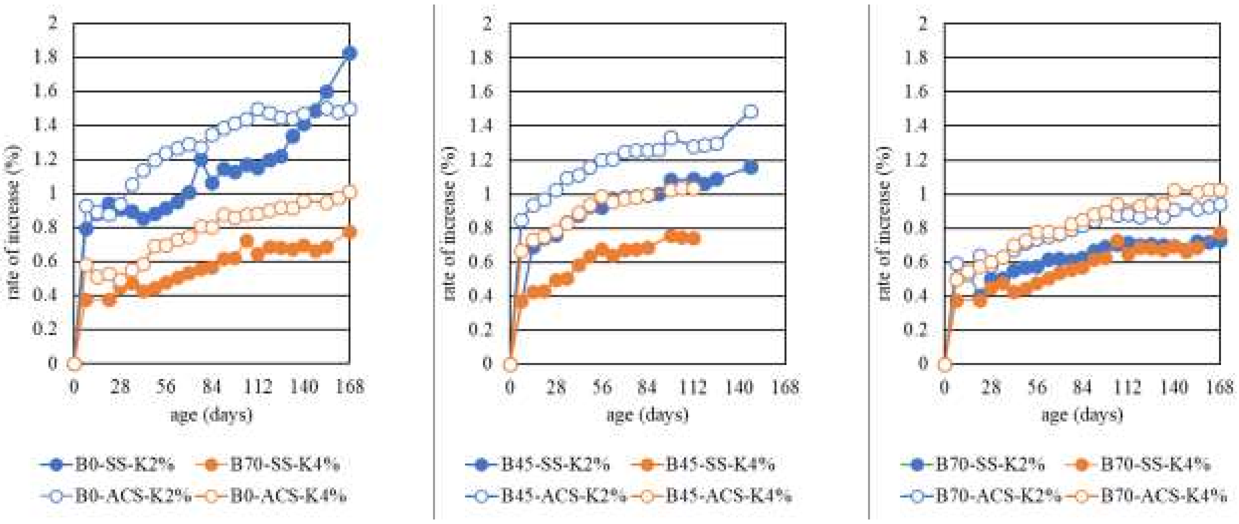


Figure 6 Change over time in the rate of mass weight

3.4 Relationship between mass weight change and length change

The relationship between the rate of mass gain and the rate of expansion at 91 days is shown in Figure 7. Focusing on the specimen using standard sand, the results show that the rate of mass gain of B0-K4, which is expanding, and B70-K4, which is not expanding, are almost equal. For the specimens with air cooling slag fine aggregate, there was no expansion in any of the mix proportion, but the mass gain varied from 0.5% to 1.5%. From these results, it is clear that there is no relationship between the mass gain rate and the expansion rate.

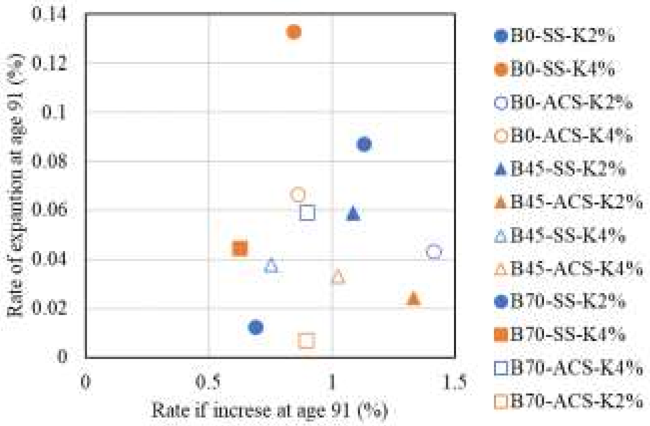


Figure 7 Relationship between mass weight change and length change

3.5 Relationship between strength and expansion rate

The figure 8 shows the compressive strength at 28 days and the expansion rate at 91 days, when there is no obvious expansion of DEF.

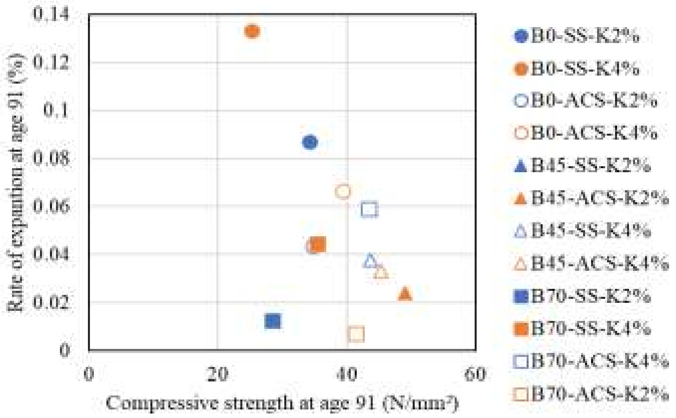


Figure 8 Relationship between strength and expansion rate

The smaller the compressive strength, the more likely it is to expand. The strength of the paste may affect whether or not expansion occurs during delayed formation of ettringite. The strength of the paste may affect whether or not it expands during the delayed formation of ettringite. However, strength does not necessarily affect expansion in all cases, as some cases show expansion while others do not, even at roughly equal strength. Here, we look at the relationship between compressive strength and expansion for B0-SS-K2% and B0-ACS-K4%, which showed expansion. The relationship between compressive strength at 28 days and expansion at 140 days of age is shown in Fig 10. B0-SS-K2% showed significant expansion, while B0-ACS-K2 did not show much expansion. In other words, even though the strength of ettringite affects the delayed generation and expansion of ettringite, after cracking, the expansion seems to be influenced more by the growth and shape of ettringite crystals than by the local area. It is clear from this that the amount and shape of ettringite may have a strong influence on the DEF expansion, so we analyzed the ettringite.

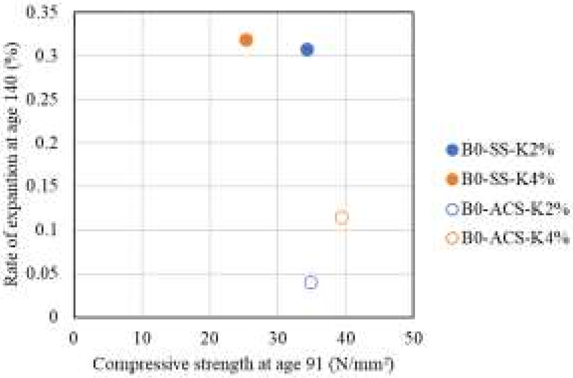


Figure 10 Relationship between strength and expansion rate at B0

4. Analysis and Discussion

In order to understand whether the expansion was caused by DEF, SEM was conducted to confirm the formation of ettringite in the expanded B0-SS-K4% and non-expanded B0-ACS-K4%, and powder X-ray diffraction (XRD) was conducted to examine whether there was a relationship between the amount of ettringite formed and the expansion.

4.1 Analysis Outline

4.1.1 Powder X-ray diffraction (XRD)

The mortar specimens were hydrated with acetone, crushed, and sieved through a 150 μm sieve to remove the fine aggregate. Quantitative analysis was carried out using the internal standard method at 9.1°, the peak of ettringite, and 52.5°, the peak of α-Al_2O_3. The comparison was made on the basis of the amount of ettringite per cement paste, the amount of ettringite other than fine aggregate contained in the powder obtained from the specimens, considering the case where all fine aggregate was not removed.

4.1.2 Scanning Electron Microscope

For the purpose of confirming the surface morphology and size of the generated ettringite, cross-sections of the specimens were observed by reflection electron images at a material age of 6 hours during high temperature curing and at a material age of 100 days or more, when the specimens were fully cured in water and showed a significant tendency to expand as shown in Figure 6 B0.

4.2 Change in the amount of ettringite due to high temperature curing

Figure 10 shows the variation of ettringite amount during high temperature curing and Figure 11 shows the XRD profiles of B0-SS-K4% and B0-ACS-K4%. The amount of ettringite produced during pre-curing is higher for B0-ACS-K4% with air cooling slag fine aggregate. B0-SS-K4% with standard sand wanted to measure ettringite when it reached 90°C. It is considered that the ettringite disappeared when the high temperature was reached. On the other hand, in B0-ACS-K4%, ettringite disappeared while it was kept at 90°C. It is considered that ettringite is formed at an early stage by using the air cooling slag fine aggregate because it has more aluminum than the standard sand.

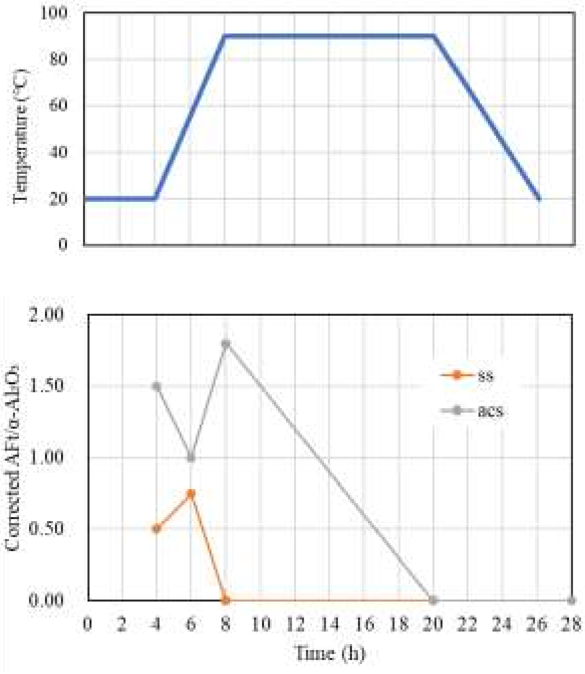


Figure 10 Change in the amount of ettringite due to high temperature curing

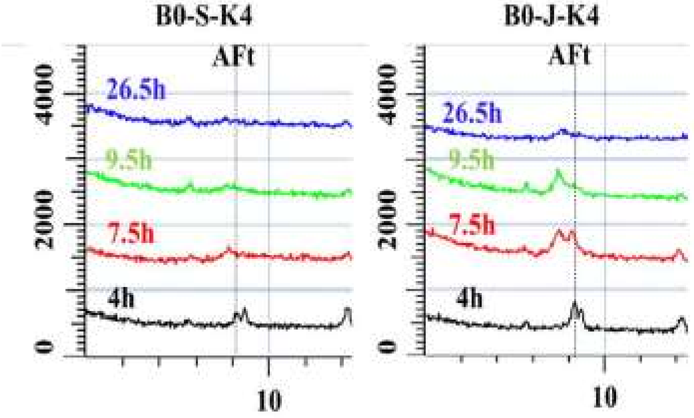


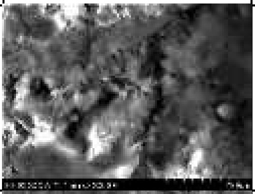
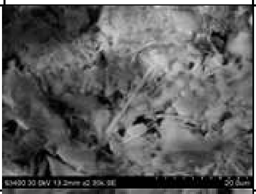
Figure 11 XRD profile

4.3 Changes in ettringite

4.3.1 Ettringite volume change

The Table 3 shows the corrected Aft/α-Al_2O_3 excluding fine aggregate and the reflected electron image by SEM. The values of Aft/α-Al_2O_3 are almost equal at 125 days for the specimens after sufficient curing in water, which indicates that approximately the same amount of ettringite has been re-generated. Although the same amount of ettringite was produced, B0-SS-K4% showed significant expansion, while B0-ACS-K4% showed only slight expansion, indicating that DEF expansion does not necessarily occur even when DEF occurs.

Table 3 Change over time of ettringite

	B0-SS-K4%		B0-ACS-K4%	
	SEM	AFt/Al_2O_3	SEM	AFt/Al_2O_3
6h		0.75		1.02
125day		3.24		3.31

4.3.2 Ettringite shape transformation

The reflected electron images by SEM shown in Table 3 were compared. The ettringite produced during the high temperature curing process in the early stage, is thin and small. After 125 days, the re-generated ettringite was clearly thicker and larger, while the B0-SS-K4% had multiple needle-like crystals of ettringite spreading like flowers from a single point. On the other hand, in B0-ACS-K4%, individual needle crystals were observed to be thick and self-standing. It is possible that the difference in the formation of the re-generated ettringite caused the difference in whether it caused expansion or not.

4.4 Difference in expansion

In the case of using B0 standard sand, a large expansion occurred, while in the case of using air cooling slag fine aggregate, only a small expansion was observed. The difference was considered as follows. In the case of using standard sand, DEF, which is a phenomenon in which ettringite changes to monosulfate hydrate at high temperature and then forms again when the temperature returns to room temperature, occurred, resulting in large expansion. On the other hand, the slight expansion in the slow-cooled slag fine aggregate is considered to be due to the residual SO_3. From previous studies, when the pre-curing period of high temperature curing is short in concrete using cement with high blast furnace slag content, DEF, in which ettringite is formed at room temperature, occurs due to the residual $S0_3$ added in excess after high temperature curing. However, it shows only a slight expansion and is different from the DEF expansion behavior. The slight expansion of the specimen using the air cooling slag fine aggregate is thought to be due to the fact that the SO_3 added as the air cooling slag fine aggregate and potassium sulfate remained unreacted after curing at high temperature, and although DEF was generated, it did not shift to a large expansion behavior.

5. Summary

(1) A large expansion occurred in mortar using standard sand after curing in water at high temperature. The expansion was greatly reduced by using blast furnace slag fine powder.

(2) In the mortar with 4% SO_3 content using air cooling slag fine aggregate, slight expansion was observed after high temperature curing in water. This phenomenon is thought to be due to the formation of ettringite by SO_3 remaining after high temperature curing.

(3) At 4 hours of preloading, the specimens with slow-cooled slag fine aggregate produced more ettringite than the specimens with standard sand, which disappeared after holding at 90°C. On the other hand, it was clear that the DEF in the specimen with standard sand did not necessarily result in expansion.

(4) There was a difference in the expansion even when approximately the same amount of ettringite was produced. It is clear that delayed formation of ettringite does not necessarily lead to expansion.

(5) The different shapes of the re-generated ettringite suggest that the timing and shape of ettringite formation affects the bochiyu.

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