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BASIC PROPERTIES OF CEMENT PASTE MIXED WITH CALCIUM HYDROXIDE-ETTRINGITE COMPOSITE TYPE EXPANSIVE ADDITIVE

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Abstract

In this study, we targeted a calcium hydroxide and ettringite composite-type expansive additive (EA) and obtained the basic characteristics of the EA mixed cement paste in order to create a method for calculating volume expansion based on the hydration reaction of the PC-EA system. Expansion strain, setting time, and compressive strength were measured. In addition, we observed the state of EA after hydration using a micro-CT scanner and scanning electron microscope, and elucidated the expansion mechanism.

Our results show that strain rapidly increased and the compressive strength decreased when the replacement ratio of the EA (C_{rep}) exceeds 6.4%. At the same time, radial cracks were generated from the hydrated EA particles, suggesting that the EA itself grew to expand the cement paste. Although no ettringite was confirmed inside the EA when the C_{rep} was 5.1%, when the C_{rep} was 10.3%, ettringite was formed vertically from the surface of C_3A with a large amount of pores. These results show that simultaneous formation of ettringite and pores causes rapid expansion.

Keywords: Expansive additive, Calcium hydroxide, Ettringite, micro-CT scanning, SEM

1. INTRODUCTION

In order to maintain the durability and aesthetics of reinforced concrete structures over a long period of time, it is necessary to prevent the occurrence of cracks such as drying shrinkage cracking. For example, reducing drying shrinkage strain is effective at preventing cracks, and expansive additive (EA) can be used for this purpose. Although there are many types of EA, calcium hydroxide-ettringite composite type EA is an admixture for concrete that has long been used, and its components are mainly composed of free-lime (f-CaO), anhydrite (CS) and hydraulic minerals such as calcium aluminate (C_3A) or calcium aluminoferrite (C_4AF) [1]. These minerals change into calcium hydroxide (CH) and ettringite (AFt) respectively. They have a large volume evolution, and thus give a cement paste (CP) a macroscopic volume expansion that compensates for shrinkage.

Up to now, regarding studies on the volume change mechanism of CP mixed with EA, Yamamoto et al. proposed the radius evolution of the EA from measurement data such as reaction degree of each mineral and volume of CH and AFt [2]. In addition, Choi calculated the expansion strain of CP by mathematical modeling based on Yamamoto's data [3]. However, some challenges remain, such as the radius evolution proposed by Yamamoto is not a value calculated based on the chemical reaction formula, and the particle size distribution is not taken into consideration.

This study aims to create a method for calculating the volume expansion of CP based on the hydration reaction and radius evolution of the calcium hydroxide-ettringite composite type EA. In this study, experiments were conducted to measure the basic properties of CP mixed with EA. These included expansion strain, setting time, compressive strength and static modulus of the CP mixed with EA. In addition, the state of EA after the hydration was observed using a micro-CT scanner and scanning electron microscopy (SEM) to elucidate the expansion mechanism.

2. EXPERIMENTS

2.1 Sample preparation

All samples were prepared using moderate-heat Portland cement (PC) adapted JIS R 5210 [4] as Japanese standard, EA (powder), Polycarboxylic acid-based super plasticizer (Ad) and deionized water. The water-binder ratio was 0.45. The applied CP mix design is shown in Table 1. All samples were cured at room temperature (20 °C). The CP for micro-CT scanning and SEM was casted in a cylindrical resin bottle with 24mm diameter and 39mm height.

Table 1: Mix-design for cement paste specimen and compressive strength

| Name | Replacement ratio for cement C _{rep} (weight.%) | Water-Binder ratio (%) | Composition | | | | | Compressive strength | | |
|-----------|--|------------------------|-------------|----------|----------|--------|-------|----------------------|--------|--------|
| | | | Water (g/L) | PC (g/L) | EA (g/L) | Ad | | [MPa] | | |
| | | | | | | (mL/L) | (B×%) | 1 day | 3 days | 7 days |
| Reference | 0% | | 590.9 | 1313.2 | 0.0 | | | 4.42 | 12.1 | 21.7 |
| EA26 | 2.57% | | 590.6 | 1278.7 | 33.7 | | | 3.97 | 14.2 | 23.8 |
| EA51 | 5.14% | | 590.3 | 1244.3 | 67.5 | | | 5.71 | 15.6 | 23.6 |
| EA64 | 6.43% | 45% | 590.2 | 1227.2 | 84.3 | 7.2 | 0.55 | 6.98 | 14.1 | 23.7 |
| EA103 | 10.29% | | 589.7 | 1175.7 | 134.8 | | | 4.10 | 8.7 | 13.2 |
| EA109 | 10.93% | | 589.6 | 1167.1 | 143.2 | | | 5.11 | 8.4 | 11.7 |
| EA129 | 12.86% | | 589.4 | 1141.4 | 168.4 | | | Not conducted | | |

2.1 Setting time

In the expansion by EA, the force caused by the expansion is, unless it is a completely enclosed space, transmitted to the rebar or restrained member only when the mortar matrix is hardened and transmits the expansion pressure. That is, even if the unhardened paste expands, no stress is generated, so that it has no meaning in the structural design. Therefore, in this study, we focused the expansion that occurs after hardening of CP begins.

The modified initial setting time determined by the modified Vicat Needle test was adopted for the starting age of hardening. Instead of the water-cement ratio that produces the “normal

consistency” paste proposed in JIS R 5201 [5], water-binder ratio was kept constant at 0.45 and the test was conducted. This standard is almost the same as ASTM C191-13 [6], with slightly different conditions. The diameter of the needle for initial setting is 1.13mm. For the modified initial setting time, the material age when the penetration depth of the Vicat needle was 1 mm from the bottom was adopted.

2.2 Expansion strain

Expansion strain of CP is measured using 50 x 400(X axis direction) x 10mm specimen. A 10 mm square aluminum bar was installed to the end of the specimen, and the change in length of x axis was measured by a non-reaction force LVDT. In order to reduce the frictional force, the CP was casted into the polyester film, and a Teflon sheet was installed between the form on the bottom and the specimen.

2.3 Compressive strength

Compressive strengths were measured using a cylindrical specimen 50(diameter) x 100(height) mm. 24 hours after casting, the CP specimens were carefully removed from their plastic moulds, sealed in polyethylene plastic film.

2.4 Observation by micro-CT scanning

Slices with a thickness of 2-3 mm were cut from the sample in resin bottle and then ground using a thin sectioning machine. Next, micro dicing machine was used and slices were processed into square bars. The length of bar was approximately 0.92 to 1.02 mm. The bars were immersed in isopropanol until testing. Phoenix Nanotom m was used for the test.

2.5 Observation and elemental analysis by E-SEM

On the 3 days of age, the sample was crushed with a hammer to a size of about 5-10 mm, and hydration was stopped with liquid nitrogen. The sample was immediately placed in a freeze-dryer and dried for 1 month. One month later, the sample was impregnated with epoxy resin while performing vacuum defoaming and cured. After the resin has hardened, each sample was grinded and polished on a lapping table with 6 μm , 3 μm , 1 μm and 0.25 μm diamond paste. In between each paste the samples were submerged in ethanol and ultrasonicated to remove debris. Following polishing samples were kept in a desiccator until testing. Philips XL 30 ESEM was used for testing.

3. RESULTS

3.1 Setting time

Test results of setting time are shown in fig 1. The setting time tended to be faster when the C_{rep} was up to 6.4%, but when the C_{rep} exceeded 6.4%, the setting time became slower as C_{rep} increased.

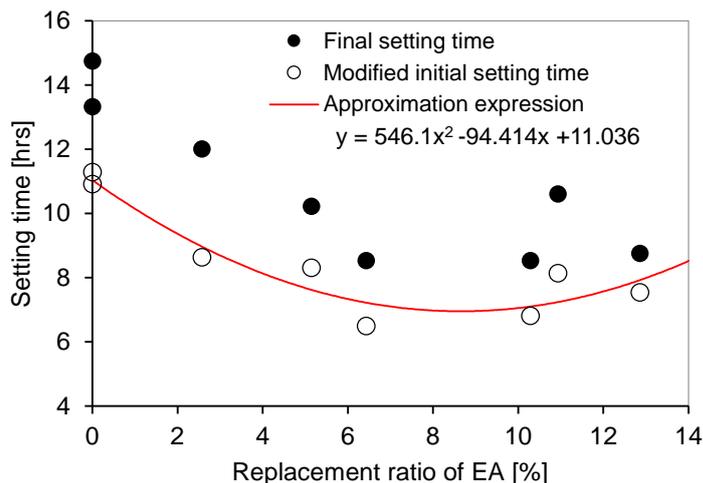


Figure 1: Relationship between C_{rep} and modified initial setting time

3.2 Expansion strain

Test results of expansion strain at 7 days of age are shown in fig 1. For all strains, the strain at the modified initial setting time was set to 0. The strain increases sharply when the replacement ratio of EA (C_{rep}) exceeds from 6.4%.

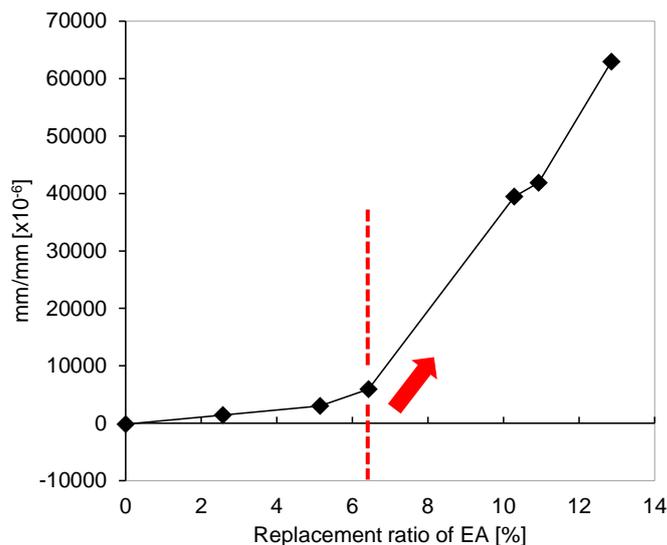


Figure 2: Relationship between C_{rep} and expansion strain at 7 days of age

3.3 Compressive strength

Test results of compressive strength at 1day, 3days and 7 days of age are shown in table 1 and strength ratio compared to reference is shown in fig 3. Compressive strength tended to decrease when the C_{rep} exceeded 6.4%.

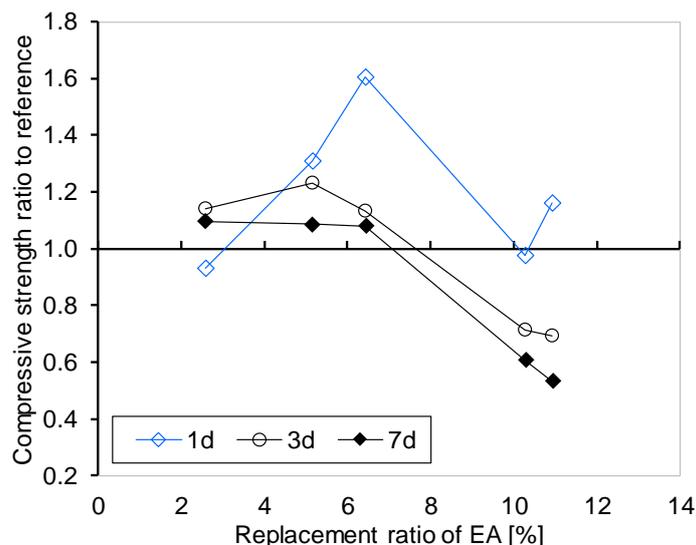


Figure 3: Relationship between C_{rep} and compressive strength

3.4 Observation by micro-CT scanning

A cross section image obtained by CT scanning is shown in Fig 4. Microcracks are radially generated from the aggregated portion of the hydration products. Hydration products such as this is not generated in the case of PC alone, and it is considered that the EA particle have grown. This result shows that the strength decreasing is caused by the expansion of the EA particles themselves.

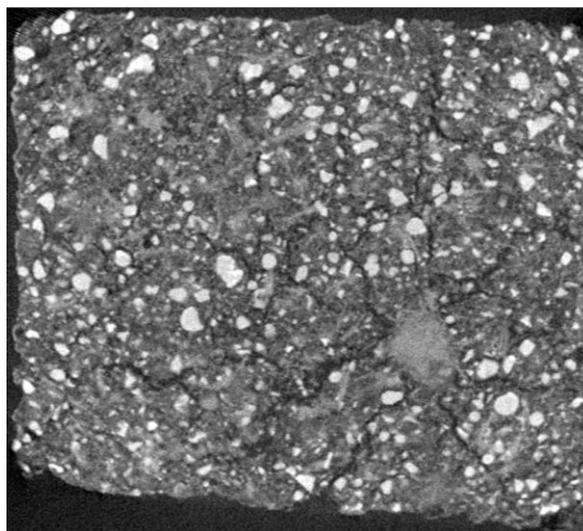


Figure 4: CT scanning image of hardened cement paste bar ($C_{rep} = 10.3\%$)

3.5 Observation and elemental analysis by E-SEM

Fig 5 shows BSE images of raw EA particle and hydrated EA particle at 3 days of age. The EA particles have a structure in which f-CaO is the main constituent mineral, and the gaps are filled with C_3A , C_4AF and anhydrite.

From observation results of EA $C_{rep} = 10.3\%$ (b), we confirmed a larger amount of AFt was produced than in 5.1% (c). (For example, a part surrounded by the red dash line in (b))

The enlarged image of the formation location of AFt is shown in (d). Mono-sulphate (AFm) exists on the surface of C_3A , and needle-like AFt grows vertically from above. In addition, a large quantity of pore was simultaneously formed around the AFt. This result shows that rapid strain expansion occurring near C_{rep} exceeding 6.4% is caused by vertical generated AFt with pores. Also, as with Delayed Ettringite Formation, we have concluded that anhydrite dissolves in water once and AFt can be produced only when the sulphate ion concentration exceeds a certain threshold.

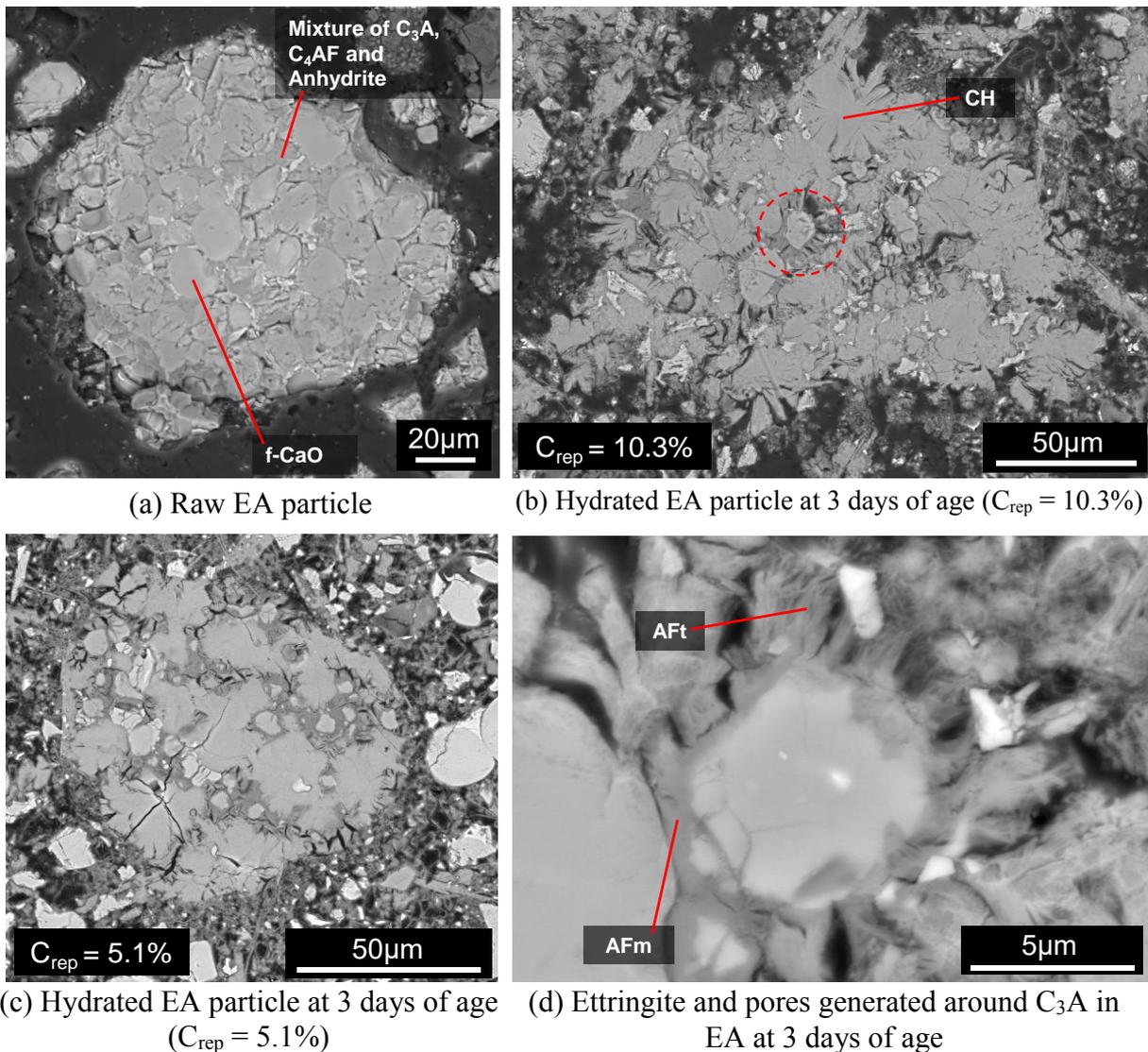


Figure 5: BSE images of raw EA material and HCP mixed with EA

4. CONCLUSIONS

- The expansion strain increases sharply when the replacement ratio of EA (C_{rep}) exceeds from 6.4%.
- The setting time tended to be faster when the C_{rep} was up to 6.4%, but when the C_{rep} exceeded 6.4%, the setting time became slower as C_{rep} increased.

- Compressive strength tended to decrease compared to reference when the C_{rep} exceeded 6.4%.
- From the cross-section image of C_{rep} 10.3% obtained by CT-scanning, microcracks are radially generated from the aggregated portion of the hydration product. This result shows that the strength decreasing is caused by the expansion of the EA particles themselves.
- From the image of the formation location of AFt in EA particle of C_{rep} 10.3% paste, AFm exists on the surface of C_3A , and needle-like AFt grows vertically from above. In addition, a large quantity of pore was simultaneously formed around the AFt. This result shows that rapid strain expansion occurring near C_{rep} exceeding 6.4% is caused by this vertical generated AFt with pores. Also, as with Delayed Ettringite Formation, we have concluded that anhydrite dissolves in water once and AFt can be produced only when the sulphate ion concentration exceeds a certain threshold.

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