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Influence of Some Chemical Admixtures on Growth Behavior of Ettringite from Aqueous Solution

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The growth of ettringite crystal by combining calcium hydroxide and aluminum sulfate solutions including some admixtures have been investigated using the microscope with high magnifications up to 3000 degrees. The nucleation, growth rate and morphology of ettringite were observed to clear the effect of admixtures.

Key words: Ettringite, Crystal growth, Chemical admixture, Nucleation

1. INTRODUCTION

Ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$, is a rarely occurring mineral in nature, whereas this is a very important mineral to cement technology since this mineral is detectable within a few hours and relates an early stage hydrate of Portland cement. [1] The growth of ettringite within the matrix of any solidified body, however, poses significant structural problems. In particular, morphologically ettringite crystallizes into a needle-like crystal habit with a large aspect ratio and the growth of these needle-like crystals in the matrix can exert substantial dilative stresses on the object which results in microcracking, swelling and eventually failure. [2] The relaxation of these stresses will be enabled enough if factors concerning growth morphology of ettringite such as acicular become clear. Furthermore, many chemical admixtures are employed in concrete and related materials, and these admixtures may be also considered to influence the morphology of ettringite. There are, however, few papers investigating the morphology change by the addition of chemical admixtures except for a series ofpapers by A.M. Cody et al. [3-5]
The use of these admixtures will increase in future, and thus it is important to clarify the influence of the addition to the growth behavior of ettringite crystals.

We have been investigating to clear the growth behavior of some crystals from high temperature solution by using in-situ observation microscope with high magnifications and crystal growth theory. In particular, Komatsu et al. one of authors, observed the growth of alite (Ca_3SiO_5), major constituent in Portland cement clinker with in-situ observation microscope, and revealed that alite crystals grew by heterogeneous nucleation and the production temperature and time for Portland cement clinker could be decreased by slight addition of cement clinker in raw materials before firing. [6-7] These results indicate that added clinker powder act as preferential sites for the nucleus of grown crystals, which leads to the increase of the growth rate and the decrease of firing temperature. In the growth of ettringite from the aqueous solution including admixture, the increase of crystal growth will be also enough expected if proper admixtures act as preferential sites.

As for the growth of ettringite, two methods have commonly been employed: (a) by reaction of aluminum sulphate solution with lime-water and (b) by mixing a calcium aluminate solution with one of lime and gypsum. There may be not any significant differences between the products employing both methods. In this study, method (a) was selected and the microscopic observation of growing ettringite crystals has been performed. This observation is easier compared with that of alitem because ettringite crystals grow at room temperature.
In this paper, two typical admixtures (superplasticizer and thickner) were chosen and the morphology change and the delay of nucleation of ettringite crystal by the addition of each admixture were examined, compared with the growth behavior without the addition. The growth behavior of ettringite crystals by the addition of admixtures was observed using the microscope for the first time.

2. EXPERIMENTAL

The reagent Ca hydroxide ($Ca(OH)_2$) and aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) were used as starting materials. A poly carboxylic acid-based compound (PC) and hydroxypropyl methyl ether-based compound (HPMC) were used as superplasticizer and thickener, respectively. The quantity of addition is from 0.02 g/L to 2 as shown in Table I. Primarily, a saturated solution of calcium hydroxide (=1.85 g/L) was made by adding Ca(OH)2 to distilled water and stirring the covered solution for 2h with a magnetic stir, and an aluminum sulfate solution was also produced by adding 2.417 g of aluminum sulfate to 1 L of distilled water. Each chemical admixture was added to an aluminum sulfate solution. Next, 360 ml of saturated $Ca(OH)_2$ solution was placed in a plastic container and 450 ml of aluminum sulfate solution were added to this container. The container was then capped and solution was stirred with magnetic stir bar. The slight quantity solution was taken off in a container every constant time for 14days after starting of stirring and grown crystals were observed with microscope with high magnifications. Precipitates in each container were filtered and examined with powder X-ray diffraction (XRD) and scanning electron microscope (SEM).

Table I A kind and the quantity of chemical admixtures used in experiments.

No.	Chemical admixture	Quantity of addition (g/L)
1	No admixture	0
2	PC superplasticizer	0.2
3	PC superplasticizer	2
4	PC superplasticizer	0.02
5	HPMC thickner	0.1
6	PC + HPMC	0.2 + 0.1

3. RESULTS and DISCUSSION

Morphology change of ettringite

XRD patterns of each precipitates obtained in main three experiments are shown in Fig.1. This indicates that main crystalline phase in precipitates is ettringite, and small quantity of calcite and hydration aluminum is also included. Calcite precipitates is due to CO_2 contamination during mixing. In three experiments, regardless of longer duration of mixing in sample No.3, the peak of ettringite is weak in comparison with that of other samples. This originates from low relative amount of ettringite in this sample due to the formation of amorphous phase such as gel or colloid. The amorphous phase was formed during the observation with microscope, and thus the formation of amorphous phase is due to the rapid evaporation of water in the sample taken from the solution and the addition of superplasticizer does not support the formation of amorphousphase.

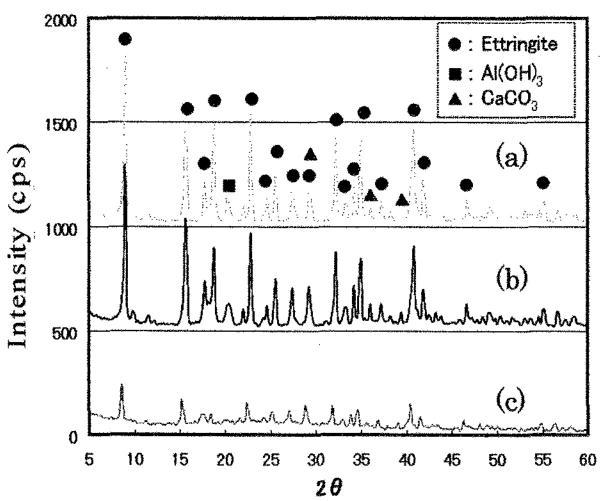

Fig. 2 XRD patterns of each precipitates in three experiments: (a) after 2days in No.1, (b) after 2days in No.5 and (c) after 10days in No.2.

Figure 2 shows SEM microimages of each sample. Ettringite crystals, grown in solutions with thickner and without additive, have dendritic shape with similar aspect ratio, whereas that with superplasticizer has thin needle-like crystal with large aspect ratio. This revealed clearly that the morphology of ettringite crystals was remarkably influenced by the addition of superplasticizer.

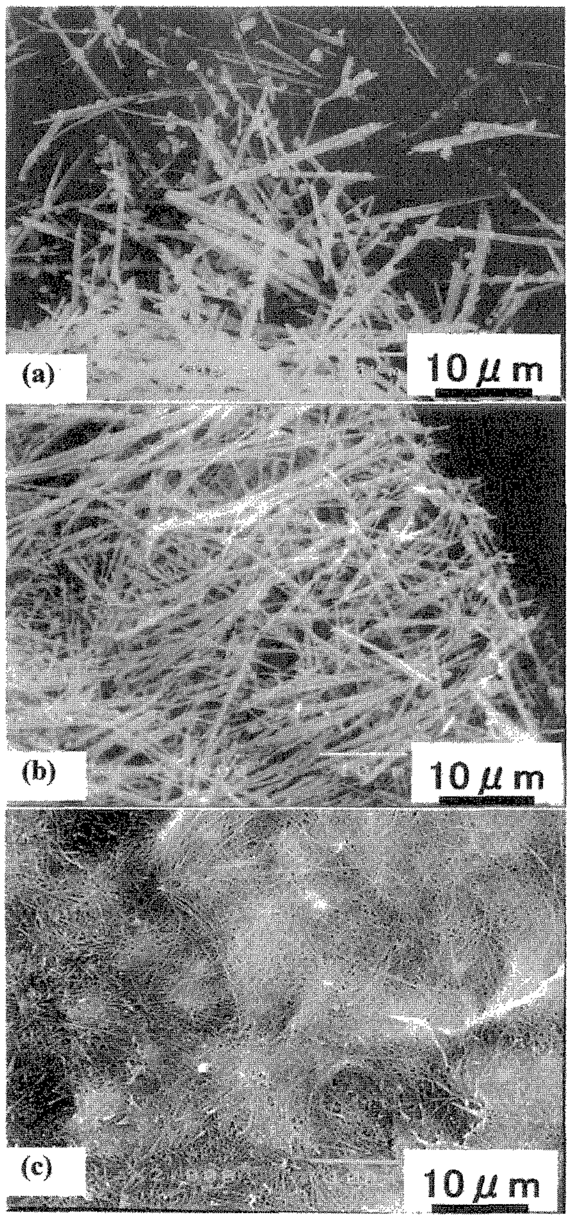

Fig.2 SEM microimages of each precipitates after 1day in main three experiments: (a) No.1, (b) No.5 and (c) No.2.

Effect of duration of mixing

Firstly, the size change of ettringite crystals was investigated using microscope. Figure 3 shows photoimages of three samples (No.1, No.2 and No.5) after the duration of 7days. The size of growing crystals in experiments of No.1 and No.5 is similarly same, which shows that the addition of thickner does not affect the morphology of crystal. In contrast, the shape of crystals grown in the solution with superplasticizer (No.2) is almost observed thin needle-like. These observation results are the same as that of SEM as shown in Fig.3. This clearly indicates that crystal growth may affect by the addition of superplasticizer until the duration of 7 days. Superplasticizer may preferentially adhere to certain faces of the crystals and prevent or slow the growth on those faces.

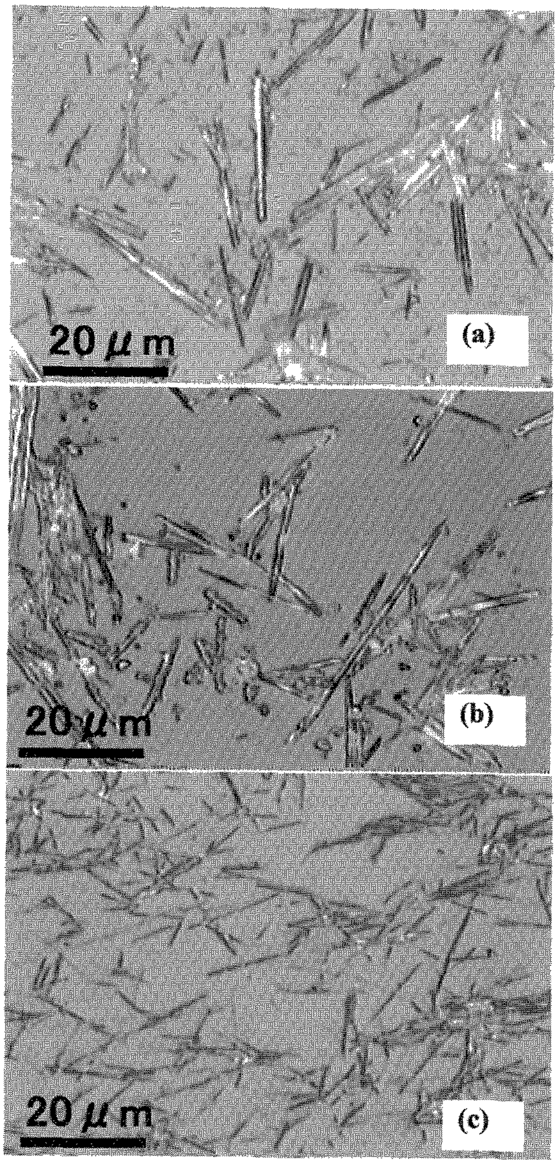

Fig.3 Photoimages of grown ettringite crystal after 7 days in main three experiments: (a) No.1, (b) No.5 and (c) No.2.

Photoimages after duration of 14 days are also shown in Fig.4. A clear difference is not seen in the shape and size of crystals in each sample, unlike the observation results in Fig.3. This indicates that the effect of superplacticizer gradually became weak. Although the origin is not clear enough, the decomposition or the change of superplasticizer for long duration may be possible. Further investigation is required.

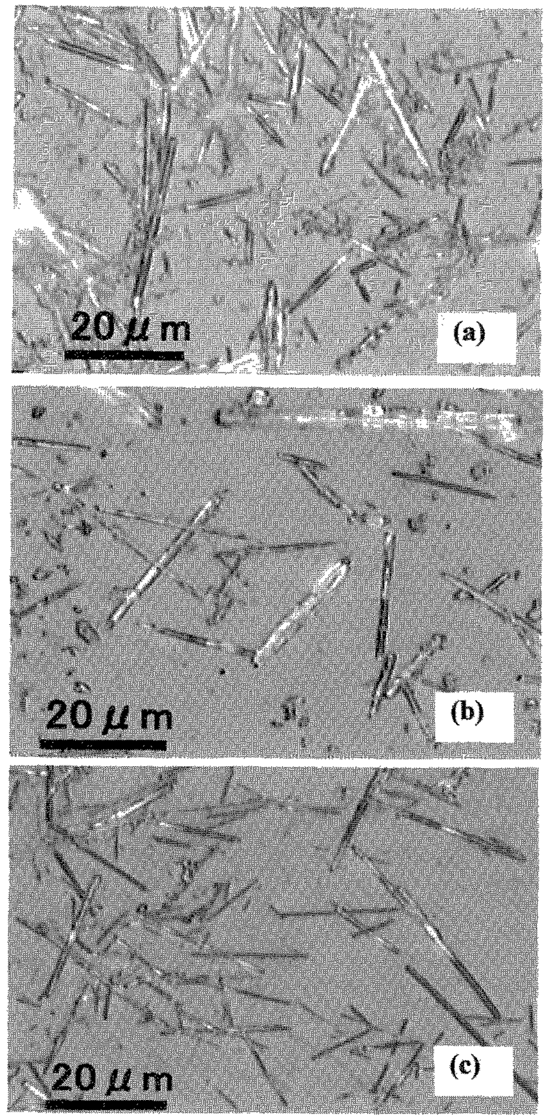

Fig.4 Photoimages of grown ettringite crystal after 14 days in main three experiments: (a) No.1t, (b) No.5 and (c) No.2.

Next, the induction time of ettringite crystal growth was investigated with the in-situ observation microscope, as shown in Fig.5. Ettringite crystal in the solution without the additive was observed to grow after the duration of 0.5 hr, whereas crystal in the solution with superplasticizer was detected after the duration of 3 hr. Ettringite density in the solution without the additive is also larger than that in the solution with superplasticizer. This indicates that superplasticizer results in the delay of nucleation and the decrease of nucleation density. Although the origin is not clear, something change of structure in solution by the addition of superplasticizer happens and this change may lead to such growth phenomena.

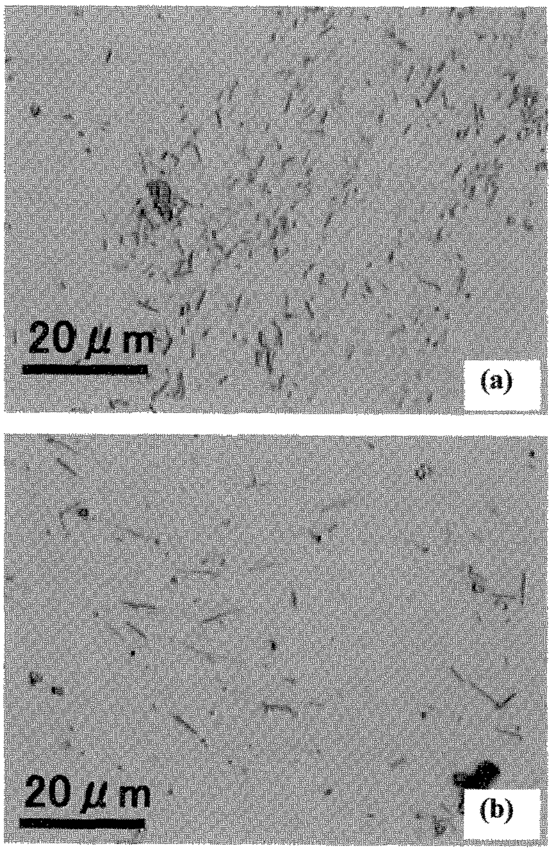

Fig.5 Photoimages of growing ettringite crystal: (a) after 0.5 hr in No.1, and (b) after 3 hr in No.2.

4. CONCLUSIONS

The influence of admixtures on the growth behavior of ettringite crystals was investigated using the microscope with high magnifications up to 3000 degrees for the first time. The thickner such as hydroxypropyl methyl ether-based compound (HPMC) had no influence. In contrast, the superplasticizer such as poly carboxylic acid-based compound (PC) was very effective in inhibiting ettringite nucleation and growth and a smaller quantity of thin needle-like ettringite crystals resulted. Further study is needed to reveal the mechanism of inhibiting.

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