

Morphological Change of Ettringite Crystals Grown in an Aqueous Solution by Addition of Chemical Admixtures

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

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

1. INTRODUCTION

Ettringite, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$, 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 related to an early stage hydration 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 dilatative 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 of papers 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 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 decrease by slight addition of cement clinker to 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 not be any significant differences between the products employing both methods. In this study, method (a) was chosen and the microscopic observation of growing ettringite crystals has been performed.

In our previous paper, two typical admixtures (superplasticizer and thickner) were chosen, and the morphology change and the growth of ettringite crystals by the addition of each admixture were examined, compared with the growth behavior without the addition. The growth behavior of ettringite crystals was observed using the microscope for the first time. As the result, it was revealed that superplasticizer delayed the timing of nucleation and the crystal growth rate and changed the morphology of ettringite in aqueous solution, compared with the ettringite without additives. [9]

In this paper, other two typical admixtures, retarder and accelerator, were chosen and the morphology change and the growth behavior of ettringite crystal by the addition of each admixture were examined, compared with the growth behavior with superplasticizer and without the addition.

2. EXPERIMENTAL

The reagents Ca hydroxide ($\text{Ca}(\text{OH})_2$) and aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) were used as starting materials. A polycarboxylate-based compound (PC), H_3BO_3 and Li_2CO_3 were used as superplasticizer, retarder and accelerator, respectively. The quantity of addition is 0.2 g/L as shown in Table I.

Primarily, a saturated solution of calcium hydroxide (=1.85 g/L) was made by adding $\text{Ca}(\text{OH})_2$ 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. Beforehand, each chemical admixture was added to an aluminum sulfate solution. Next, 360 ml of saturated $\text{Ca}(\text{OH})_2$ solution was placed in a plastic container and 450 ml of aluminum sulfate solution was added to this container. The container was then capped and solution was stirred with magnetic stir bar.

A slight quantity of solution was taken off a container every constant time for 14days after starting of stirring and grown crystals were observed with the microscope with high magnifications. Precipitates in each container were filtered and washed by distilled water, and examined with powder X-ray diffraction (XRD) and scanning electron microscope (SEM)

Table I. Chemical admixtures used in experiments

No.	Chemical admixture	Quantity of addition (g/L)
1	Without additive	0
2	PC superplasticizer	0.2
3	H_3BO_3 retarder	0.2
4	Li_2CO_3 accelerator	0.2

3. RESULTS and DISCUSSION

3.1 Identification of each precipitate

XRD patterns of each precipitate obtained in main experiments (Table I) are shown in Fig.1. These indicate that the main crystalline phase in precipitates is ettringite, and small amounts of calcite and aluminum hydroxide are also included. Calcite precipitates may be due to CO_2 contamination from air during mixing except for experiment No.4 (with Li_2CO_3). In experiment No.4, calcite precipitates are due to CO_3^{2-} in Li_2CO_3 solution.

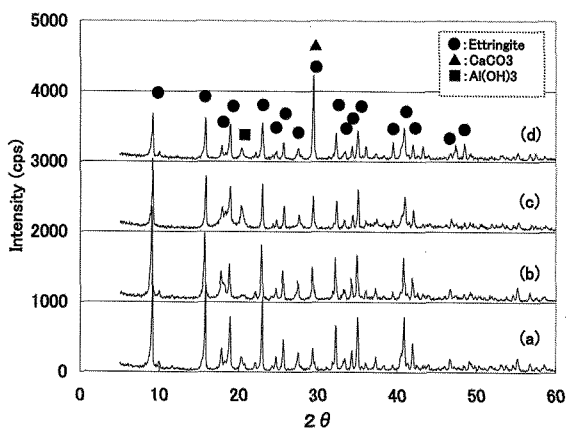


Fig.1. XRD patterns of precipitates in the four experiments: (a) after 2days without additive, (b) after 10days with superplasticizer, (c) after 12days with H_3BO_3 , (d) after 1days with Li_2CO_3 .

3.2 Morphology change of ettringite crystals and effect of duration of mixing

The variations of size and morphology of ettringite crystals with time were investigated with the in-situ observation microscope. Photoimages of grown ettringite crystals are shown in Fig.2 and 3.

Ettringite crystals grown in solution without additive (No.1) have dendritic shape as shown in Fig.2(a), whereas those grown in solution with superplasticizer

(No.2) show thin needle-like crystals with large aspect ratio (Fig.2(b)). With time, the size of these crystals was grown but the morphology did not change. The origin of

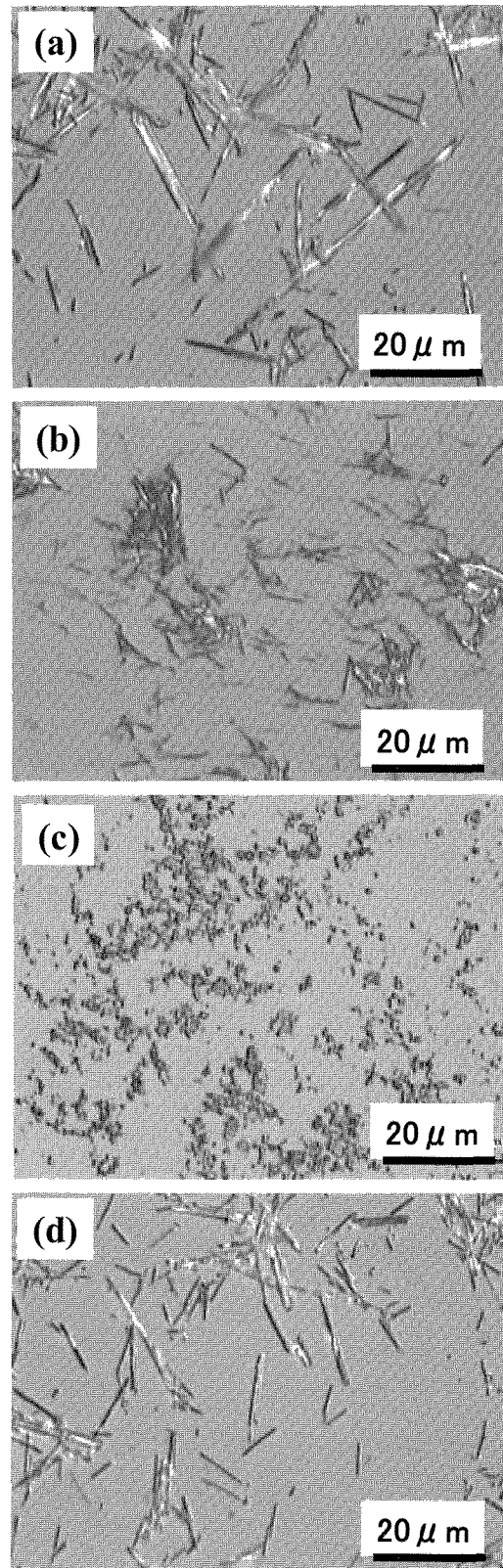


Fig.2. Photoimages of grown ettringite crystals after 1 day: (a) without additive, (b) with superplasticizer, (c) with H_3BO_3 and (d) with Li_2CO_3 .

this morphology isn't clear, but superplasticizer may preferentially adhere to certain faces of the crystals and prevent or slow the growth on those faces. After 14 days, a clear difference is not seen in the shape and size of crystals between with and without superplasticizer (Fig.3(a)). For this reason, it may be considered that the effect of superplasticizer gradually weakens by the decomposition or the change of superplasticizer. Further investigation is required.

The induction time of ettringite crystal was investigated with the in-situ observation microscope, as shown in Fig.4. Ettringite crystals in the solution without the additive were observed to grow after the duration of 0.5 hr (Fig.4(a)), whereas crystals in the solution with superplasticizer were detected after the duration of 3 hrs (Fig.4(b)). This indicates that superplasticizer results in the delay of nucleation and the decrease of nucleation density.

Addition of H_3BO_3 (No.3) dramatically makes the morphology of ettringite crystals change from dendrites to smaller non-dendritic crystals as shown in Fig.3(b). The shape of these crystals was not observed after 1 days and 3 days (Fig.3(b)), and thus observation using SEM was performed. SEM microimages were shown in Fig.5. According to XRD result, precipitates after 1 days is almost amorphous phase (Fig.5(a)), and ettringite was detected after 3 days. These ettringite crystals after 3 days are prismatic (Fig. 5(b)). In addition, it was revealed that H_3BO_3 delayed the timing of nucleation.

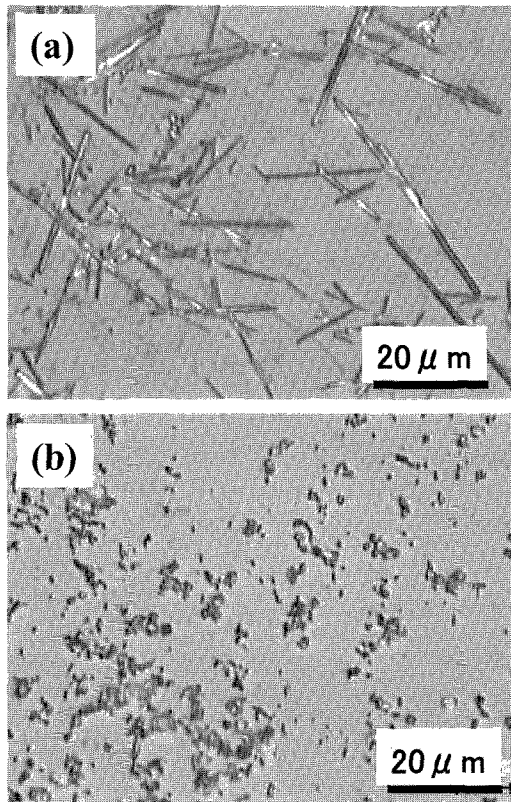


Fig.3. Photoimages of grown ettringite crystals: (a) after 14 days without additive, (b) after 3 days with H_3BO_3 .

BO_3^{3-} is exchangeable for SO_4^{2-} of ettringite and is able to be incorporated in the crystal structure of ettringite. [8] Therefore, BO_3^{3-} also may be preferentially absorbed to certain faces of the crystals and prevent or slow the growth on those faces.

The shape of crystals grown in the solution with Li_2CO_3 (No.4) was dendritic and the size was slightly smaller than those grown without the additive (Fig.2 (d)). But ettringite crystals in the solution with Li_2CO_3 after the duration of 0.5 hr were observed to grow fast and the ettringite crystals density in the solution with Li_2CO_3 is also high (Fig.4(c)), compared with those in the solution without the additive. This indicates that Li_2CO_3 results in the acceleration of nucleation and the increase of nucleation density.

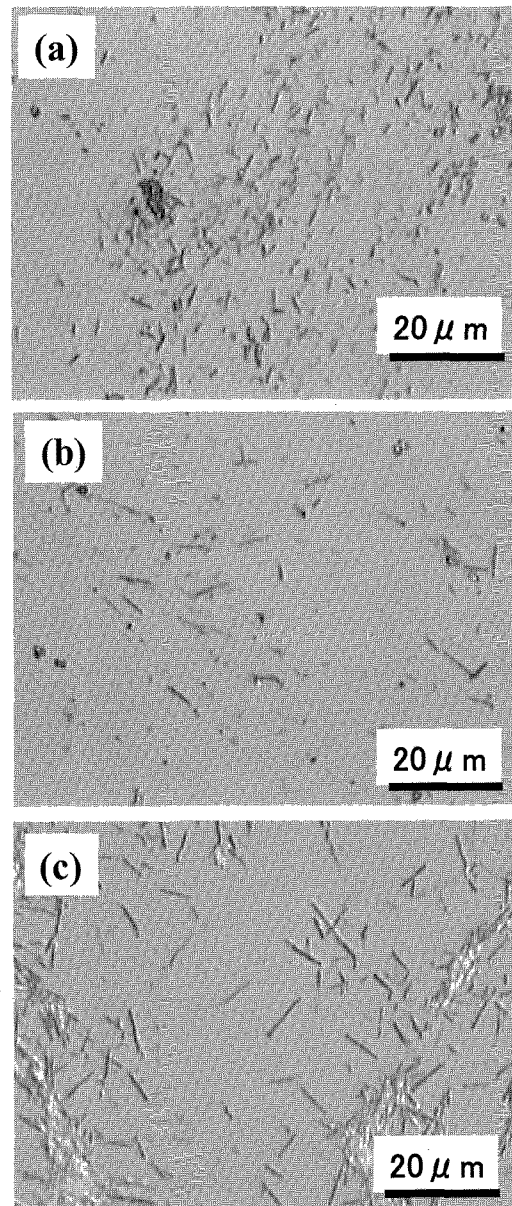


Fig.4. Photoimages of grown ettringite crystals: (a) after 0.5 hr without additive, (b) after 3 hr with superplasticizer and (c) after 0.5 hr with Li_2CO_3 .

The acceleration of nucleation may be due to initial precipitate of calcite that came from Li_2CO_3 and $\text{Ca}(\text{OH})_2$ in the solution, and the calcite was detected with XRD (Fig.1(d)) and the cubic crystals were observed with SEM in an early stage (Fig.6). The higher nucleation density may make the size of ettringite crystals smaller.

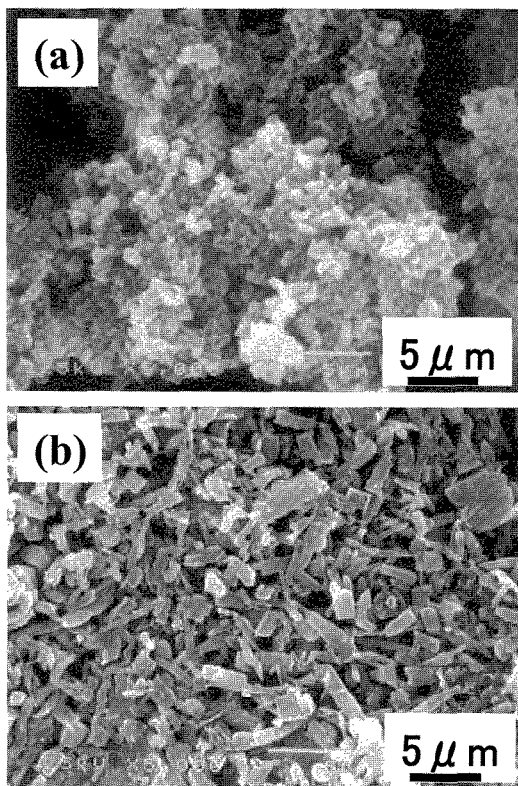


Fig.5. SEM microimages of precipitates with H_3BO_3 : (a) after 1 day, (b) after 3 days.

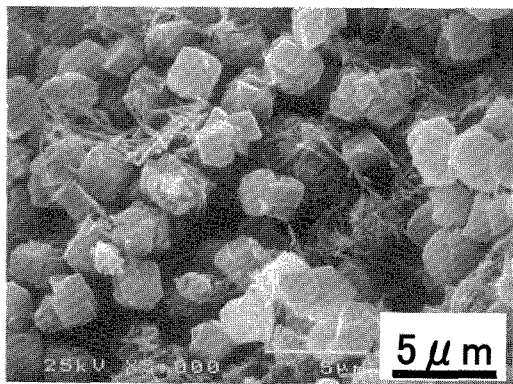


Fig.6. SEM microimage of precipitates after 0.5 hr with Li_2CO_3 .

Fig.7 shows microphotograph of the ettringite crystals in the static solution with the in-situ observation microscope. Spherulite consisting of ettringite dendrites was observed, and calcite was detected in the core of this spherulite. [10] Calcite precipitates resulting from Li_2CO_3 and $\text{Ca}(\text{OH})_2$ solution may act as nucleation site of ettringite crystal growth. In addition, many ettringite dendrite crystals were also observed around each

spherulite. This may be due to the secondary nucleation [11] from dendrites in spherulite. From these phenomena, Li_2CO_3 acts as an accelerator for the nucleation and the growth of ettringite crystals in an early stage.

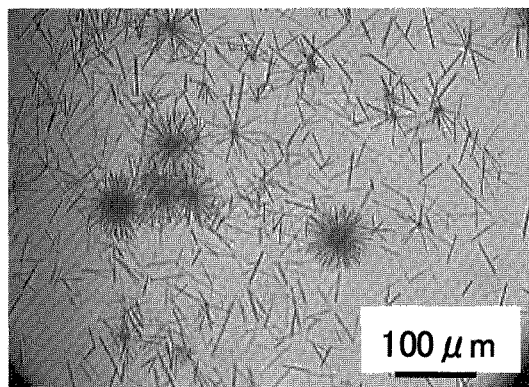


Fig.7. Photoimages of spherulite and dendrite of ettringite crystals in the static solution with calcite.

4. CONCLUSIONS

The influence of admixtures on the growth behavior of ettringite crystals was investigated using a microscope with high magnification up to 3000 for the first time. A polycarboxylate-based compound (PC) as superplasticizer was effective in inhibiting ettringite growth, and thin needle-like ettringite crystals resulted. The retarder (H_3BO_3) was also very effective in inhibiting ettringite nucleation and growth, and smaller prismatic ettringite crystals resulted. The accelerator (Li_2CO_3) was effective in accelerating ettringite nucleation and growth in an early stage. Further new observation study of each crystal faces using AFM microscope is needed to reveal the growth behavior of ettringite crystal.

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