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Phase formation in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at $23 \pm 1^\circ\text{C}$

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Abstract

Soluble borates are known to interfere with the hardening of cement. Phase formation in the quaternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at $23 \pm 1^\circ\text{C}$ was studied and the range of mole ratios permitting the removal of soluble borates from solution has been established. Hydrating the powder composition with molar ratio $\text{Ca}(\text{OH})_2:\text{H}_3\text{BO}_3:\text{C}_3\text{A}^1 = 3:4:1$ resulted in the formation of phase pure $6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3 \cdot 39\text{H}_2\text{O}$ after 3 months of equilibration. During the early stages of hydration, though, the hexagonal calcium aluminate hydrate $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{B}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ and the calcium borate hydrate $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ crystallized but were later consumed by the reaction to form phase pure $6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3 \cdot 39\text{H}_2\text{O}$. At powder ratios of 3:3:1 and 3:2:1, $6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3 \cdot 39\text{H}_2\text{O}$ and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{B}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ were present together at equilibrium. When powders were mixed in the molar proportion of 1:2/3:1, well crystallized $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{B}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ formed directly as a single phase within 5 h. The present study also demonstrates that boron may take on two coordinations, depending on which hydrate forms. Similarities between the hexagonal hydrates $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{B}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CO}_2 \cdot 12\text{H}_2\text{O}$ suggest boron to be three-coordinated in the AFm structure, whereas the literature shows boron to be four-coordinated in $6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3 \cdot 39\text{H}_2\text{O}$, which has the ettringite structure. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Boro-ettringite; Phase formation; Cement hydration

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¹ In cement nomenclature, $\text{C}_3\text{A} = 3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (tricalcium aluminate).

1. Introduction

Encapsulation by concrete has been shown to significantly reduce the leachability of hazardous heavy metals [1]. It is essential, however, that the final waste-form solidifies to a stable solid, renders the contaminants as immobile as possible and achieves adequate strength for safe transport. Boron is widely used in the nuclear power industry and is dissolved in either the secondary coolant water or pools where spent fuel is stored. When waste streams contaminated with boric acid or other soluble borates are utilized for the cement-based solidification/stabilization of nuclear waste, the resulting cement paste often experiences an accelerated set (flash set) and a drastic increase in the time it takes to harden [2]. Pre-treatment of the water may be required to remove as much of the soluble boron as possible. According to Csetenyi and Glasser [3], soluble borates can be insolubilized via their incorporation into the ettringite structure. Ettringite is an important secondary hydration product commonly found in concrete [4]. However, the relevant phase relationships involving the borates have not been determined.

Ettringite, $6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 32\text{H}_2\text{O}$ (alternatively written as $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$), is a quaternary double salt belonging to a group of compounds generally referred to as AFt phases, an acronym which stands for calcium alu \bar{m} inate or ferrite tri-substituted hydrates. Ettringite is characterized by a morphology comprising hexagonal prisms or needles (Fig. 1a) with the SO_4^{2-} oxyanions lying within channels that run lengthwise parallel to the *c*-axis [5]. A wide range of oxyanions, including those of toxic elements such as CrO_4^{2-} and AsO_4^{3-} have been shown to substitute either completely or partially for sulfate in the ettringite structure [6]. Trivalent metals such as Fe^{3+} and Cr^{3+} have been shown to substitute for Al^{3+} , whereas divalent metals such as Zn^{2+} and Cd^{2+} have been shown to substitute for Ca^{2+} in the structure [7].

Another family of quaternary double salts, generally known as AFm phases, or calcium alu \bar{m} inate or ferrite mono-substituted hydrates, are also commonly formed from the hydration of portland cement [8]. The sulfate–AFm phase has the formula $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot 12\text{H}_2\text{O}$, or alternatively, $\text{C}_3\text{A} \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ (sulfate–AFm). A wide range of anions can replace sulfate, the most important of which include OH^- , CO_3^{2-} , and Cl^- [5,9]. Structurally, AFm phases are similar to the mineral hydrocalumite, the

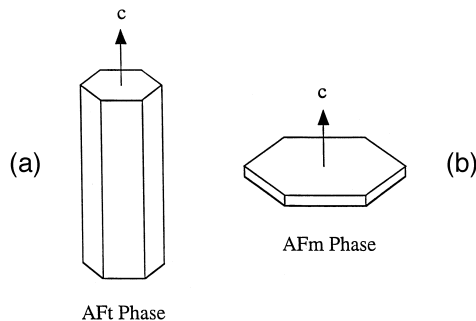


Fig. 1. Characteristic crystal morphologies of (a) AFt and (b) AFm phases. Basal spacing in AFm crystal structure dependent on the type of anion, such as CO_3^{2-} , OH^- , Cl^- and SO_4^{2-} , within interlayer region.

crystals of which are morphologically recognizable as thin hexagonal plates, as shown in Fig. 1b. In contrast to the AFt phases, the anions are bound within interlayer regions which run perpendicular to the *c*-axis. The thickness of this interlayer region thus depends on the size and nature of this anion and the number of water molecules which also reside there [5].

It is known that boron can substitute completely for sulfur in both AFm and AFt phases. Two boro-ettringites have been reported [10]. There is the high-boro-ettringite with the chemical formula $6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3 \cdot 39\text{H}_2\text{O}$, alternatively written as $\text{C}_3\text{A} \cdot 2\text{Ca}(\text{B}[\text{OH}]_4)_2 \cdot \text{Ca}(\text{OH})_2 \cdot 30\text{H}_2\text{O}$ (B-AFt), and the low-boro-ettringite with the formula $\text{C}_3\text{A} \cdot \text{Ca}(\text{B}[\text{OH}]_4)_2 \cdot 2\text{Ca}(\text{OH})_2 \cdot 36\text{H}_2\text{O}$. The high-boro-ettringite can be synthesized via the hydration of calcium aluminate pastes provided the molar ratio $\text{H}_3\text{BO}_3:\text{Al}_2\text{O}_3$ exceeds 0.25 and the temperatures is below 40°C [10]. Phase pure low-boro-ettringite has only been synthesized from aqueous lime–sucrose solutions and stoichiometric amounts of $\text{NaAl}(\text{OH})_4$ and boric acid. In both cases, IR spectroscopy shows boron to be four-coordinated, i.e. $\text{B}(\text{OH})_4^-$, within the ettringite structure [10,11].

Wenda and Kuzel [10] also synthesized and characterized a fully boron substituted AFm phase with chemical formula $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{B}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$, alternatively written as $\text{C}_3\text{A} \cdot \text{CaHBO}_3 \cdot 11.5\text{H}_2\text{O}$ (B-AFm). It was determined that this phase has pseudo-hexagonal symmetry and goes through a displacive monoclinic to trigonal phase transition at 60°C.

The hydration product, $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$, which forms within the ternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ has been extensively studied with regards to the hydration of C_3A [12–14]. The objective of the current study is to determine the conditions under which this and the quaternary hydrates, B-AFt and B-AFm, are stable within the quaternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at $23 \pm 1^\circ\text{C}$. Forming these compounds and establishing the conditions under which they form provides a mechanism for removing boron from solution, thereby permitting normal cement hydration.

2. Experimental methods

To determine the phase assemblages in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ system at $23 \pm 1^\circ\text{C}$, six powder compositions were hydrated. The first three had molar proportions $\text{Ca}(\text{OH})_2:\text{H}_3\text{BO}_3:\text{C}_3\text{A} = 3:4:1, 3:3:1$ and $3:2:1$. The other three had molar proportions $\text{Ca}(\text{OH})_2:\text{H}_3\text{BO}_3:\text{C}_3\text{A} = 1:2/3:1, 1:3/4:1, 1:1:1$. These compositions were prepared by mixing C_3A , $\text{Ca}(\text{OH})_2$ and reagent grade boric acid, H_3BO_3 . For comparison, sulfate-AFm was prepared by hydrating a molar 1:1 mixture of gypsum and C_3A . The C_3A was synthesized by firing an intimate mixture of CaCO_3 and $\text{Al}(\text{OH})_3$ at 1250°C for 2 h. After cooling in air to room temperature, the C_3A was hand ground using a mortar and pestle. The $\text{Ca}(\text{OH})_2$ was synthesized by hydrating CaO in boiling water followed by drying in a vacuum oven to avoid carbonation. The CaO , in turn, was prepared by calcining CaCO_3 at 1050°C for 2 h.

All mixtures were hydrated in de-ionized water at a liquid-to-solids weight ratio of approximately ten. The slurries, along with five pieces of ZrO_2 milling media, were contained in 120 ml high density polyethylene bottles that were tightly sealed with

electrical tape as an extra precaution against carbonate uptake. The mixtures were periodically agitated and stored at room temperature ($23 \pm 1^\circ\text{C}$) for at least 3 months to ensure that equilibrium was reached. Periodic pH measurements were taken of the samples so as to monitor the progress toward equilibrium. For some samples, a portion of the suspension was removed and then diluted by as much as 400%. The large solids content of the suspensions allowed equilibrium to be reached from undersaturation within a month. Identical pH values in both the diluted and mother slurries indicated that equilibrium had been reached. Upon equilibration, the slurries were filtered to remove the solids which were air-dried and then characterized by X-ray diffraction.

3. Results and discussion

The powder composition mixed in the proportion $\text{Ca}(\text{OH})_2:\text{H}_3\text{BO}_3:\text{C}_3\text{A} = 1:2/3:1$ crystallized primarily B–AFm along with a small amount of $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$. This same phase assemblage was produced from the compositions 1:3/4:1 and 1:1:1. TGA analysis on the hydration products confirmed the formula to be $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{B}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$. Fig. 2 shows the X-ray diffraction pattern of the B–AFm phase and the single intense Bragg reflection characteristic of such AFm phases. This Bragg reflection corresponds to a longest basal (interlayer) spacing of around 8.25 Å, a value that agrees well with the one in the literature for the same compound [10]. Interestingly, the diffraction pattern of B–AFm is also very similar to that of the hemi-carbonate-AFm, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CO}_2 \cdot 12\text{H}_2\text{O}$, which has the longest basal spacing of 8.20 Å [15]. In fact, Wenda and Kuzel [10] demonstrated the existence of a complete solid solution series between B–AFm and the hemi-carbonate-AFm. These similarities indicate the coordination of the boron in B–AFm to be three-fold, i.e. $(\text{HO})\text{BO}_2^{2-}$, as with CO_3^{2-} , rather than four-fold, i.e. $\text{B}(\text{OH})_4^-$.

Periodic characterization of the solids during the course of reaction produced additional information concerning the manner in which the B–AFt and B–AFm phases formed. From the composition with molar proportion $\text{Ca}(\text{OH})_2:\text{H}_3\text{BO}_3:\text{C}_3\text{A} = 1:2/3:1$, the solids were extracted and characterized at various times during the reaction to establish the evolution of phase development. As shown by the diffraction patterns in Fig. 3, B–AFm formation was detected within 30 min, and was well crystallized after

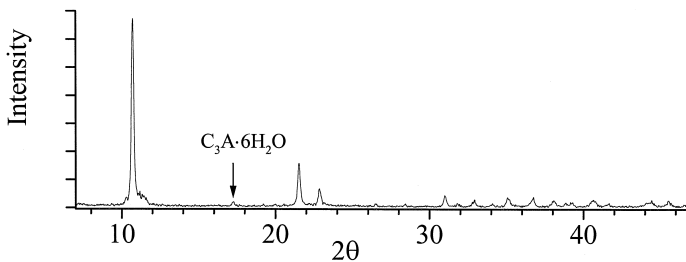


Fig. 2. X-ray diffraction pattern of the quaternary B–AFm phase showing a small amount of the cubic ternary hydrate, $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$.

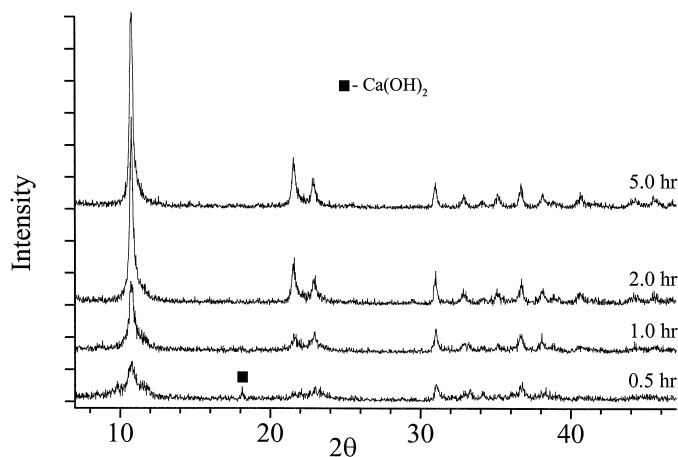


Fig. 3. X-ray diffraction patterns showing the phase development of B–AFm as a function of time.

5 h. Calorimetric studies establishing the kinetics of this reaction confirmed that B–AFm crystallization occurred during this period and established that the AFm phase forms rapidly and directly from the hydration of C_3A in the presence of boric acid and $Ca(OH)_2$ [16]. When this same mixture was allowed to equilibrate for an additional month with only periodic agitation, $C_3A \cdot 6H_2O$ precipitated. This observation raises questions as to the stability of B–AFm. The sulfur analog, $4CaO \cdot Al_2O_3 \cdot SO_3 \cdot 12H_2O$ (sulfate–AFm), was shown to be metastable in the system $CaO-Al_2O_3-SO_3-H_2O$ eventually converting to the stable cubic phase, $C_3A \cdot 6H_2O$ [14]. However, in the present system, characterization of the solids from the 1:2/3:1 and 1:3/4:1 compositions after more than 3 1/2 years of equilibration show only traces of $C_3A \cdot 6H_2O$ with B–AFm still the predominant phase. In a follow-up study, $Ca(OH)_2$, H_3BO_3 , and the stable hydrate $C_3A \cdot 6H_2O$ were combined in the molar proportions 1:1:1 with de-ionized water and were allowed to react for approximately 1 month. Periodic characterization of the solid phases during that time period showed, initially, the presence of highly crystalline $CaO \cdot B_2O_3 \cdot 6H_2O$ along with unreacted $C_3A \cdot 6H_2O$. With time, the B–AFm phase nucleated and grew at the expense of $CaO \cdot B_2O_3 \cdot 6H_2O$ and after 1 month of reaction, became the predominant phase. This observation clearly shows that $Ca(OH)_2$ reacts rapidly with boric acid upon hydration to form the hydrate, $CaO \cdot B_2O_3 \cdot 6H_2O$. Its subsequent reaction with $C_3A \cdot 6H_2O$ to produce B–AFm is rate limiting. These observations indicate that B–AFm is a stable phase at $23 \pm 1^\circ C$ and does not undergo conversion to $C_3A \cdot 6H_2O$. An SEM micrograph showing the crystal morphology of this phase assemblage is presented in Fig. 4. Large, flat, hexagonally shaped crystals of B–AFm and smaller $C_3A \cdot 6H_2O$ crystals, which are in the form of octahedrons, can both be observed. Though all solids were dried in open air, an attempt to dry and store them in a vacuum desiccator resulted in the complete decomposition of the B–AFm phase but not the B–AFm phase.

Fig. 5 shows the diffraction patterns of the solids extracted at different times during hydration of the powder composition mixed in the molar proportion

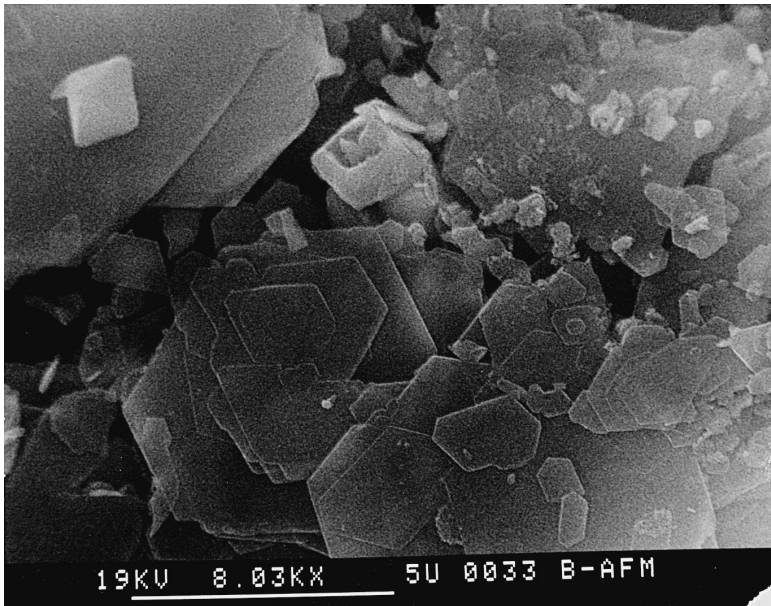


Fig. 4. SEM micrograph showing the large, platy, hexagonally shaped crystals of B-AFm and the small octahedrally shaped crystals of the cubic $C_3A \cdot 6H_2O$.

$Ca(OH)_2:H_3BO_3:C_3A = 3:4:1$. By comparing these diffraction patterns, the succession of solid phases which precipitated and then re-dissolved during the course of equilibration can be discerned. After 2 weeks of reaction, B-AFt, B-AFm and $CaO \cdot B_2O_3 \cdot$

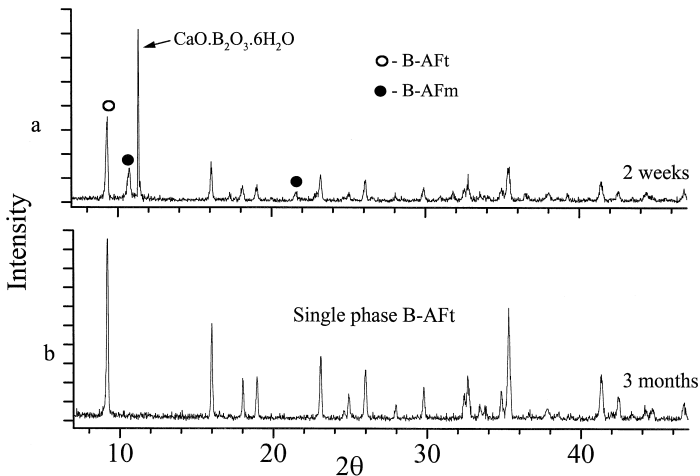


Fig. 5. X-ray diffraction patterns of the composition with molar proportion $Ca(OH)_2:H_3BO_3:C_3A = 3:4:1$ after (a) 2 weeks and (b) 3 months of equilibration.

$6\text{H}_2\text{O}$ were present. After 3 months of equilibration (Fig. 5b), only B-AFt remained as the stable phase, which compositionally, contains the same molar ratio of solids, $\text{Ca}(\text{OH})_2$, H_3BO_3 , and C_3A (3:4:1) as the starting powder composition. The SEM micrograph in Fig. 6 shows the morphology of the high-boro-ettringite (B-AFt) synthesized in this study. The crystals possess a small aspect ratio and appear to be faceted.

In an attempt to synthesize the low-boro-ettringite, the amount of boric acid was decreased while the relative proportions of $\text{Ca}(\text{OH})_2$ and C_3A remained constant. Decreasing the proportion of boric acid in the initial mix to 3:3:1 does not provide sufficient boron to produce phase pure B-AFt (i.e., high-boro-ettringite). After 2 weeks of equilibration, B-AFm, $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, B-AFt, and unreacted $\text{Ca}(\text{OH})_2$ were present, as shown in Fig. 7a. In comparison to the 3:4:1 mixture, the 3:3:1 mixture has less $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ yet more B-AFm after 2 weeks of reaction. After 3 months, $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ was completely consumed and the resulting phase assemblage consisted of B-AFt and B-AFm only (Fig. 7b).

Decreasing the amount of boric acid further to 3:2:1 resulted in the crystallization of B-AFt and B-AFm after 2 weeks of equilibration with unreacted $\text{Ca}(\text{OH})_2$ present as well. This phase assemblage remained unchanged throughout the course of study.

The solids present after 2 weeks of reaction and after 3 months, along with the pH values of the 3-month saturated solutions are listed in Table 1. The solution from which B-AFt crystallized as a single phase showed the lowest equilibrium pH of the four compositions studied. As the relative boric acid concentration decreased, the pH of the equilibrium solution increased. Table 1 shows the equilibrium pH of the 3:3:1 and 3:2:1

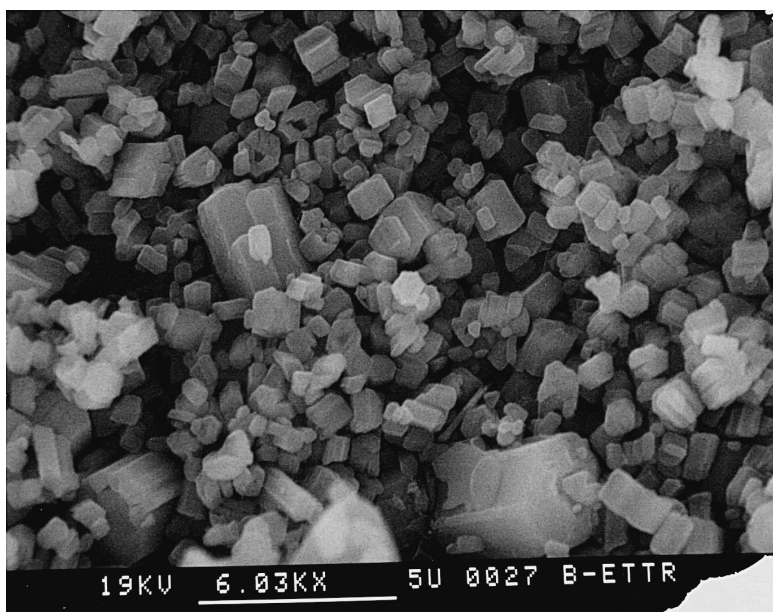


Fig. 6. SEM micrograph showing crystal morphology of the high-boro-ettringite phase (B-AFt).

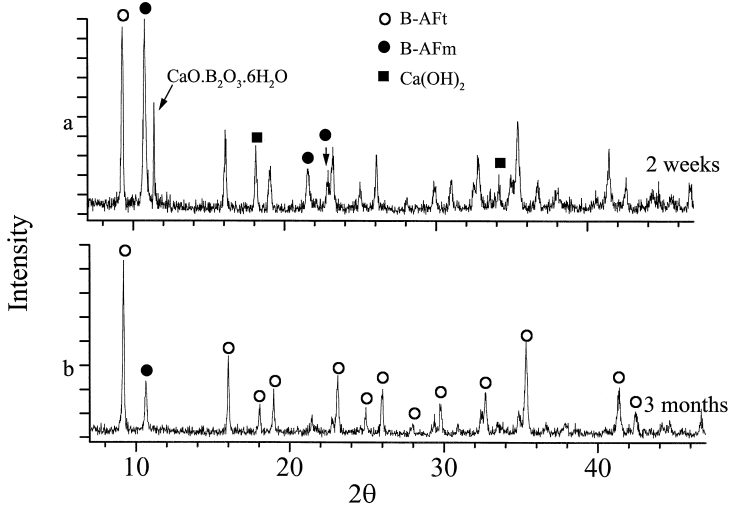
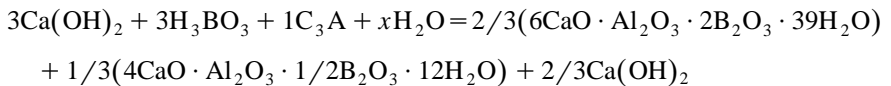


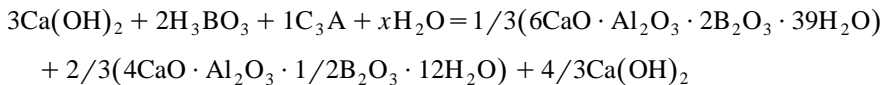
Fig. 7. X-ray diffraction patterns of the composition with molar proportion $\text{Ca(OH)}_2:\text{H}_3\text{BO}_3:\text{C}_3\text{A} = 3:3:1$ after (a) 2 weeks and (b) 3 months of equilibration.

compositions to be 12.54 and 12.58, respectively. These values are close to the pH of a saturated solution of Ca(OH)_2 . This observation suggests Ca(OH)_2 to be in solution at equilibrium in both these compositions. This is consistent with the relative amounts of Ca(OH)_2 in the initial powder mixes and with the compositions of the quaternary double salts which were present at equilibrium. Mole balances are:

3:3:1 Powder Mix:



3:2:1 Powder Mix:



It can be seen from these mole balances that decreasing the relative amount of boric acid in the initial powder mixes results in an increasing amount of Ca(OH)_2 present in solution at equilibrium. In the 3:3:1 composition, even though the solution pH and the above mole balance dictate that solid Ca(OH)_2 is present at equilibrium, it could not be observed by X-ray diffraction. Alternatively, the quantity of unreacted Ca(OH)_2 in the 3:2:1 composition was large enough to be detected by X-ray diffraction. In both cases, the low-boro-ettringite was not observed.

The relatively rapid formation of B-AFm may be the result of the planar conformation [17] of the BO_3^{3-} oxyanion. The CO_3^{2-} oxyanion is also planar and the formation of the hemi-carbonate-AFm also is rapid. According to Roberts [15], the presence of the

Table 1

Equilibrium phase assemblages and solution pH from powder mixes containing C_3A , $Ca(OH)_2$ and boric acid hydrated in water at $23 \pm 1^\circ C$

Composition of initial powder mix in the molar proportion: $Ca(OH)_2:H_3BO_3:C_3A$	Phases present after 2 weeks of reaction	Phases present after 3 months	pH of suspension after 3 months
3:4:1	$CaO \cdot B_2O_3 \cdot 6H_2O^a$, B–AFt, B–AFm	B–AFt ^a	11.87
3:3:1	$CaO \cdot B_2O_3 \cdot 6H_2O$, B–AFt, B–AFt, $Ca(OH)_2$	B–AFt ^a , B–AFm	12.54
3:2:1	B–AFt, B–AFm ^a , $Ca(OH)_2$	B–AFt, B–AFm ^a , $Ca(OH)_2$	12.58
1:1:1	Not available	B–AFm ^a , $C_3AH_6^b$	12.48
1:3/4:1	Not available	B–AFm ^a , C_3AH_6	12.30
1:2/3:1	B–AFm (5 h)	B–AFm ^a , C_3AH_6	12.43

^aDominant phase.^bBarely detectable on diffraction pattern.

often mis-characterized hemi-carbonate-AFm, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CO}_2 \cdot 12\text{H}_2\text{O}$, may account for many of the conflicting results found in studies done on the hydration of C_3A . Ternary hydrates, such as $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ (OH-AFm), often convert to the quaternary hemi-carbonate-AFm upon drying and even during X-ray characterization of the moist solids due to incorporation of atmospheric CO_2 . The relative ease with which these carbonated AFm phases form may be attributed to the planar CO_3^{2-} oxyanion, the geometry of which appears to be more suitable for the two-dimensional ‘sandwich-like’ structure of the AFm phases (see Fig. 1b). The rapidity with which B-AFm forms indicates boron is also three-coordinated in the AFm structure.

To further demonstrate this point, a 1:1 mixture of C_3A and gypsum was mixed with water and then continuously agitated for 8 h. The solids were removed and characterized at various times during the reaction. As shown in Fig. 8, sulfate-ettringite formed within the first hour of hydration. There was also a substantial amount of unreacted anhydrous C_3A present at this point. Two hours into the reaction, the C_3A appeared to have been consumed in conjunction with the ettringite being re-dissolved. About 8.5 h into the reaction, conversion to the sulfate-AFm took place. These observations agree with the established mechanisms of C_3A hydration in the presence of gypsum [18–21]. However, the preferential formation of ettringite during the early stages of hydration is analogous to that of the AFm phase in the borate system. In addition, sulfate-AFm forms in much the same manner as does B-AFt; via the precipitation and re-dissolution of transitory phases. Based on the order of phase evolution, these similarities clearly show that tetrahedral oxyanions such as SO_4^{2-} and $\text{B}(\text{OH})_4^-$ have a preference for the more three-dimensional columnar-like structure of the AFt phases.

The observed sequence of phases which formed during the hydration of C_3A in the presence of both borate and sulfate is consistent with Ostwald’s Law of Stages or *Stufenregel* [22]. In describing crystallization in supersaturated solutions and super-cooled melts, Ostwald states that a system left in an unstable state ‘will change not into the most stable form, but into the form the stability of which most nearly resembles its own; i.e., into that transient stable modification whose formation from the original state

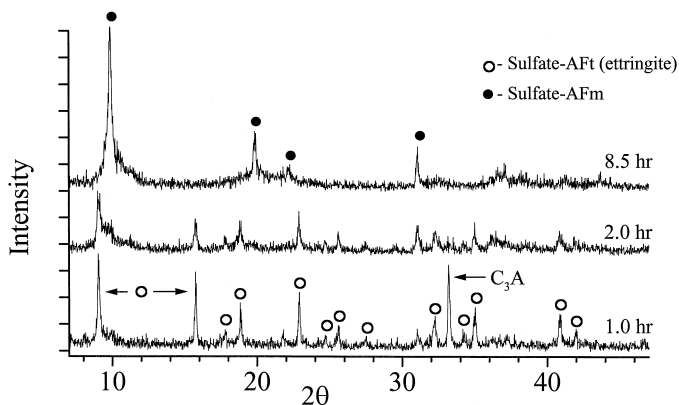


Fig. 8. X-ray diffraction patterns showing the phase development of a 1:1 molar mixture of C_3A and gypsum in water as a function of time.

is accomplished by the smallest loss of free energy.' Therefore, the metastable formation of B–AFm in the 3:4:1 composition and the metastable formation of sulfate–AFt can be considered kinetically favorable under the conditions of this study; the structural compatibility between the oxyanion and the structure of its host phase being the basis for the evolution of phases.

4. Conclusions

The high-boro-ettringite (B–AFt) is a stable phase in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at $23 \pm 1^\circ\text{C}$ and can coexist invariantly with B–AFm and $\text{Ca}(\text{OH})_2$. B–AFm was also shown to be a stable phase which can coexist univariantly with the cubic hydrate, $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$. However, the fact that $\text{C}_3\text{A} \cdot 6\text{H}_2\text{O}$ was present in the 1:1:1 composition as well seems to suggest that B–AFm may be an incongruent solid.

The rate at which X-ray phase pure B–AFt forms is slow, crystallizing fully in approximately 3 months. Such slow crystallization is due to the initial formation of the transient phases, $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ and B–AFm. Eventually, $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ and B–AFm re-dissolve leaving fully crystallized B–AFt as the only phase.

Equilibrium involving B–AFt is reached more rapidly when the $\text{H}_3\text{BO}_3/\text{C}_3\text{A}$ molar ratio is decreased, or equivalently, when the solution from which it precipitates becomes enriched with respect to $\text{Ca}(\text{OH})_2$. Under those conditions, less intermediate $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ and more B–AFm forms. It also appears that decreasing the boron content without changing the relative proportions of calcium and aluminum does not result in the formation of the low-boro-ettringite. This is in accordance with the observation that phase pure low-boro-ettringite can only be synthesized by using the saccharate method [3,10,11]. By decreasing the boron concentration further relative to C_3A , and reducing the $\text{Ca}(\text{OH})_2/\text{C}_3\text{A}$ molar ratio to 1, B–AFm crystallizes directly as the predominant phase within minutes.

In the context of being the more suitable host phase for boron, B–AFm has some advantages over B–AFt. It was reported by Csetenyi and Glasser [3] that high carbonate concentrations in solution decompose the low-boro-ettringite phase, and in the present study, a vacuum was shown to have a similar effect on the high-boro-ettringite (B–AFt). In contrast, rather than being decomposed by the carbonate ion, B–AFm forms a stable solid solution with it. In the sulfate system, AFm phases are more stable at higher alkali concentrations and temperatures than are AFt phases [23]. These facts point toward the direct crystallization of B–AFm as the desired route when the goal is the complete and efficient removal of dissolved boron.

Boron is unusual in that it establishes two stable coordinations depending on which phase crystallizes [11]. In the B–AFt structure, boron is four-coordinated as $\text{B}(\text{OH})_4^-$. In the B–AFm structure, boron appears to be three-coordinated, most likely as the planar oxyanion, $(\text{HO})\text{BO}_2^-$.

Comparing the mechanistic paths of B–AFt and B–AFm formation illustrated a correlation between the geometry of the oxyanion and the structure of the hydrate which forms initially. B–AFm and sulfate–AFt form most readily during the early stages of C_3A hydration in the presence of boric acid and sulfate, respectively. Early B–AFm

formation suggests a preference of the planar oxyanion for the more two-dimensional 'sandwich-like' structure of the AFm phases. Early sulfate–AFt formation suggests a preference of the tetrahedral oxyanion for the more three-dimensional columnar-like structure of the AFt phases.

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