

EFFECT OF BORAX ON CALCIUM SULFOALUMINATE CEMENT PROPERTIES

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This work reports the effect of borax on the performance of calcium sulfoaluminate (CSA) cements which contain different amounts of gypsum. The heat evolution, setting time, compressive strength, dimensional stability and hydration products were investigated. The results indicated that borax significantly retards the early hydration and setting time of CSA cement. The setting time is prolonged with an increased amount of additional borax. The addition of gypsum influences the early hydration of CSA cements with borax. The early strength of the mortars with borax suffers a decrease for mortars containing 5 % gypsum. The addition of borax leads to an increase in the mechanical strength of the mortars with 15 % and 20 % gypsum. An appropriate amount of borax as a retarder is beneficial to the strength development of CSA cements. The shrinkage and expansion rates of the cements with borax are limited. The presence of borax inhibits the hydration of ye'elimite and the depletion of gypsum at 1 day. The effect of borax on the ettringite formation is related to the gypsum content of the CSA cements.

INTRODUCTION

The production of Portland cement (PC) consumes a large quantity of energy and generates 5 ~ 10 % of the anthropogenic CO₂ emissions [1]. The cement industry is trying to seek innovative solutions to conserve energy and reduce CO₂ emissions. One method is the development of alternative low-carbon binders. Calcium sulfoaluminate (CSA) cement is a promising alternative cement to traditional PC because this type of cement requires less energy and emits lower CO₂. Although CSA cements have different compositions, they consist of ye'elimite (C₄A₃S̄) and belite (C₂S). Additionally, other phases, such as gehlenite (C₂AS), aluminoferrite (C₄AF) and anhydrite (C̄S), may also exist in these cements. CSA cements are obtained by grinding the cement clinker with 10 - 25 % gypsum or anhydrite [2]. The main performance of CSA cements is the rapid setting, high early strength, shrinkage compensation and good resistance to corrosion and sulfate-rich environments, which is associated with the hydration of C₄A₃S̄ [3-4]. CSA cements are usually used in small-scale repairs and construction in winter. Although CSA cements have gained increasing attention in recent years, many barriers prevent their extensive use, such as high production costs and lack of mixture design methodology.

The hydration mechanism of CSA cements is associated with the rapid reaction of ye'elimite with calcium sulfates [5-7]. The produced hydration products consist of ettringite, monosulfate and aluminium hydroxide. Different types or quantities of calcium sulfate have a significant influence on the amount of ettringite and monosulfate at early ages [8]. This will cause the setting time, porosity, mechanical strength and dimensional stability to be also affected by calcium sulfates [9]. The slow hydration reaction of belite leads to the formation of calcium silicate hydrate, which is, in turn, related to the long-term strength development in the CSA cement.

Compared with PC, CSA cements react fast and produce a large amount of hydration heat on the first day [10]. Therefore, the use of retarders in CSA cements is necessary to ensure the sufficient time for mixing and placing. Several chemical additives can be used to slow down the hydration of ye'elimite and, thus, control the setting time of CSA cements. Hydroxylic organic admixtures, like citric, tartaric or gluconic acids, as well as their salts, are used as set retarders of CSA cements [11-12]. The commonly used inorganic additives are boric acid and its salt (sodium borate) [13-15]. The borate ions retard the hydration of CSA cement, possibly due to the high gypsum content in the binder [13].

This study reported that the formation of ulexite with poor crystallinity was found in the hydration process of CSA cements containing sodium borate. The transient formation of ulexite was found to play a significant role in controlling the cement hydration. Reducing the gypsum content or increasing the sodium content are two effective ways to prevent the precipitation of ulexite and, thus, decrease the retardation of cement hydration. Thus, the influence of sodium borate on the hydration is clearly associated with the addition of gypsum. Some works have studied the retarding effect of borax (sodium tetraborate) [12]. The results showed that the presence of borax significantly lowered the pH of the solution and prevented the dissolution of ye'elimite. Bullerjahn et al. studied the effect of boron on the early hydration of belite ye'elimite ferrite cement [15]. The addition of boron decreased the workability and improved the compressive strength of the mortar. Similarly, the dissolution of ye'elimite was slowed down or inhibited in case of a high concentration of boron. The presence of boron further accelerated the precipitation of ettringite, the consumption of calcium sulfate and the subsequent monosulfate formation. This study assumed that boron was initially absorbed on the surface of amorphous hydrates. At later ages, boron was further depleted by exchanging with the sulfate bound in ettringite and monosulfate. Therefore, boron has a notable impact on the hydration kinetics. However, the mechanism of the hydration of CSA cements with boron is not well known. Deep research on the property development of CSA cements with boron is also limited.

It is well known that gypsum plays a significant role in the hydration process of CSA cements. The amount of gypsum can have an impact on the retardation of CSA cements by borate ions. Consequently, the aim of this work is to investigate the impact of borax on the performance of CSA cements containing different amounts of gypsum, as well as the hydration process involved. This research will help to understand the hydration mechanism of CSA cements with the addition of boron and, thus, facilitate the application of CSA cements in construction engineering.

EXPERIMENTAL

Raw material

A CSA cement clinker, which was manufactured by Liujiu Cement Co. Ltd (China), was used in this work. Natural gypsum (NG) was incorporated into this work to prepare the CSA cement. The chemical and phase composition of the CSA cement clinker and NG are described in Table 1. In the CSA cement clinker, $C_4A_3\bar{S}$ and C_2S are the main minerals. The other minor phases include ferrite, mayenite ($C_{12}A_7$) and anhydrite. The cement clinker has a Blaine surface of $3500 \text{ cm}^2 \cdot \text{g}^{-1}$. Chemical grade borax (sodium tetraborate decahydrate) was employed as the retarder.

Five cementitious compositions with different gypsum contents were investigated in this paper. The CSA cement clinkers were blended with different amounts of NG (0 %, 5 %, 10 %, 15 % and 20 %), and they were labelled as A0, A1, A2, A3 and A4, respectively. The dosage of borax was by the mass of cement (0.0 %, 0.1 %, 0.3 % and 0.5 %). Borax was dissolved in water beforehand in order to ensure that borax was evenly dispersed in the cement.

Test methods

The setting time was tested using a standard Vicat apparatus in line with GB/T 1346-2011. The mortars were prepared with a sand/cement ratio of 3 and a water/cement ratio of 0.5. The mortars were cast in moulds with dimensions of $40 \text{ mm} \times 40 \text{ mm} \times 160 \text{ mm}$. The moulds were then moved to the curing room where the temperature was 20°C and the relative humidity was 95 %. After demoulding, the mortars were continuously cured in water at 20°C until the strength testing. The compressive strengths of the mortars were measured in line with GB/T 17671-2021. The strength result represented the average of the strengths from six specimens. For dimensional stability testing, the mortars were also prepared with a sand/cement ratio of 3 and a water/cement ratio of 0.5. The mortars were cast in moulds with a different size of $25 \text{ mm} \times 25 \text{ mm} \times 280 \text{ mm}$. The moulds were then cured under the same conditions as for the compressive strength test. After 1 d of curing, the mortars were removed from the moulds. The initial length was recorded accordingly. The specimens

Table 1. Chemical and mineralogical composition of the raw materials (%).

Component			Phase		
	CSA clinker	Gypsum		CSA clinker	Gypsum
CaO	42.1	32.3	Ye'elimite	65.0	-
SiO ₂	10.5	2.0	Belite	18.7	-
Al ₂ O ₃	32.0	1.0	Ferrite	5.5	-
Fe ₂ O ₃	1.9	0.5	Mayenite	6.5	-
MgO	1.4	1.3	Anhydrite	4.3	-
Na ₂ O	0.1	0.6	Gypsum	-	96.5
K ₂ O	0.3	1.2	Anhydrite	-	2.9
SO ₃	9.0	39.5	Quartz	-	0.6

were cured in water and air, respectively. Finally, the expansion/shrinkage rate can be calculated based on the length changes at the different curing ages.

The heat evolution was monitored by a TAM AIR calorimeter. Cement pastes with 2 g of cement and 1 g of water were prepared externally. The experiment was carried out at 20°C.

The cement pastes were mixed with water at a water/cement (w/c) mass ratio of 0.4. At the testing age, the samples were broken into small pieces in an agate mortar. In order to stop hydration, the small samples were soaked in ethanol for 2 days. Finally, the specimens were dried in a vacuum desiccator at 40°C for further analysis.

X-ray diffraction (XRD) was adopted to identify the mineral development in the hydrated samples. The samples were milled in order to pass through a 0.08 mm sieve before the XRD analysis. The XRD patterns were obtained by using a diffractometer (Bruker D8 Advance, Cu K α radiation). The diffractometer was operated at 40 kV and 40 mA with step scans taken from 5 to 65° with a step size of 0.02°. TOPAS 4.2 software was used for the Rietveld quantitative phase analysis. The microstructure of the hydrated samples was observed by using scanning electron microscopy (SEM). Prior to the SEM test, the fractured surfaces of the specimens were coated with gold in order to promote the electrical conductivity.

RESULTS AND DISCUSSION

Heat of hydration

Figure 1 displays the heat flow released during the hydration of the CSA cements with the addition of borax. The initial peak occurs after being in touch with water is related to the dissolution of the cement minerals and the occurrence of the hydration reactions [12, 16]. After the initial peak, the hydration heat flow decreases and the samples show an induction period. The main

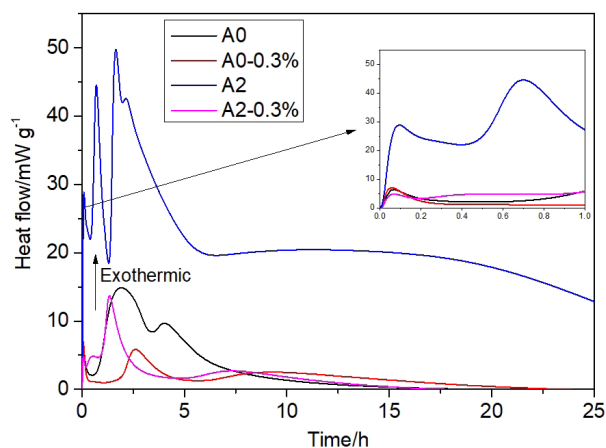


Figure 1. Hydration heat flow of the CSA cements with borax.

hydration period of sample A0 is characterised by two peaks with their maxima at 1.9 h and 4 h. The first peak reflects the period of the consumption of ye'elimite and the formation of ettringite [17-18]. The second peak is ascribed to the deficiency of gypsum, leading to the precipitation of ettringite as well as monosulfate [17-18]. In the presence of borax, the induction period of sample A0 is prolonged. After the induction period, sample A0 with 0.3 % borax shows the first heat peak at 2.6 h. The second heat peak at 9.3 h is quite weak. Therefore, the addition of borax significantly retards the hydration of the clinker and decreases the heat flow of those heat peaks. There are also two peaks for sample A2 in the heat flow curves. The two peaks occur at 0.7 h and 1.6 h. The shoulder appeared at 2.1 h possibly due to the deficiency of gypsum. It is seen that the hydration of CSA cements is prominently enhanced by the presence of gypsum. By comparison, sample A2 with 0.3 % borax shows the first hydration peak at 1.3 h and the second weak peak at 7.3 h. The decrease in intensities of the peaks is distinctly found. As stated above, ettringite is the main hydrate during the first heat peak, whereas it is monosulfate during the second hydration peak. The presence of borax seems to decelerate the precipitation of ettringite and, thus, causes the slower depletion of sulfate. Consequently, the onset of the monosulfate peak appears later. It is seen that borax also retards the hydration of CSA cements. Besides that, the addition of gypsum results in a shift in the heat peaks to an earlier time.

Setting time

Table 2 demonstrates the initial and final setting times of the CSA cements with the different amounts of gypsum. The setting times of the CSA clinker (A0) are also given for comparison. It can be seen that the setting times of CSA cements are much shorter than PC. The hydration reaction of ye'elimite with calcium sulfate is rapid and promotes the precipitation of ettringite, resulting in the fast setting of the CSA cement [19]. The cement with 5 % gypsum (A1) shows a similar setting time to the clinker (A0). The initial and final setting times of the cements with 10 % and 15 % gypsum (A2 and A3) are significantly shortened, while the setting times of cement with 20 % gypsum (A4) are slightly prolonged compared with the clinker. This indicates that the addition of 10 % and 15 % gypsum promotes the setting process of the cements at early ages.

Table 2. Setting times of the CSA cements with different amounts of gypsum (min).

Cements	Initial setting time	Final setting time
A0	37	64
A1	36	62
A2	23	38
A3	28	43
A4	40	76

The setting times of the CSA cements with different dosages of borax is depicted in Figure 2. The influence of borax on the setting time varies for the different cements. A dosage of 0.1 % demonstrates a weak retarding effect for samples A0, A1 and A4. When the dosage of borax increases to 0.3 %, a significant retardation in the setting time can be observed in samples A0, A1 and A4. While for samples A2 and A3, the addition of borax causes a significant retardation in the setting time. The initial and final setting times are extended with the increased amount of borax in samples A2 and A3. When the dosage of borax increases to 0.5 %, the initial and final setting times of CSA cements are remarkably extended to more than 250 min and 300 min, respectively. For cement A1, the initial and final setting time are extended from 36 min and 62 min to 366 min and 420 min, respectively. The longest setting time is observed for cement A4, the initial and final setting times being 397 and 491 min, respectively. The result indicates that borax retards the setting process of the CSA cements, which is in accordance with the hydration heat of CSA cements shown in Figure 1. The initial and final setting times of the CSA cements were related to the time of the heat peak [20]. The retardation of borax may be caused by hindering the dissolution of ye'elimite [21]. In the presence of borax, as the amount of gypsum increases, it seems that the setting times of the cements are prolonged. However, the setting times of cement A2 and A3 are significantly shorter than samples A0 and A1 in the presence of 0.5 % borax. These phenomena are related to the influence of gypsum on the early hydration of CSA cements with borax.

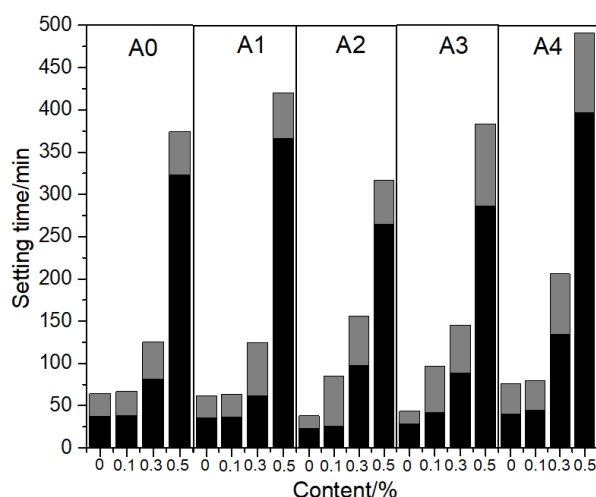


Figure 2. Influence of borax on setting times of the CSA cements with the different amounts of gypsum (the black parts represent the initial setting time, while the grey parts represent the time between the initial and final setting time).

Compressive strength

The evolution of the compressive strengths of the clinkers with the addition of borax is shown in

Figure 3. It can be found that the main strength increase occurs after 3 days of hydration. The addition of borax significantly enhances the compressive strength of the mortars prepared with the CSA clinkers. The borax dosage has little effect on the strength development at 1 d. The mortars with 0.1 % and 0.3 % borax achieve a similar strength level at all the ages. Using borax at a dosage of 0.5 % results in the highest strength after 3 days of hydration.

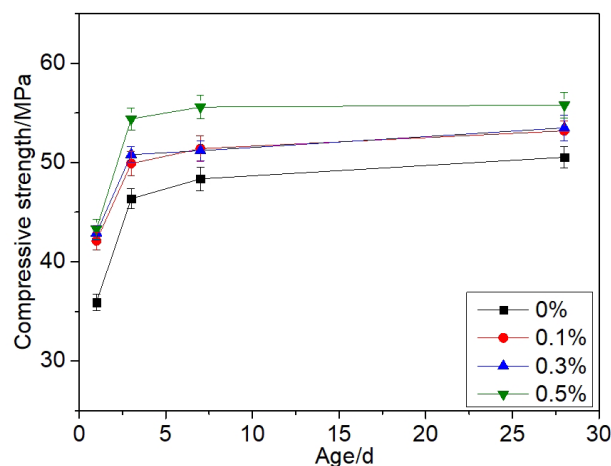


Figure 3. Influence of borax on the compressive strength of sample A0.

Figure 4 demonstrates the influence of borax on the compressive strength development of the CSA cements with the different amounts of gypsum. The addition of gypsum improves the compressive strength of the CSA cements, particularly after 1 day of hydration. It is found that the optimum gypsum dosage is around 5 % for strength development of the CSA cements. The strength of the CSA cements at the early ages is due to the hydration of ye'elimite with calcium sulfate [22-23]. After 7 days of hydration, a slight strength increase is observed due to the slow hydration rate of belite and the formation of calcium silicate hydrate, as shown in Equation 1 [24-25]. The effect of borax on the compressive strength varies for the cements containing different amounts of gypsum. In the presence of 5% gypsum, the strength after curing for 1 day suffers a decrease by adding borax. After 3, 7 and 28 days of hydration, the addition of borax leads to a similar strength development. For cement A2, the presence of borax causes similar strength levels at 1, 3 and 7 days. The strength of cement A2 with borax at 28 days is significantly increased compared with the blank cement. The highest strength (around 60 MPa) is reached for mortars with 0.3 % borax at 28 days. On the other hand, with a gypsum content of 15 % and 20 %, the addition of borax leads to mortars with a much higher mechanical resistance. For cement A3, with the

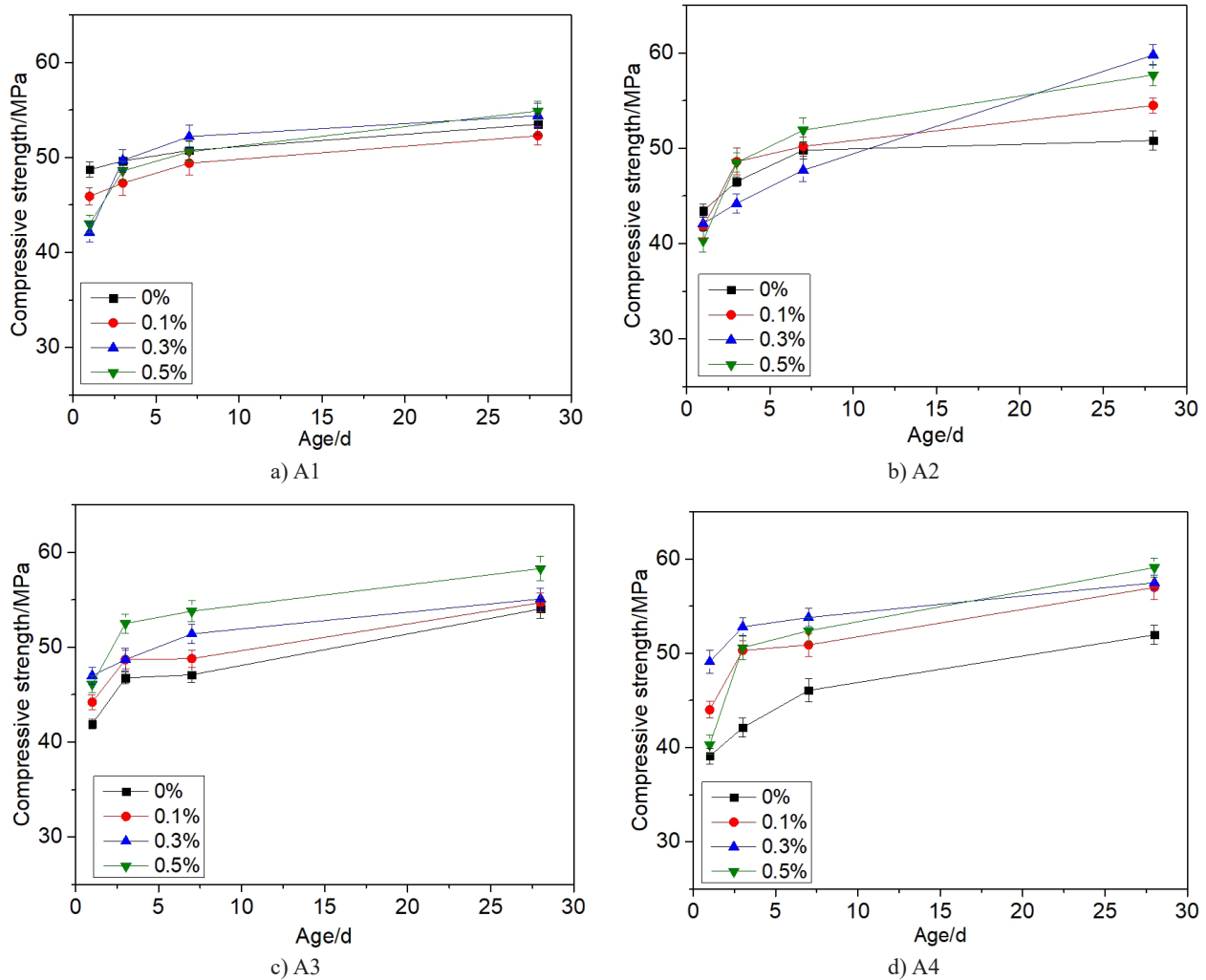
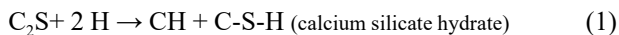


Figure 4. Compressive strength of the CSA cements with borax.

increasing borax contents, it can be found that a higher strength is gained. Cement A4 with 0.3 % borax shows the highest strength at 1 day. A similar strength is obtained for cement A4 with an increased content of borax after 3, 7 and 28 days of hydration. The results indicate that an appropriate amount of borax as a retarder is beneficial to the strength development of CSA cements.



Dimensional stability

It is known that CSA cements show volume expansion in the process of hydration and hardening. The hydration reaction of ye'elimite with calcium sulfate produces ettringite, which is associated with the expansion and strength development [19]. When a large amount of ettringite produces after hardening, expansion and even cracking can occur [26]. Consequently, the dimensional stability of CSA cement should be studied. Figure 5 and 6 present the dimensional stability of mortar A2 and mortar A4 which contain different contents of

borax in different curing conditions. When cured in air, the borax-added samples demonstrate relatively higher drying shrinkage at 1 day compared with the reference sample. After 7 days, the shrinkage rate of mortar A2 with 0.1 % and 0.5 % borax is close to the reference mortar. Mortar A2 with 0.3 % borax yields the highest shrinkage at all the ages. The mortars show rapid shrinkage during 7 days of hydration, and, afterwards, the shrinkage reaches a plateau. Mortar A4 shows lower drying shrinkage than mortar A2 due to the increased content of gypsum (Figure 4b). Similarly, the higher shrinkage is also attained for the mortars with borax compared with the reference mortars. The increased borax contents result in much lower drying shrinkage of mortar A4 within the curing age. Mortar A4 with 0.1 % borax shows the highest shrinkage among the four different mortars.

When cured in water, 0.3 % and 0.5 % of borax lead to a much lower rate of expansion for sample A2. The sample with 0.1 % borax shows a higher expansion rate than the blank sample at the early ages, but reaches a similar expansion rate after 14 days of hydration. Note

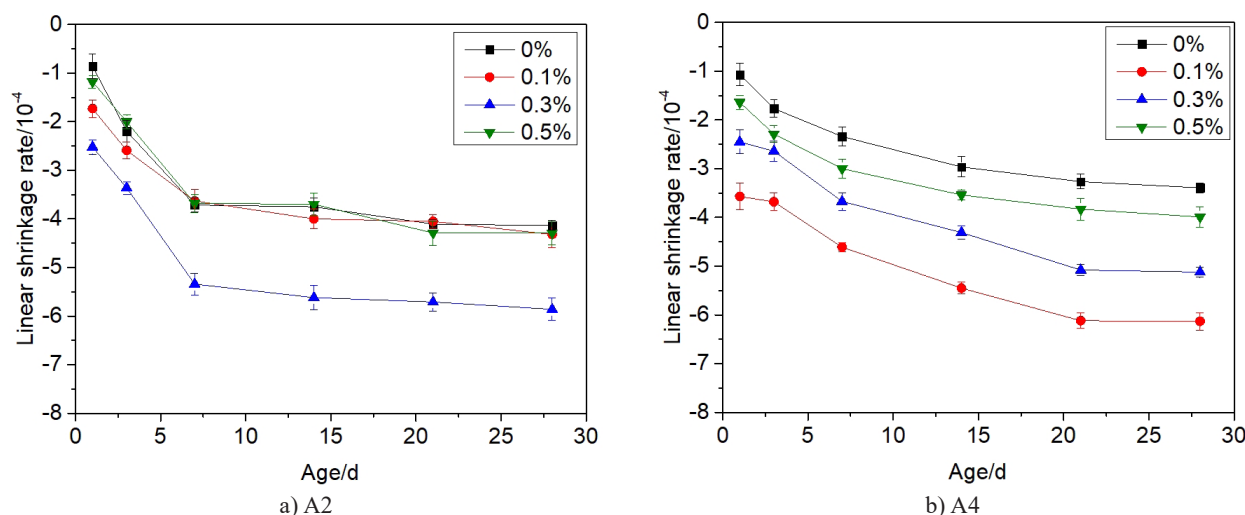


Figure 5. Influence of borax on the dimensional stability of the CSA cements cured in air.

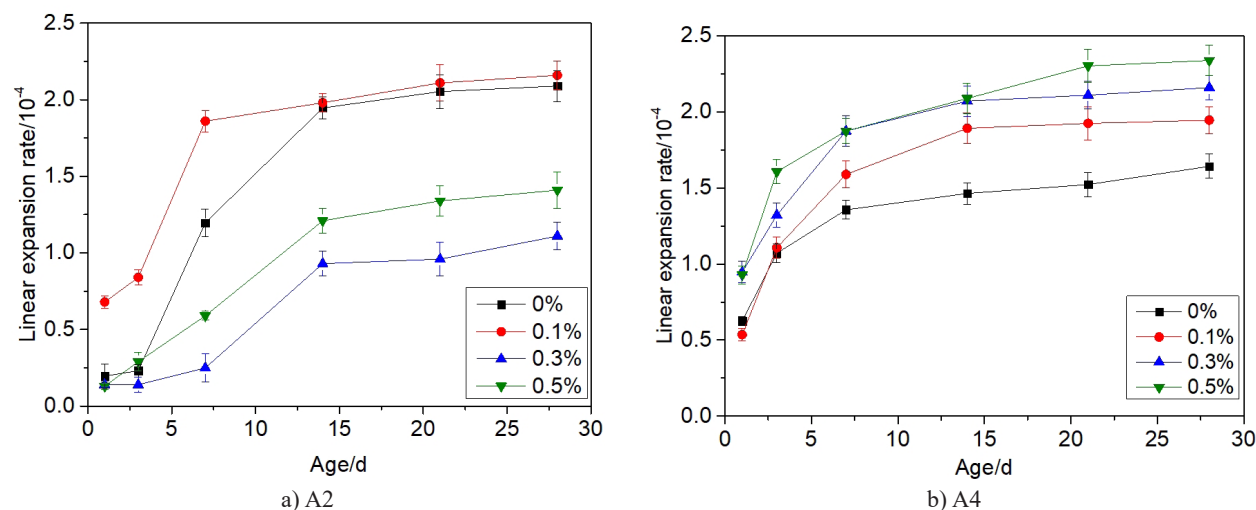


Figure 6. Influence of borax on the dimensional stability of the CSA cements cured in water.

that the increased content of gypsum causes the lower expansion of the mortars. With increasing borax contents, it can be found that a higher expansion rate is gained for sample A4. The expansion rate of sample A4 with 0.1 % borax is much lower than that of sample A2 with 0.1 % borax, while in the presence of 0.3 % and 0.5 % borax, the expansion rate of sample A4 is much higher than that of sample A2. The expansion rates of sample A4 with 0.5 % borax are within 2.5×10^{-4} at 28 days, which is still limited. The results indicate that the presence of borax does not increase the risk for expansion, even if more gypsum is added to the cement.

Hydration product

The XRD patterns of the CSA cements with the different contents of borax at 1 day of hydration are displayed in Figure 7. It can be found that ettringite is the main hydration product of the retarded and non-retarded cements. Ye'elimite is not completely depleted after 1 day of hydration. Traces of aluminium hydroxide are

not observed by the XRD analysis because its crystallised structure is poor [27-28]. In the absence of gypsum (A0), ettringite only forms after one day of hydration. This indicates that despite the absence of gypsum, the hydration of ye'elimite can still yield ettringite by Equation 2 [27, 29]. However, no AFm (calcium monosulfoaluminate hydrate) phase can be detected by means of the XRD analysis. With the increasing gypsum contents, ye'elimite is consumed much faster, and, thus the ettringite formation accelerates according to Equation 3. However, ye'elimite is depleted slowly in the cement with 20 % gypsum (A4). The diffraction peak of gypsum is also identified in cement A4.

The addition of borax has a significant effect on the hydration of ye'elimite. It is seen that borax inhibits the hydration of ye'elimite. The ettringite content in the pastes without gypsum significantly decreases with the addition of borax, while the intensity of ye'elimite peaks increases (A0). For cement A2, the dissolution of ye'elimite is strongly inhibited due to the incorporation of borax. Gypsum is observed in the presence of borax

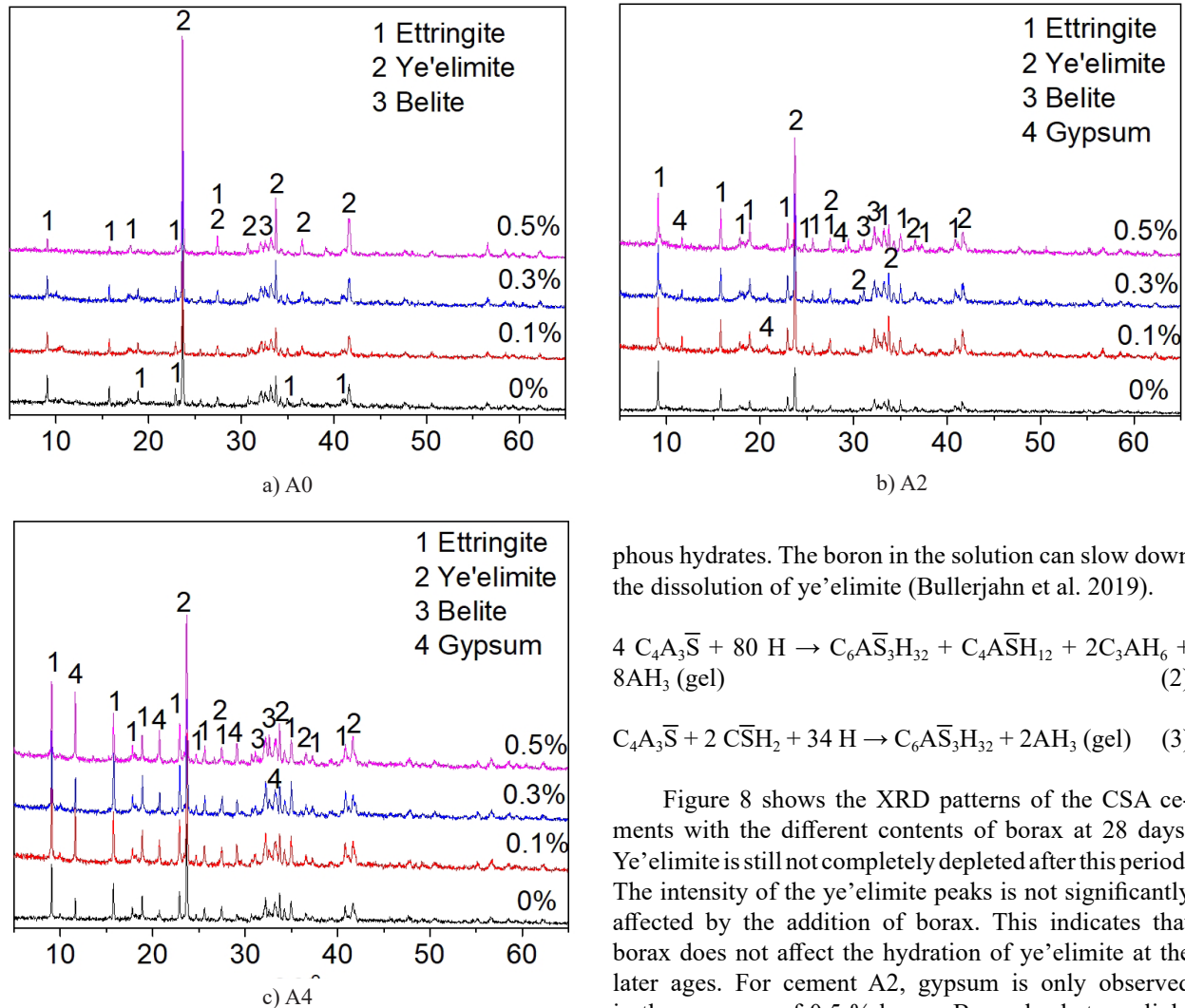


Figure 7. XRD patterns of the cements with the different contents of borax at 1 d.

while gypsum is fully consumed in the paste without borax. However, the effect of the borax dosage is not significant. Borax does not remarkably affect the formation of ettringite. For cement A4, the higher borax content causes much more gypsum to be present in the paste. It seems that the borax leads to an increase in the intensity of the ettringite peaks. The formation of ettringite of cement A2 and A4 is closely associated with the compressive strength at 1 day, as shown in Figure 3. Therefore, the effect of borax on the dissolution of ye'elimite and the precipitation of ettringite at the early ages is linked to the gypsum content. It was reported that, in the case of borax, ulexite with poor crystallinity was produced temporarily, which caused the retardation of the hydration [30]. The stability of ulexite depends on the alkalinity and the boron contents [12]. However, in the present experiment, amorphous ulexite is not identified by the XRD analysis. Boron dissolves fast, and its concentration decreases during cement hydration. It was assumed that boron was initially adsorbed on the amor-

phous hydrates. The boron in the solution can slow down the dissolution of ye'elimite (Bullerjahn et al. 2019).

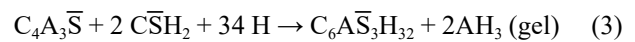
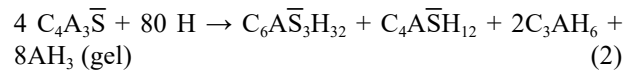


Figure 8 shows the XRD patterns of the CSA cements with the different contents of borax at 28 days. Ye'elimite is still not completely depleted after this period. The intensity of the ye'elimite peaks is not significantly affected by the addition of borax. This indicates that borax does not affect the hydration of ye'elimite at the later ages. For cement A2, gypsum is only observed in the presence of 0.5 % borax. Borax leads to a slight decrease in the intensity of the ettringite peaks. The XRD pattern of cement A4 with borax shows similar phase development as for that of cement A2 with borax. Traces of gypsum are also identified in cement A4 regardless of borax dosages, indicating that 20 % of gypsum is excessive. A slight decrease in the ettringite can be also observed in cement A4 with borax. The results show that the impact of borax on the hydration of ye'elimite and the formation of ettringite at the later ages is not significant. Ettringite can uptake boron from the solution at the later ages [31], which results in the depletion of boron and the increased strength development [15]. The increased 28-day strength of cements with borax in Figure 3 may be due to the incorporation of boron in ettringite.

The microstructure of the cement pastes with borax is shown in Figure 9 and 10. The morphology observations reveal that, after 1 day of hydration, needle-shaped ettringite has formed in the pastes without gypsum. Ettringite crystals could be embedded in the hardened pastes as shown in Figure 9. It is observed that cement A2 contains a large amount of ettringite needles and plate-like grains. The needle shape is well-defined because they show the typical hexagonal crystals.

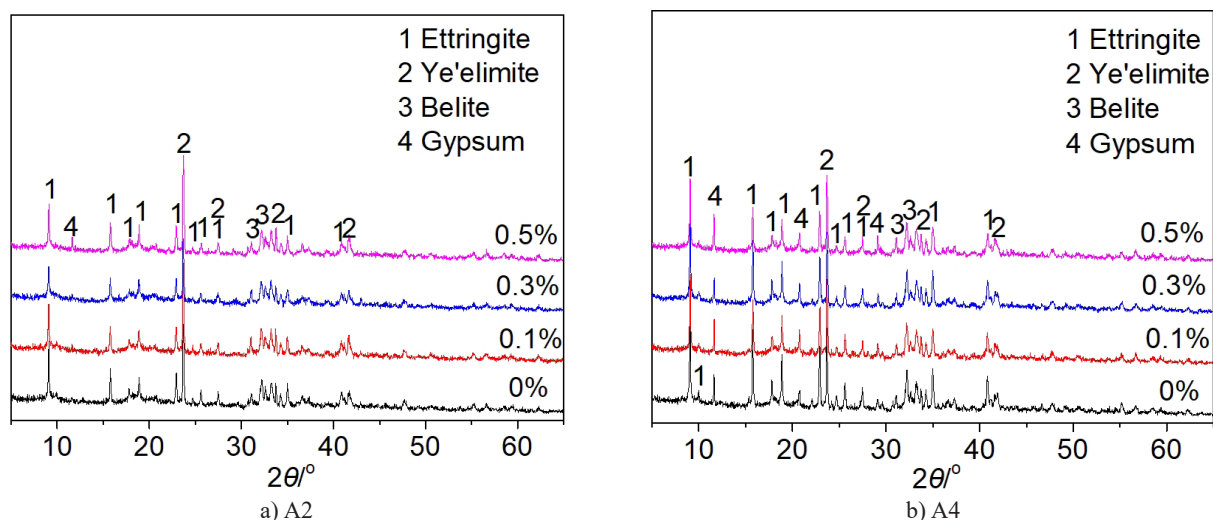
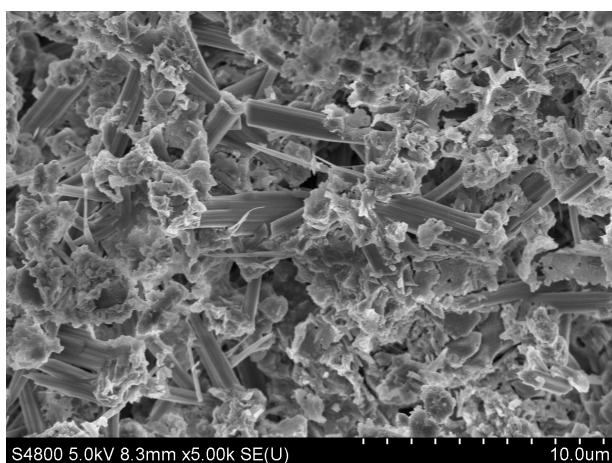


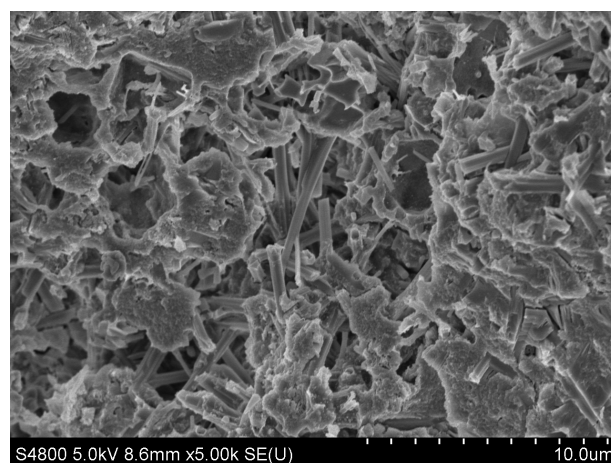
Figure 8. XRD patterns of the cements with the different contents of borax at 28 d.

The needle thickness is larger than in the pastes without gypsum. Moreover, the cement A2 paste has a denser film compared with the cement A0 paste. This may

explain the higher strength development of cement A2. The morphology of the hydrates differs when borax is added. The ettringite sizes of the cement pastes with

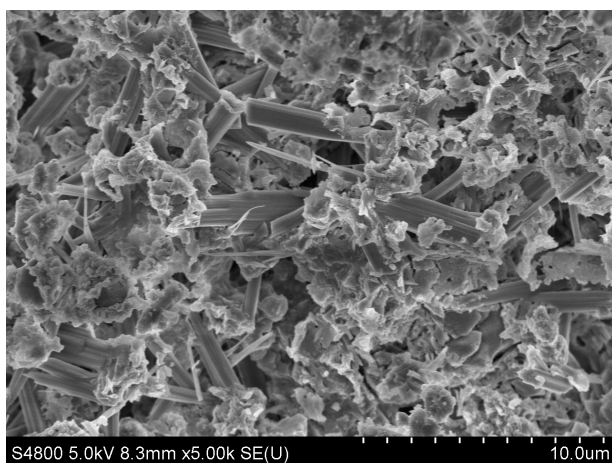


a) 0 % borax

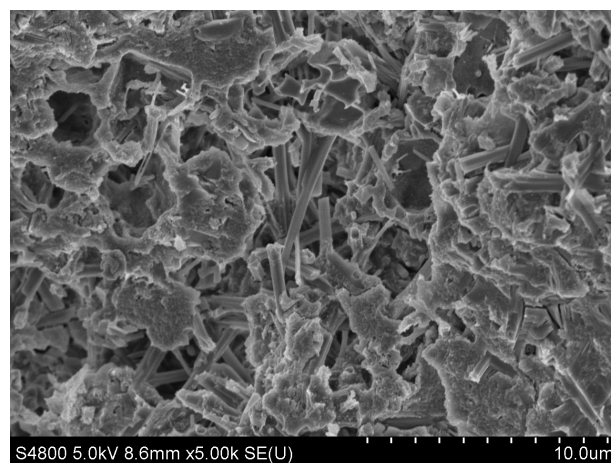


b) 0.3 % borax

Figure 9. SEM images of sample A0 at 1 d of hydration.



a) 0 % borax



b) 0.3 % borax

Figure 10. SEM images of sample A2 at 1 d of hydration.

borax become smaller. In addition, the platelet-like grains of cement A2 with borax grows bigger than the reference cement. This indicates that borax can promote the formation of ettringite.

CONCLUSIONS

The influence of borax on the hydration and properties of CSA cements with variable contents of gypsum was studied. Therefore, the following conclusions can be drawn:

- (1) The addition of borax retards the hydration process of CSA cements and causes a significant retardation in the setting time. The setting time is prolonged with the increased amount of borax. The addition of gypsum can influence the early hydration of CSA cements with borax.
- (2) The early strength of mortar A1 with borax suffers a decrease. At 28 days of hydration, cement A2 with borax shows higher strength values than the blank cement. When 15 % and 20 % of gypsum are incorporated, the addition of borax results in mortars with much higher mechanical strength. An appropriate amount of borax as a retarder is beneficial to the strength development of CSA cements.
- (3) Mortar A2 with 0.3 % borax yields the highest shrinkage at all the ages, while that with 0.1 % and 0.5 % shows similar values compared with the reference samples. The increased borax contents result in the much lower drying shrinkage of mortar A4. The expansion rates of mortars with borax are limited, which does not cause expansion and cracking in the CSA cement.
- (4) Borax has a notable effect on the hydration at the early ages. After 1 day of hydration, the addition of borax inhibits the hydration of ye'elimite and the consumption of gypsum. The effect of borax on the precipitation of ettringite is related to the gypsum content of the CSA cements.

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