

氧化硼对铝酸钙水泥水化性能的影响

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摘要: 对比研究了含与不含氧化硼对铝酸钙水泥水化行为的影响。通过测试水泥净浆的水化放热曲线, 对比分析了铝酸钙水泥中的氧化硼杂质含量对水泥水化速率的影响, 以及水泥水化时的电导率随养护时间的变化, 阐述了该杂质对水泥溶解沉淀速率的影响。通过冷冻真空干燥的方法中止水泥水化, 继而用 X 射线衍射和热重分析研究了上述两种水泥净浆的水化产物组成。用维卡仪测定了水泥砂浆的凝结时间, 用跳桌法测定了水泥结合浇注料的流动值衰减。结果表明: 铝酸钙水泥中的氧化硼杂质缩短了水泥的水化诱导期, 加速了水泥水化形成大量沉淀的进程, 从而促进了水泥的水化, 缩短了砂浆的凝结时间, 并加快了水泥结合浇注料的流动值衰减速度。

关键词: 铝酸钙水泥; 水化; 氧化硼; 凝结时间

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Effect of B₂O₃ on Hydration Behavior of Calcium Aluminate Cement

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Abstract: The hydration behavior of calcium aluminate cements in the presence and absence of B₂O₃ was investigated. The hydration rate of these two cements was determined via the exothermic temperature development of cement pastes. The dissolution-precipitation rates of the cement aqueous suspensions were evaluated by means of electrical conductivity. The cement hydration was terminated via vacuum freeze drying, and the resultant hydration products were analyzed by X-ray diffraction. The setting behavior of the mortars was determined by a Vicat apparatus, and the flow values of the castables containing the cements were measured on a vibration table. The results indicate that the presence of B₂O₃ in the cement shortens the induction period of the cements and accelerates the massive precipitation of the hydrates. B₂O₃ contained in the cement promotes the cement hydration rate, reduces the setting time of the mortar and leads to the flow decay of the castable.

Keywords: hydration; calcium aluminate cement; boron oxide; setting time

1 Introduction

Calcium aluminate cements (CACs) are widely used as a binder in refractory castables. The impurities presented in calcium aluminate cement (CAC) have an impact on the hydration rate and setting behavior of the hydraulic phases^[1], consequently affecting the placement

of CAC bonded castables^[2]. It was reported that the hydration rate of C₁₂A₇ is accelerated by adding silica as an impurity, because the thickness of the gelatinous hydrate layer formed is reduced due to the reducing solvation rate of C₁₂A₇^[3]. Also, the hydration rate of CAC with the higher SiO₂ contents in the raw mixes is faster because the silicate phases formed from SiO₂ interfere

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the grain growth of the hydraulic phases and consequently make the hydraulic phases have a higher surface activity^[1]. Some studies on high alumina cements showed that the hydration and setting rates of the cements are increased due to the inclusions of TiO₂, Fe₂O₃, MgO and SiO₂ in bauxite of the raw mixes^[4]. That is because the minor phases of calcium titanate (CaTiO₃), ferrite mineral phase, spinel (MgO·Al₂O₃) and gehlenite (2CaO·Al₂O₃·SiO₂) phases in the cements serve as crystal nucleus for hydrates, resulting in the decrease of the induction period of the cements^[2,4].

Some CAC contains 0.2%–0.3% B₂O₃ because the alumina source in the cement production is alumina dust, which is recovered from production of alumina *via* the Bayer process and includes 0.5%–1.0% boric oxide. It was reported that boric acid retards the setting of CAC bonded castables as an amorphous calcium borate layer precipitates around the cement particles^[5–6]. However, it is unclear whether the presence of B₂O₃ in the cement has an effect on the hydration and setting behaviors of CAC. Little study on this particular aspect has been reported.

This work investigated the hydration behavior of CAC in the presence and absence of B₂O₃.

2 Experimental

Commercial calcium aluminate cements (Zhengzhou Aluminates Co., China) with B₂O₃ (alumina source is from alumina dust) and without B₂O₃ (alumina source is from the Bayer alumina) were used. Tables 1–3 show the chemical composition, the major phase composition, and the fineness of the cements, respectively.

Table 1 Major chemical composition of cement w/%

Cement	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	B ₂ O ₃
Without B ₂ O ₃	0.47	69.93	28.92	0.20	0.00
With B ₂ O ₃	0.48	68.55	29.17	0.22	0.21

w is mass fraction.

Table 2 Major phase composition of cements w/%

Cement	CA	CA ₂	C ₂ AS
Without B ₂ O ₃	48.79	46.07	1.50
With B ₂ O ₃	46.31	49.42	0.85

Table 3 Fineness of cements with and without B₂O₃

Cement	Blaine surface area/(cm ² ·g ⁻¹)	Particle size D ₅₀ /μm
Without B ₂ O ₃	416	10.00
With B ₂ O ₃	435	10.15

The exothermic temperature profiles of the cement pastes were measured by a semi-adiabatic method. The water–cement ratio of the cement pastes was 0.36. The temperature caused by the exothermic heat as a function of time was recorded by a type-T thermocouple

immersed in the paste and this thermocouple was connected to a data capture system that can record temperature and time. The conductivity of the cement aqueous suspensions with water–cement ratio as 5 at 20 °C and 80% relative humidity (RH) was measured by a model Inlab731 conductivity electrode (Mettler Toledo Co., Switzerland). The cement mortars were prepared with a cement–sand ratio of 1 and a water–cement ratio of 0.349. The setting times of cement mortars were determined by a Vicat apparatus based on the Chinese standard GB/T 1346—2011.

The cement pastes above after curing at 20 °C for designed times were frozen at –40 °C for 1.5 h to halt the hydration of the cement pastes. The frozen pastes were immediately dried in a vacuum box under a pressure of 60 Pa at 20 °C. The phase compositions of the dried cement pastes were characterized by a model D8 Focus X-ray diffractometer (XRD) (Bruker Co., Germany). The thermal property was determined by a model STA 449 thermogravimetric analysis (TG) instrument (NETZSCH Co., Germany), using a heating rate of 10 °C/min with nitrogen flow and using α-Al₂O₃ as a correction standard. The relative weight loss of the cement hydrate phases between the initial and final temperatures was determined *via* the TG results.

The influence of B₂O₃ in the cement on the flow decay of the corundum based castables at different time was also investigated. The mixtures were dry-mixed for 1.5 min, followed by 3.5-min wet mixing in a Hobart mixer. Afterwards, the castables were placed into a stainless steel cone with a diameter of 100 mm at the bottom, a diameter of 70 mm at the top and a height of 50 mm. The castables were allowed to flow under vibrating for 15 s at 50 Hz on a vibration table after the cone were lifted up. Then the average of the samples with two perpendicular diameters was measured to calculate the flow value. Furthermore, the changes of the flow value with time were determined at each interval time of 30, 45 and 60 min, respectively.

3 Results and discussion

As shown in Tables 1–3, the chemical composition, major phase composition and fineness of the two cements with and without 0.21% B₂O₃ are similar. Figure 1 shows the exothermic heat evolution of the cement pastes of CAC with and without B₂O₃ as a function of time. Clearly, the dormant period of the paste without B₂O₃ completes at approximately 5 h. However, the dormant period of the paste with B₂O₃ stops at 2.8 h. Also, the peak of main reaction for hydrate precipitation of the paste without B₂O₃ after hydration appears for 6.2 h, and the peak of the main reaction for hydration of the paste with B₂O₃ occurs at 3.8 h. This indicates that the main reaction in the B₂O₃-containing paste occurs much earlier than that of the paste without B₂O₃. The results above indicate that the presence of B₂O₃ in the cement accelerates the hydration of CAC at 20 °C.

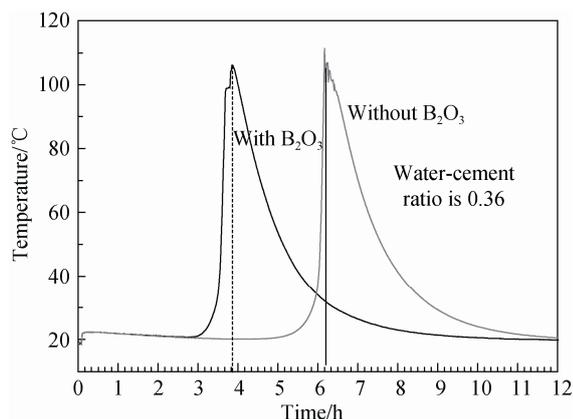


Fig. 1 Exothermic temperature curves for CAC with and without B_2O_3 at $20\text{ }^\circ\text{C}$

Figure 2 shows the conductivity of the cements with and without B_2O_3 at $20\text{ }^\circ\text{C}$ as a function of time. It is seen that, initially, the conductivity of the cements with and without B_2O_3 increases, indicating that the presence of B_2O_3 in the cement does not affect the dissolution process of the cement. However, the induction period of the B_2O_3 -containing cement is shorter than that of the B_2O_3 -free cement, which is consistent with the shorter dormant period of the former cement than that of the latter one (see Fig. 1). As a result, the sharp decrease in the conductivity of the cement including boric oxide occurs much earlier than that of the cement without boric oxide (see Fig. 2), indicating that the massive precipitation of hydrates starts much earlier in the former cement than in the latter one. The results above indicate that the presence of B_2O_3 in the cement promotes the oversaturation of Ca^{2+} and $Al(OH)_4^-$ ions in solution with respect to the hydrates and results in the accelerated precipitation of the hydrated calcium aluminate phases. The presence of B_2O_3 in the cement does not affect the dissolution process of the cements, but accelerates the induction period of the cements and the massive precipitation of the hydrates.

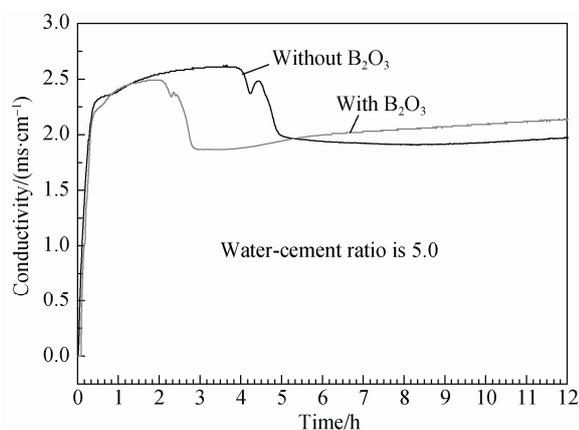


Fig. 2 Conductivity of CAC with and without B_2O_3 at $20\text{ }^\circ\text{C}$

Figure 3 shows the XRD patterns of the hydrated cements with and without B_2O_3 after hydration at $20\text{ }^\circ\text{C}$ for 10 h. It is seen that C_2AH_8 is the major noticeable hydrate in the cement with and without B_2O_3 after hydration for 10 h. However, there is more AH_3 in the cement with B_2O_3 than in the cement without B_2O_3 after the hydration. As AH_3 is the by-product of C_2AH_8 transformed from metastable hydrates such as CAH_{10} ,^[2,7-8] the more amount of AH_3 in the B_2O_3 -containing cement means that B_2O_3 in the cement should generate a higher content of metastable hydrates such as CAH_{10} . As a result, the presence of B_2O_3 in the cement accelerates the hydration of the cement and the formation of hydrates. With respect to the exothermic temperature and conductivity of the cement pastes, the promoted formation of AH_3 in the cement with B_2O_3 after hydration for 10 h (see Fig. 3) is compatible with the shorter dormant period of the B_2O_3 -containing cement (see Figs. 1 and 2). Nevertheless, the mechanism of the presence of B_2O_3 in the cement facilitated the hydration of CAC needs to be further investigated.

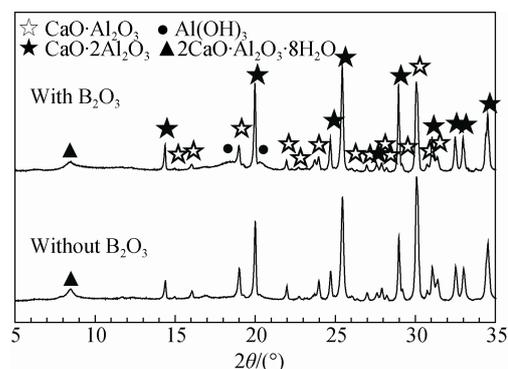


Fig. 3 XRD patterns of the hydrated cements with and without B_2O_3 after hydration for 10 h at $20\text{ }^\circ\text{C}$

Figure 4 shows the TG diagram of the cements with and without B_2O_3 after hydration at $20\text{ }^\circ\text{C}$ for 10 h. The different dehydration stages at various temperatures are attributed to removal of surface bonded water, dehydration of aluminium hydroxide gel, dehydration of CAH_{10} to C_2AH_8 , dehydration of C_2AH_8 to C_3AH_6 , and dehydration of C_3AH_6 to anhydrous CA, respectively.^[9] Table 4 shows the weight losses at different temperatures caused by different hydrates. It is seen that the weight loss of the cement paste without B_2O_3 at $70\text{--}90\text{ }^\circ\text{C}$ is 0.63%, while the weight loss of paste with B_2O_3 is 1.30%. The greater weight loss could be ascribed to the more amount of AH_3 in the paste with B_2O_3 ,^[10] which is in agreement with the more AH_3 in the cement with B_2O_3 (see Fig. 3). Table 4 also exhibits that the mass loss of 1.96% caused due to the decomposition of CAH_{10} in the paste with B_2O_3 is greater than that in the paste without B_2O_3 (*i.e.*, 1.65%). Moreover, the temperature ranges for dehydration of C_2AH_8 , AH_3 and C_3AH_6 are obviously overlapped.^[10-11] It is thus difficult to differentiate the weight losses of the cement pastes caused by C_2AH_8 ,

AH₃ and C₃AH₆. However, the total mass loss of the paste with B₂O₃ at 160–350 °C resulting from dehydration of C₂AH₈, AH₃ and C₃AH₆ is 7.34%, while that is 4.27% in the paste without B₂O₃, also indicating more hydrates in hydrated cement with B₂O₃. The weight losses between the hydrated cements with and without B₂O₃ demonstrates that B₂O₃ in cement promotes the cement hydration process, which is consistent with the results from the XRD results (see Fig. 3).

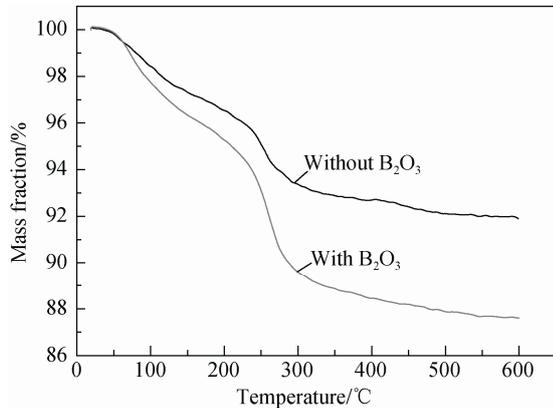


Fig. 4 TG diagrams for the hydrated cements with and without B₂O₃ after hydration for 10 h at 20 °C

Table 4 Mass loss of hydrated cements with and without B₂O₃ after hydration for 10 h at 20 °C

Temperature range/°C	Hydrates decomposed at the temperature	Mass loss of samples/%	
		With B ₂ O ₃	Without B ₂ O ₃
70–90	AH ₃ gel	1.30	0.63
90–160	CAH ₁₀	1.96	1.65
160–350	AH ₃ , C ₂ AH ₈ and C ₃ AH ₆	7.34	4.27

Figure 5 shows the initial and final setting time of the mortars including the cements with and without B₂O₃ at 20 °C. Clearly, the mortar containing the cement without B₂O₃ has an initial setting time of 133 min and a final setting time of 158 min. However, the initial setting time and the final setting time of the mortar including the cement with B₂O₃ are 55 and 90 min, respectively. This indicates that the hydration of the cements is accelerated in the presence of B₂O₃ in the cement.

Figure 6 shows the time-dependent decay of the flow values of corundum-based castables including the cements with and without B₂O₃ at 20 °C. Clearly, the presence of B₂O₃ in the cement does not affect the flow values of the castable within the initial 30 min. However, the flow value decay of the castable is more pronounced with the cement with B₂O₃, due to the accelerated induction period and faster precipitation behavior of the cement containing B₂O₃. These results confirm that the hydration of the cements in castables is accelerated in the presence of B₂O₃ in the cement.

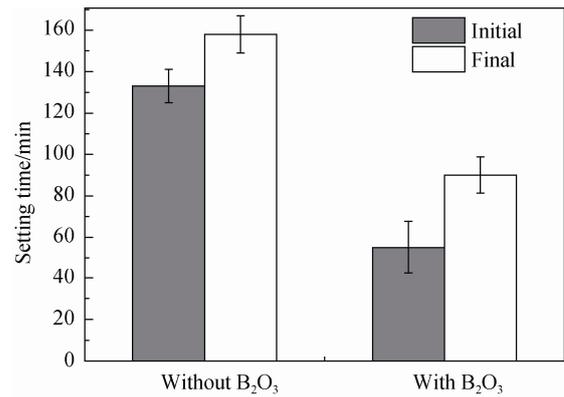


Fig. 5 Setting time of cement mortars with and without B₂O₃

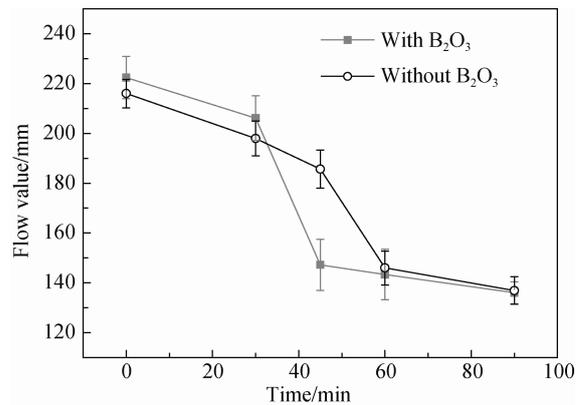


Fig. 6 Flow values of the corundum based castables including the cements with and without B₂O₃ at 20 °C

The accelerated hydration of the cement with B₂O₃ is probably related to the deformation of the crystal structures of the hydratable phase (CA and CA₂) caused by incorporation of B₂O₃ as solid solution. This aspect is still under investigation.

4 Conclusions

The presence of B₂O₃ in the cement did not affect the dissolution process of the cements, but shortened the induction period of the cements and accelerated the massive precipitation of the hydrates. The accelerated hydration caused in the presence of B₂O₃ in the cement occurred due to the greater amount of hydrates in the hydrated cement with B₂O₃. Consequently, the initial setting time and the final setting time of the mortar including the cement with B₂O₃ were reduced and the flow value of the castable containing the cement with B₂O₃ decayed faster than that of the castable without B₂O₃.

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