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Hydration of hydratable alumina in the presence of various forms of MgO

G. Ye, T. Troczynski [*]

Department of Materials Engineering, University of British Columbia, Vancouver, BC, Canada V6T 1N5

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Abstract

This work investigates hydration behavior of hydratable alumina in the presence of several forms of magnesia used for production of refractory castables. The mixtures of hydratable alumina with reactive magnesia, fused magnesite and deadburnt magnesite were hydrated at 20 °C and 110 °C. The hydration products were determined with X-ray diffractometer and the hydration extent was calculated from thermogravimetric analysis. The results revealed significant difference in the hydration products between the hydratable alumina-reactive magnesia mixture and the hydratable alumina-fused magnesite or deadburnt magnesite mixtures under the hydration conditions. The relationships of the compositions of hydrotalcite-like hydrates with different types of magnesias are elucidated. The bonding formed between hydratable alumina and magnesite aggregate in castables and its effect on the strength of the castables dried at 110 °C and fired at 816 °C was discussed.

Keywords: D. MgO; E. Refractories; Hydration; Hydratable alumina; Castable

1. Introduction

Low, ultralow and no cement castables have been widely used in recent years because the presence of lime in refractory castables unfavorably influences the high-temperature properties of castables [1]. Therefore, hydratable alumina is a preferable binder to calcium aluminate cement. As a result, formulations for refractory castables including hydratable alumina as the binder are being developed [2].

The hydration behavior of transition alumina (commercially referred to as "hydratable alumina") has been investigated extensively [3–5]. Transition alumina first reacts with water to yield pseudoboehmite gel and then transforms to predominantly bayerite with traces of boehmite [3,5]. However, crystalline bayerite formation strongly depends on the hydration temperature. Bayerite was not observed when hydration was performed at 5 °C for 8 days; and bayerite accounted for 48% and 57% after transition aluminas were hydrated for 8 days at 25 °C and 50 °C, respectively [3]. It was also observed that transition alumina was not completely hydrated in the temperature range of 15 °C and 55 °C for 24 h [4].

Hydratable alumina behavior in castables is similar as if hydrated alone, when the aggregates and matrixes of the castables are composed of alumina [2,6,7]. However, the presence of reactive magnesia accelerates the hydration of hydratable alumina and the hydration products include a hydrotalcite-like compound [8]. Hydratable alumina in the presence of reactive magnesia forms the hydrotalcite hydrate when it has been hydrated for 24 h at 20 °C and 30 °C [8]. This is beneficial because formation of hydrotalcite-like hydrate in castables bonded by hydratable alumina increases the strength of the castables after drying at 110 °C and firing at 816 °C [9]. Secondly, formation of the hydrotalcite hydrate could make the heat-up of castables safer. It has been reported [2,6,7] that the castables bonded by hydratable aluminas are more liable to explosion spalling during drying and initial heat-up than the castables bonded by calcium

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[*] Corresponding author. Tel.: +1 604 822 2612; fax: +1 604 822 3619.
E-mail address: troczyns@interchange.ubc.ca (T. Troczynski).

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aluminate cements because alumina gel formed from hydratable alumina lowers the permeability and porosity of the castables. Formation of hydrotalcite hydrate would facilitate drying and heat-up of the castables because the dehydration of the hydrotalcite-like compound would generate a micro-porous network in the bonding systems [8], and this porous network would provide channels for vapor escape during heating-up.

The hydration behavior of hydratable alumina in the presence of reactive magnesia has been investigated at room temperature [8]. However, in industrial practice, deadburnt and fused magnesias, rather than reactive magnesia, are normally used for production of refractory castables. The difference in reactivity and hydration between reactive magnesia and deadburnt or fused magnesia could be significant. Therefore, the mixtures of hydratable alumina and non-reactive magnesias may exhibit different hydration behavior from those of hydratable alumina and reactive magnesia. Moreover, in industrial practice, hydration of hydratable alumina in castables happens not only during curing of the castables at room temperatures, but also continues during drying/heating-up of the castables. Consequently, the hydration temperatures for hydratable alumina should include room temperature reflecting the curing of the castables and the temperatures reflecting the drying/heating-up of the castables.

In this work, hydratable alumina mixed with reactive magnesia, deadburnt magnesite and fused magnesite, respectively, were hydrated under the conditions representing curing and drying/heating-up of the castables in industrial vessels. The objective of this work is to determine the difference in the hydration products between the mixtures of hydratable alumina with reactive magnesia and those of hydratable alumina with deadburnt or fused magnesite powder at the temperatures of 20 °C and 110 °C, and to understand why hydratable alumina-bonded castables with magnesia aggregates have higher strength after drying at 110 °C and firing at 816 °C than the castables with magnesium aluminate spinel aggregates [9].

2. Experimental procedures

The raw materials were hydratable alumina (Alphabond 300, $d_{50} = 2.1–2.9\ \mu m$) from Almatis (Bauxite, USA), reactive magnesia ($d_{50} = 3.09\ \mu m$) from Fisher Scientific, 98.0% MgO deadburnt magnesite (−200 mesh) from Martin Marietta (P-98, Baltimore, USA) and 96–98% MgO fused magnesite (−200 mesh) from Washington Mills (Dynamag K, Niagara Falls, USA).

Twenty five grams of the as-received individual oxides as well as three mixtures of hydratable alumina and magnesia with a $MgO:Al_2O_3$ weight ratio of 84:16 were mixed with 20 g of distilled water. The three mixtures were composed of hydratable alumina and reactive magnesia (Mixture I), hydratable alumina and fused magnesite (Mixture II) and hydratable alumina and deadburnt magnesite (Mixture III). Two hydration conditions were employed: Hydration-A for 48 h at 20 °C in sealed polyethylene bags, and Hydration-B for 48 h at 20 °C in sealed polyethylene bags and then additionally for 12 h at 110 °C in steam at a pressure of 34.5 kPa (5 psi) in an autoclave. All the samples were dried at 110 °C for 24 h in air following hydration. The phase composition of the hydrated samples was determined by X-ray diffraction (XRD, model 5000, Siemens). The hydration extent of the hydrated samples was investigated using thermogravimetry (TGA, TG-96, Setaram) at a heating rate of 10 °C/min under a flow of helium. The weight loss due to evaporation of adsorbed water was subtracted from the overall weight loss measured.

3. Results and discussion

Fig. 1a shows that bayerite and boehmite were formed in hydratable alumina hydrated under Hydration-A and Hydration-B conditions. Compared with the sample hydrated under Hydration-A, the peak intensity of boehmite and bayerite was increased under Hydration-B, indicating that crystallization of bayerite and boehmite from the hydratable alumina was improved under hydration at the higher temperatures. The TG results (Fig. 1b) show that the mass loss (from 150 °C to 800 °C) of hydratable alumina after Hydration-A is 14.20 wt.%, indicating that about 31% of hydratable alumina was hydrated under Hydration-A. DTA results (not shown here) illustrated that the dominant hydration product was bayerite. In Hydration-B, about 70% of hydratable alumina was hydrated and the dominant hydration products were bayerite and pseudoboehmite. The results indicate that hydratable alumina was not completely hydrated under both Hydration-A and Hydration-B.

Fig. 2 compiles XRD data for the hydration products of reactive magnesia, fused magnesite and deadburnt magnesite under the A and B conditions. Brucite is the predominant crystalline phase in the reactive magnesia under Hydration-A. In contrast, relatively weak peaks of brucite are visible in fused magnesia samples and no brucite peaks are noticeable in the deadburnt magnesia under the same hydration condition. TG results for the same samples of magnesia (Fig. 3a) show that the weight losses of the reactive, deadburnt and fused magnesia after Hydration-A were 27.7%, 4.4% and 3.2%, respectively, confirming that the reactive magnesia was hydrated to a significantly higher extent than the deadburnt and fused magnesia. Crystallization of brucite from reactive magnesia was promoted under Hydration-B (Fig. 2b), as compared to Hydration-A (Fig. 2a). Under Hydration-B, the brucite peaks are strong also for the fused and deadburnt magnesites (Fig. 2b), but periclase peaks are still noticeable in the two samples. TG results (Fig. 3b) showed that the weight losses of reactive magnesia, fused magnesite and deadburnt magnesite hydrated under Hydration-B were approximately 28.6%,

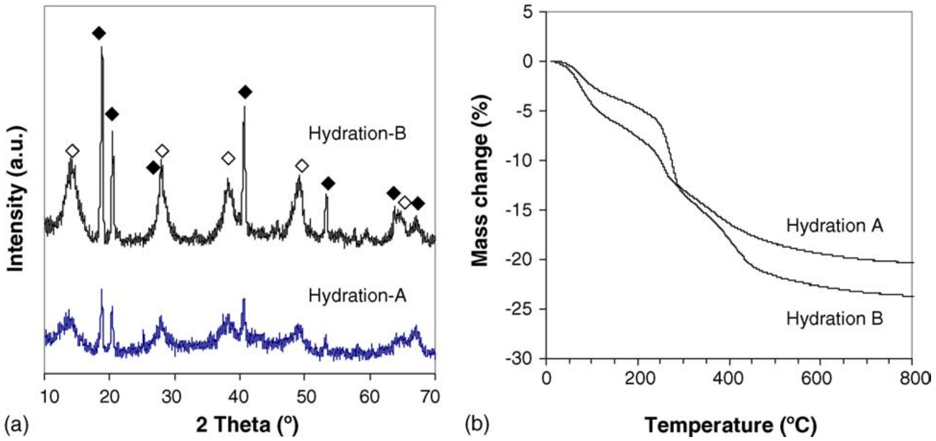

Fig. 1. (a) XRD patterns and (b) TG curves of Alphabond 300 hydrated under Hydration-A (48 h at 20 °C) and Hydration-B (48 h at 20 °C and 12 h at 110 °C) conditions (◇: boehmite and ◆: bayerite).

26.9% and 24.8%, respectively. Comparing with the theoretical water content of 30.9% in brucite ($Mg(OH)_2$), the TG results indicate that the reactive magnesia was hydrated to a higher degree than the fused and deadburnt magnesites in Hydration-B. The XRD results (Fig. 2) and TG results (Fig. 3) indicate that reactive magnesia is more liable to hydration at room temperature and 110 °C than the fused and deadburnt magnesites.

Fig. 4a shows that, under both hydration conditions, brucite [$Mg(OH)_2$] and hydrotalcite-like compound [$(Mg_{10}Al_2)(OH)_{24}(CO_3)(H_2O)_9$] were formed in Mixture I. On the other hand, neither brucite nor hydrotalcite-like compound was formed in Mixture II and Mixture III under Hydration-A. The TG results (Fig. 5a) indicate that the weight losses of Mixture II and Mixture III after Hydration-A were only 6.9%; in contrast, the weight loss of Mixture I was 37%. The higher weight loss of Mixture I in Fig. 5a resulted from the hydration of both reactive magnesia (Figs. 2a and 3a) and hydratable alumina (Fig. 1) and formation of the hydrotalcite-like compound (Fig. 4a) during Hydration-A. However, little deadburnt and fused magnesias were hydrated after Hydration-A (Figs. 2a and 3a) and crystalline hydrotalcite-like compound was not detected in Mixtures II and III after Hydration-A. Accordingly the weight losses of Mixtures II and III were much lower than Mixture I after Hydration-A.

It could be inferred that the presence of sufficient $Mg(OH)_2$, not the presence of MgO, in the mixtures of hydratable alumina and magnesia during Hydration-A is necessary for formation of hydrotalcite-like compound. In Mixture I, the reactive magnesia was hydrated to a high degree during Hydration-A, and accordingly the hydrotalcite-like compound was formed. On the other hand, the fused and deadburnt magnesia in Mixtures II and III, respectively, were much less hydrated during the same hydration condition, and consequently the hydrotalcite-like compound was not observed.

Fig. 4b shows that, after Hydration-B, hydrotalcite-like compound [$(Mg_{10}Al_2)(OH)_{24}(CO_3)(H_2O)_9$] was present in Mixture I, and hydrotalcite-like hydrate [$(Mg_4Al_2)(OH)_{12}(CO_3)(H_2O)_6$] in Mixtures II and III. These results confirm the above conclusion that formation of the hydrotalcite-like compounds depends on the presence of $Mg(OH)_2$ in the mixtures during hydration. It is inferred from Figs. 2b and 3b

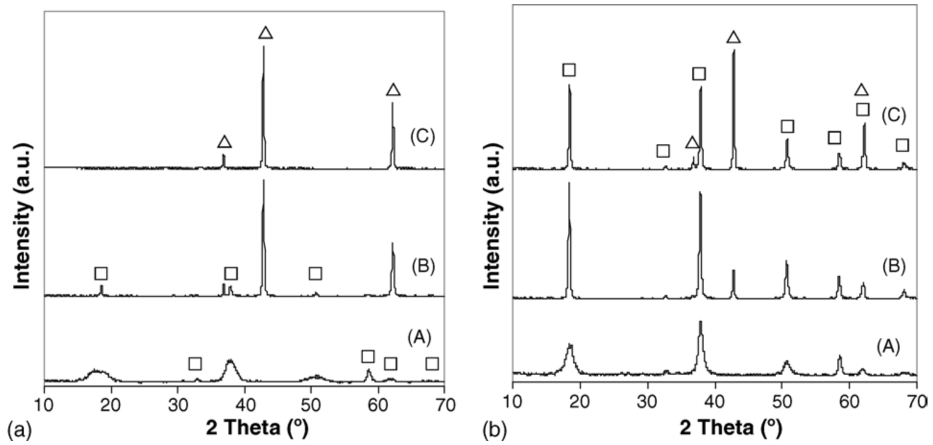

Fig. 2. XRD patterns of various forms of magnesia hydrated under (a) Hydration-A and (b) Hydration-B conditions: (A) reactive magnesia, (B) fused magnesite and (C) deadburnt magnesite (△: periclase, ◇: boehmite and □: brucite).

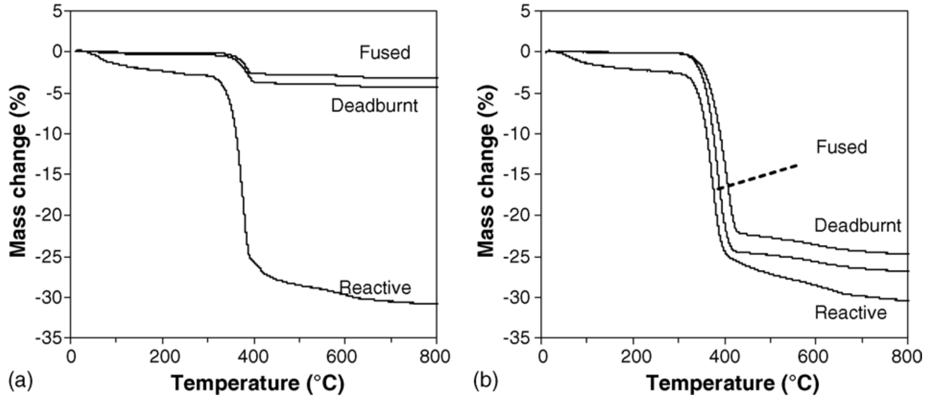

Fig. 3. TG curves for the thermal decomposition of various forms of magnesia after (a) Hydration-A and (b) Hydration-B conditions.

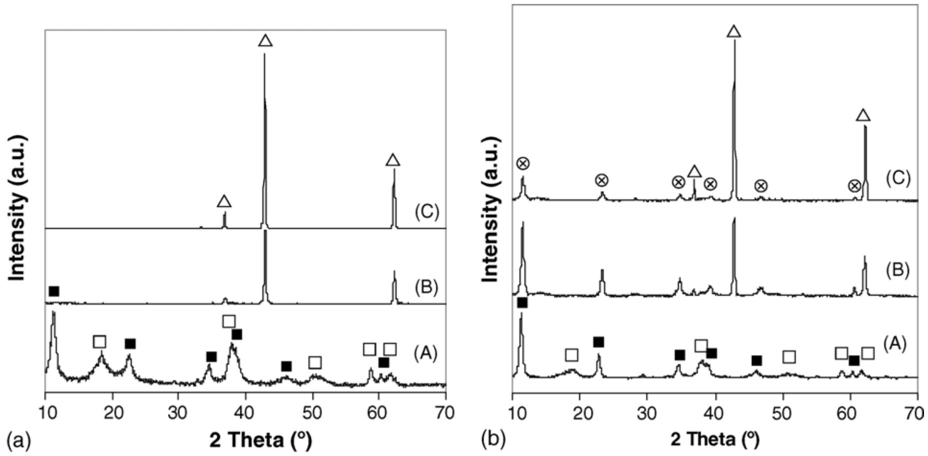

Fig. 4. XRD patterns of mixtures (with a MgO:Al_2O_3 weight ratio = 84:16) hydrated under (a) Hydration-A and (b) Hydration-B conditions: (A) Mixture I, (B) Mixture II, (C) Mixture III (■:: $(Mg_{10}Al_2)(OH)_{24}(CO_3)(H_2O)_9$, ⊗: $(Mg_4Al_2)(OH)_{12}(CO_3)(H_2O)_6$, △: periclase and □: brucite).

that the three magnesias in the three mixtures were hydrated under Hydration-B. As a result, the hydrotalcite-like compound was formed in all the three mixtures during Hydration-B.

Periclase peaks observed in Mixtures II and III after Hydration-B (Fig. 4b), indicated that only part of the magnesites was hydrated in Mixtures II and III under the Hydration-B condition. This was confirmed by the TG results (Fig. 5b) of the three mixtures after Hydration-B. The weight loss of Mixture I after Hydration-B was 37%, while the weight losses of the Mixtures II and III were 24% and 10%, respectively. The results shown in Fig. 4b also indicate that more magnesia in Mixture I was hydrated than in Mixture II and Mixture III under Hydration-B, because

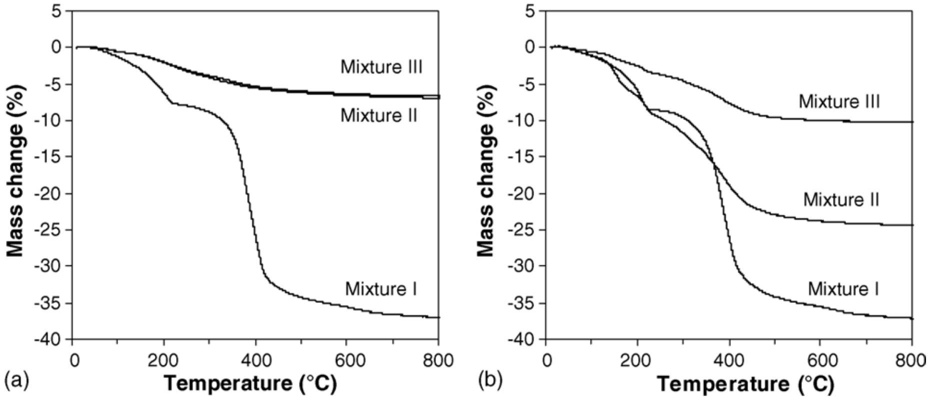

Fig. 5. TG curves for the thermal decomposition of the magnesia-alumina mixtures (with a MgO:Al_2O_3 weight ratio = 84:16) after (a) Hydration-A and (b) Hydration-B conditions.

brucite was detected in the former hydrated mixture and not detected in the latter two mixtures (Fig. 4b). These results are in agreement with those in Figs. 2b and 3b, where the three types of magnesia were individually hydrated under Hydration-B.

Fig. 4b shows that the hydrotalcite hydrates formed in Mixture I had a different composition from that formed in Mixture II and Mixture III. The hydrotalcite hydrate in the former mixture had a molar Mg:Al ratio of 5:1; by contrast, the hydrotalcite hydrate in the latter two mixtures had a molar Mg:Al ratio of 2:1, though the three starting mixtures had the same $MgO:Al_2O_3$ weight ratio of 84:16 (Mg:Al molar ratio of over 6:1). A recent investigation [8] has shown that the hydrotalcite-like hydrate formed from hydratable alumina-reactive magnesia mixture with a $MgO:Al_2O_3$ ratio of 65:35 (Mg:Al molar ratio of about 3:1) had a molar Mg:Al ratio of 3:1 $[(Mg_6Al_2)(OH)_{16}(CO_3)(H_2O)_4]$. Based on our experimental results and [9], it is proposed that the varying compositions of hydrotalcite hydrates formed through the hydration-reaction of hydratable alumina–magnesia mixtures are related to the ratio of $Mg(OH)_2$ to the hydrated-Al_2O_3 in the hydrated mixtures. In Mixture I, the reactive magnesia was completely hydrated, and correspondingly the formed hydrotalcite hydrate has a high molar Mg:Al ratio (5:1). However, deadburnt or fused magnesite was only partially hydrated under the hydration conditions. Consequently, the hydrotalcite hydrate has a low molar Mg:Al ratio (2:1) in Mixture II and Mixture III.

It was observed [9] that, after drying at 110 °C and firing at 816 °C, castables with hydratable alumina as a binder and with deadburnt or fused magnesite as the aggregate had higher strength than the hydratable alumina-bonded castables with magnesium aluminate spinel as the aggregates. This could be attributed to the hydration-reaction of hydratable alumina and magnesites as described above. It has been reported [10,11] that the addition of 0.25% co-precipitated magnesium aluminate hydrate $(MgO{\cdot}Al_2O_3{\cdot}16H_2O)$ into deadburnt magnesite samples cured at 110 °C for 24 h improved the strength of the samples dried at 110 °C because $Mg(OH)_2$ formed on the surface of the MgO particle and then hydrogen bonding was created between $Mg(OH)_2$ on the surface of the MgO particles and the magnesium aluminate hydrate. As a result, the bonding between the MgO particle and the matrixes was promoted and the strength of the samples enhanced. During heating below 1100 °C, dehydroxylation reaction of $Mg(OH)_2$ and magnesium aluminum hydrate was accompanied by polycondensation reactions [11]:

$$\begin{aligned}&\mathrm{HO{-}Mg{-}OH + HO{-}(Mg, Al){-}OH + HO{-}Mg{-}OH}\\&+ \cdots \rightarrow \mathrm{{-}O{-}Mg{-}O{-}(Mg, Al){-}O{-}Mg{-}O{-}} + n\mathrm{H_2O}\end{aligned} \tag{1}$$

This polycondensation reaction forms a bond between the aggregates and matrixes, and contributes to the strength of the materials after heat treatment under 1100 °C. In a similar mechanism, the hydrates (especially the hydrotalcite hydrate [9]) in the matrixes and $Mg(OH)_2$ on the magnesite aggregate in the castables form hydrogen bonds with the magnesite aggregates during curing and drying. It is expected that the hydrogen bond contributes to the increased strength of the castables after drying at 110 °C. During firing of the castables at 816 °C, polycondensation follows dehydration of the hydrates in the matrixes and $Mg(OH)_2$ on the surface of the magnesite aggregate as described above, and improves the fired strength of the castables.

4. Conclusions

1. Hydratable alumina was not completely hydrated at 20 °C for 48 h and then at 110 °C for 12 h. This hydration condition was similar to the curing and drying of castables, where water and steam are available for hydration of hydratable alumina.
2. After hydration at 20 °C for 48 h, a hydrotalcite hydrate was formed in the mixture of hydratable alumina and reactive magnesia, while such a hydrate was not observed in the mixtures of hydratable alumina and deadburnt or fused magnesite under the same hydration conditions. After hydration at room temperature for 48 h and then at 110 °C for 12 h, hydrotalcite compounds were formed in the mixtures of hydratable alumina with reactive magnesia, deadburnt magnesite and fused magnesite, respectively.
3. The compositions of hydrotalcite hydrates formed through the hydration-reaction of hydratable alumina and various forms of magnesia varied with the $Mg(OH)_2:Al_2O_3$ ratio in the hydrated mixtures, rather than the $MgO:Al_2O_3$ ratio in the starting mixtures.

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