Mechanochemical Synthesis of Tricalcium Aluminum Hydrate from Calcium Hydroxide-Boehmite Mixtures by Room Temperature Grinding

by Wantae KIM\(^1\) and Fumio SAITO\(^2\)

Tricalcium aluminum hydrate \((3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} : \text{CaAl}_6\text{H}_{16})\) is synthesized mechanochemically from mixtures composed of calcium hydroxide \((\text{Ca(OH)}_2)\) and pseudo-boehmite \((7 - \text{AlO(OH)})\) powders by room temperature grinding using a planetary ball mill. Use of the boehmite sample with inferior crystallinity is more favorable for the mechanochemical synthesis rather than that with well crystalline one. The time required to form \(\text{CaAl}_6\text{H}_{16}\) from the \(\text{Ca(OH)}_2 \cdot 7 - \text{AlO(OH)}\) mixture is much longer than that from the \(\text{Ca(OH)}_2 \cdot \text{gibbsite} (\text{Al(OH)}_3)\) one. Adsorbed water from air during grinding plays a significant role in the formation of \(\text{CaAl}_6\text{H}_{16}\) from the former mixture. After water addition to \(\text{Ca(OH)}_2 \cdot 7 - \text{AlO(OH)}\) mixtures ground for various times, excess hydrated calcium aluminates such as \(\text{CaAl}_6\text{H}_{16}, \text{CaAl}_{18/12}\) and \(\text{Ca}_3\text{Al}_2\text{H}_{63}\) are formed in the starting and the short time ground mixtures, while a few amount of these compounds is formed in these hydrated mixtures after prolonged grinding. Formation of these excess hydrated compounds, which belong to layered structural materials, is enhanced in the presence of free Ca, Al compounds and water.

**KEY WORDS:** Tricalcium Aluminum Hydrate, Mechanochemistry, Dry Grinding, Calcium Hydroxide, Pseudo-boehmite, Excess Hydrated Calcium Aluminate.

1. Introduction

Tricalcium aluminate, denoted as \(\text{C}_3\text{A} (3\text{CaO} \cdot \text{Al}_2\text{O}_3)\), is an important constituent of cement clinker and is usually manufactured at high calcining temperature with carefully proportioned mixtures of limestone, clay, iron ore etc. \(\text{C}_3\text{A}\) plays a significant role to determine the physico-mechanical properties of cement clinker. Especially, \(\text{C}_3\text{A}\) reacts with calcium sulfosilicate, denoted as \(\text{CSA} (3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4)\), at the presence of water in the cement slurry, this compound changes into ettringite \((3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O})\) which contributes to keep initial shape of the concrete mass and high strength properties of the hardened body. Since clinker making has been regarded so far as one of high energy consuming processes, a lot of researches have been done in the scope of the synthesis and characterization of clinker minerals especially in both tricalcium silicate \((3\text{CaO} \cdot \text{SiO}_2)\) and \(\beta\)-dicalcium silicate \((2\text{CaO} \cdot \text{SiO}_2)\), which share large portions of cement clinker by relatively low temperatures (including room temperature)\(^3\)\(^-\)\(^4\). Tricalcium aluminum hydrate, denoted as \(\text{CaAl}_6\text{H}_{16} (3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O})\) can be synthesized mechanochemically from the mixture of \(\text{Ca(OH)}_2\) and gibbsite \((\text{Al(OH)}_3)\) by room temperature grinding using a planetary ball mill\(^5\). However, no attempt has been done on the mechanochemical synthesis including grinding method of \(\text{CaAl}_6\text{H}_{16}\) from a mixture composed of other aluminum resources such as boehmite.

The main purpose of this paper is to investigate and characterize the effect of mechanochemical synthesis of \(\text{CaAl}_6\text{H}_{16}\) from different powder mixtures composed of calcium hydroxide and pseudo-boehmite, and to provide experimental data for further engineering applications on \(\text{CaAl}_6\text{H}_{16}\).

2. Experimental

2.1 Samples

Calcium hydroxide \((\text{Ca(OH)}_2)\) was a pure chemical reagent having 4.5 \(\mu\)m mean size supplied from Wako Pure Chemicals Industries Ltd. Four different types of pseudo-boehmite \((7 - \text{AlO(OH)})\) samples offered from Nippon Steel Corporation and a gibbsite \((\text{Al(OH)}_3)\) sample were used as aluminum sources. The gibbsite sample was a pure chemical reagent having 5 \(\mu\)m mean particle size. Boehmite samples are denoted as the sample number from A-1 to A-4 in this work. Each of these boehmite samples consist of very fine particles of 30 \(\mu\)m : A-1, 20 \(\mu\)m : A-2, 9 \(\mu\)m : A-3 and 1 \(\mu\)m : A-4. Crystallinity of them becomes better as the sample number increment. Weight ratio of boehmite or gibbsite to the \(\text{Ca(OH)}_2\) sample was changed from 0.7 to 2.0. The weighed two samples were mixed in an agate mortar with a pestle for 20 min before grinding, and preserved in a sealed box.

2.2 Grinding and hydration

A planetary ball mill (Fritsch, Pulverisette-7) with a pair
of zirconia pot of 50 cm³ inner volume containing seven zirconia balls of 15 mm diameter was adopted to grind the Ca(OH)₂-boehmite/gibbsite mixtures. A mixture of 3.5 g was charged in the mill pot. The mill was started, keeping constant revolution speed at 710 rpm for various duration from 15 to 120 min. In the case of the long time grinding over 30 min, the milling was stopped for 30 min to prevent from the excess temperature increase (below about 335 K) inside the mill pot.

Distilled water was added to both starting and ground mixtures at the equivalent weight for the hydration, and prepared samples were preserved in a sealed box for 2-weeks.

2.3 Characterization of ground product

Kinds of components and crystallinity of ground and hydrated mixtures as well as the starting mixture were characterized by X-ray diffraction (XRD) method using Cu-Kα radiation in an angular range from 2θ = 5° to 65° (Rigaku RAD-B System). Morphology of these samples was observed by means of a scanning electron microscope (SEM, Jeol JSM-4100). Thermogravimetric analysis was also applied to both starting and ground mixtures using a thermogravimeter (TG-DTA, Rigaku TAS-200) at 10 K/min of heating rate in air. Size distribution of these samples was also measured by a laser diffraction and scattering method using a particle size analyser (Seishin, LMS-30).

3. Results and Discussion

3.1 Mechanoochemical synthesis of Ca₃AH₆

Fig.1(A), (B) shows XRD patterns of the Ca(OH)₂-boehmite (A-1) mixture (A) and the Ca(OH)₂-gibbsite mixture (B) ground for different duration. Each of these starting mixtures is adjusted to the equivalent weight ratio of those of the corresponding two original samples. In both cases, characteristic peaks of each sample are decreased with an increase in grinding time. Ca₃AH₆ being a garnet type crystal structure is then formed in the mixture in the prolonged grinding. Ca₃AH₆ is synthesized mechanoochemically from the Ca(OH)₂-

boehmite mixture within 60 min, while it is obtained from the Ca(OH)₂-gibbsite mixture within 30 min. Equilibrium reactions in the formation of Ca₃AH₆ from both mixtures are given as follows:

3Ca(OH)₂ + 2AlO(OH) + 2H₂O → 2CaO·Al₂O₃·6H₂O  

........................................................................ (1)

3Ca(OH)₂ + 2Al(OH)₃ → 2CaO·Al₂O₃·6H₂O  

........................................................................ (2)

Two moles of water is necessary to achieve the reaction (1), while free water is not necessary in the reaction (2). The difference may affect the formation time of Ca₃AH₆ in each mixture. Anyhow, Ca₃AH₆ can be synthesized mechanoochemically from the Ca(OH)₂-boehmite mixture by its room temperature grinding. According to the thermodynamic data, the Gibbs energy change of Ca₃AH₆ is -4.46 kJ/mol at 298 K and -4.26 kJ/mol at 300 K, while positive at 400 K or higher. This implies that grinding at room temperature assists the spontaneous reaction forward thermodynamically to form Ca₃AH₆ from the

Fig. 2 XRD patterns of mixtures composed of Ca(OH)₂ and boehmite ground for 120 min.

Fig. 3 XRD patterns of 60 min ground mixtures composed of Ca(OH)₂ and boehmite (A-1) with different weight ratio of both samples.
Ca(OH)\textsubscript{2}-boehmite mixture rather than at high temperature.

In the present experiment, two starting mixtures do not coincide in stoichiometric balance of each component with those given by equation (1). However, the reaction takes place in this system, and C\textsubscript{3}AH\textsubscript{6} phase is detected as the grinding progresses. Starting powders, especially boehmite rather than Ca(OH)\textsubscript{2}, adsorb stoichiometric amount of water from air for the formation of C\textsubscript{3}AH\textsubscript{6}.

Fig. 2 shows XRD patterns of 120 min ground mixtures composed of Ca(OH)\textsubscript{2} and boehmite samples. C\textsubscript{3}AH\textsubscript{6} is formed rather effectively from the mixture containing the boehmite (A-1) sample with inferior crystallinity, by comparing peak intensities of that ground at the same period.

Fig. 3 shows XRD patterns of 60 min ground mixtures composed of Ca(OH)\textsubscript{2} and boehmite (A-1) samples with different mixing weight ratio of both samples. The peak intensity of C\textsubscript{3}AH\textsubscript{6} in the case of the ratio (A-1)/Ca(OH)\textsubscript{2} = 1.3, seems to be the highest of those of all mixtures. Comparable difference among mixtures is detected in the XRD profile, that is, Ca(OH)\textsubscript{2} disappears in the ground mixture prepared at the ratio of 1.3 or more, while it remains at the ratio of 0.7 and 1.0. According to the characteristics of the XRD analysis, disappearance of peaks of Ca(OH)\textsubscript{2} in this pattern does not always mean the perfect extinction in the mixture, but a small amount of Ca(OH)\textsubscript{2} may exist in these ground mixtures. It is worth mentioning that the mixing ratio around 1.3 of the Ca(OH)\textsubscript{2}-boehmite mixture is suitable for the reaction.

Fig. 4 shows TG curves of mixtures of Ca(OH)\textsubscript{2}-boehmite (A-1) and Ca(OH)\textsubscript{2}-gibbsite, both ground for various periods of time. As described earlier, the latter mixture changes into C\textsubscript{3}AH\textsubscript{6} within 30 min, while the former within 60 min. The dehydration temperature of a ground mixture for a long time was identified to be that of C\textsubscript{3}AH\textsubscript{6}.

3.3 Hydration of ground mixtures by water addition

Fig. 5 shows XRD patterns of hydrated mixtures composed of Ca(OH)\textsubscript{2} and boehmite (A-1) of the constant weight ratio of 1.3, after grinding for various time. Different phases of excess hydrated calcium aluminates, such as 2CaO·Al\textsubscript{2}O\textsubscript{3}·8H\textsubscript{2}O(C\textsubscript{8}AH\textsubscript{13}), 3CaO·Al\textsubscript{2}O\textsubscript{3}·8H\textsubscript{2}O (C\textsubscript{8}AH\textsubscript{13}) or 2CaO·Al\textsubscript{2}O\textsubscript{3}·6H\textsubscript{2}O (C\textsubscript{2}A\textsubscript{5}H\textsubscript{8}) were found in the starting and the short time ground mixtures. On the contrary, less
formation of these excess hydrated compounds is detected in these prolonged ground mixtures. In the starting and the short time ground mixtures, Ca(OH)\textsubscript{2} or Ca(OH)\textsubscript{2} activated by grinding reacts with boehmite (A-1) in the presence of water, to form three different phases of excess hydrated calcium aluminates. While in the case of the mixture ground for long time, the amount of free Ca(OH)\textsubscript{2} and boehmite is small, because they are already exhausted forming Ca\textsubscript{3}Al\textsubscript{2}O\textsubscript{6} as a stable compound. C\textsubscript{3}AH\textsubscript{6} is not changed into excess hydrated calcium aluminates by water addition, because of its rigid crystal structure (garnet type). This is the reason why relatively weak peaks of excess hydrated compounds are observed in hydrated mixtures after prolonged grinding.

Fig. 6 shows SEM photographs of the starting and the ground Ca(OH)\textsubscript{2}-boehmite (A-1) mixtures (A), (B) and (C) and their hydrated mixtures (D), (E) and (F)), obtained at the constant 1.3 mixing weight ratio. In photographs (A)-(C), fine particles of Ca(OH)\textsubscript{2} are dispersed and adhered on the surface of boehmite particles in the early stage of grinding. The prolonged grinding seems to form C\textsubscript{3}AH\textsubscript{6} particle aggregate. On the other hand, platy materials regarded as C\textsubscript{3}Al\textsubscript{6}O\textsubscript{12} and C\textsubscript{3}Al\textsubscript{6}H\textsubscript{15} are clearly observed in these hydrous starting and 30 min ground mixtures, although they are partly observed in the hydrated 60 min ground mixture. It can be observed from the photograph (F) that C\textsubscript{3}AH\textsubscript{6} is also included in the excess hydrated compounds. These excess hydrated compounds are kinds of layered structural materials, so that their particle shapes are somewhat different from that of C\textsubscript{3}AH\textsubscript{6} appeared mainly in the photograph (C).

4. Conclusions

Experimental results obtained from the present work are summarized as follows:

(1) C\textsubscript{3}AH\textsubscript{6}, which is a garnet type crystal structure, can be synthesized from the mixture of Ca(OH)\textsubscript{2} and boehmite only by room temperature grinding. Use of boehmite with inferior crystallinity is rather favorable for the mechanochemical synthesis than that with well crystalline boehmite.

(2) Synthesis of C\textsubscript{3}AH\textsubscript{6} was promoted by an increase in the mixing weight ratio of boehmite to Ca(OH)\textsubscript{2}, and the effective ratio was around 1.3.

(3) Time required to form C\textsubscript{3}Al\textsubscript{6}H\textsubscript{15} from the Ca(OH)\textsubscript{2}-boehmite mixture is much longer than that from the Ca(OH)\textsubscript{2}-gibbsite one. Water from air during grinding plays a significant role in the formation of C\textsubscript{3}Al\textsubscript{6}H\textsubscript{15} from the former mixture. The mechanochemical reaction was supported by the Gibbs energy change.

(4) When water is added to the mixture of Ca(OH)\textsubscript{2} and boehmite, different phases of excess hydrated calcium aluminates such as C\textsubscript{3}AH\textsubscript{6} or C\textsubscript{3}Al\textsubscript{6}H\textsubscript{15} are formed in the starting and the short time ground mixtures. Formation of these excess hydrated compounds, which belong to layered structural materials, is enhanced in the presence of free Ca, Al compounds and water.

Acknowledgments One of the authors (W. Kim) wishes to thank the Ministry of Education, Science and Culture of Japan (Mombusho) for the financial support provided through the Scholarship. The authors are grateful to Mr. S. Yamazaki, Nippon Steel Corporation for supplying the boehmite samples used in this experiment. They also wish to acknowledge the "International Fine Particle Institute, Inc. (IFPRI)" for the financial support.

References