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Influence of mechanical activation on the synthesis and hydraulic activity of calcium dialuminate

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Abstract

Calcium dialuminate (CA_2, C=CaO, A=Al_2O_3) powders were synthesized from the mechanically activated mixture of calcium hydroxide and aluminium hydroxide. Attrition mill was used for the mechanical activation. A new X-ray phase corresponding to CAH_{10} was identified after 10 min of attrition milling. The activated mixture was calcined at 1000 °C to obtain CA_2. The hydraulic activity of the prepared CA_2 was studied using XRD, DTA and compressive strength development. The XRD analysis of CA_2 hydrated for different periods indicated the faster conversion of CAH_{10}–C_2AH_8–C_3AH_6. In case of mechanically activated CA_2, the maximum compressive strength was achieved after 1-day hydration, whereas in conventional CA_2 the maximum strength was obtained after 14-day hydration. The faster conversion of hydration phases and rapid early strength development gives an indication of increased hydraulic activity of CA_2.

Keywords: Calcium dialuminate; Mechanical activation; Synthesis; Hydraulic activity; Strength development

1. Introduction

The main hydraulic phases in the CaO–Al_2O_3 binary phase equilibrium diagram are CA, CA_2 and $C_{12}A_7$ (C=CaO, A=Al_2O_3). Calcium dialuminate exhibits very low thermal expansion and excellent thermal properties and thus considered desirable phase for refractory applications [1–3]. It is usually synthesized by solid-state reaction of pure lime and alumina in two or multiple stage heating in the range of 1400–1500 °C [4]. However, the very low hydraulic activity and consequently poor early strength development restricts the use of CA_2 in larger proportion and thus, it is often used in conjunction with faster hydraulic phases like CA and $C_{12}A_7$. Increase in the reactivity of CA_2 has been a subject of much concern and attracted intensive research activities. Various methods such as addition of reactive phases like CA or $C_{12}O_7$ [5], increasing the surface area (4500 cm^2/gm) followed by curing at higher temperature (~30 °C) [6], combination of hydration and multiple firing [7] were suggested to improve the reactivity of CA_2.

The term mechanochemistry or mechanical activation is used to cover broadly those structural and other physico-chemical changes which are induced in solids as a result of applied mechanical energy [8–10]. The process of activation depends on the breakage process and the rate at which energy is supplied to the system. The solid state reaction during mechanical activation are generally believed to be favoured due to increase in surface area, stresses and defects induced in the solid structures, phase transformations, localised and overall thermal effects, repeated welding of interfaces and fracture leading to dynamic creation of fresh surfaces for reactions etc. It is possible to decrease the synthesis temperature of inorganic compounds by mechanochemical treatment of the reaction mixtures, especially if at least one component contains hydroxyl group [11,12]. Such a synthesis route is described as a "soft" mechanochemistry. Use of mechanical activation in calcium aluminate cement technology is reported [13,14]. Recently it has been observed y the present investigators that high-energy milling of cementitious material such as blast furnace slag and fly ash improves the reactivity of resulting blended cement [15,16].

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This paper reports the results of our studies on the effect of mechanochemical activation of aluminium hydroxide and calcium hydroxide in an attrition mill on the synthesis of calcium dialuminate. The investigation is focused on the reactivity during hydration reactions. Strength development after different hydration time is recorded and the results obtained are compared with conventional calcium dialuminate. An outline of the hydration mechanism of high-energy milled calcium dialuminate has also been presented.

2. Experimental

Analytical grade aluminium hydroxide (AH_3) and calcium hydroxide (CH) were used as the starting material. Molar mixture equivalent to 1 CaO:2 Al_2O_3 was prepared and intermilled for 30 min in a batch type attrition mill (NETZSCH, Germany; Model: PE-75). The medium used for milling was isopropyl alcohol. The total weight of solid and pulp used was 150 g and 250 ml, respectively, and the total weight of grinding media (2 mm steel balls) was 1.875 kg. No dispersing agent was added during the milling. The milled powder was then air dried at ambient temperature.

Siemens D500 X-ray diffractometer was used to identify the phases of AH_3, CH, and attrition-milled and ball-milled samples using Co Kα radiation. Particle size analysis of the milled powder was carried out in a Malvern Mastersizer MS1 particle size analyser. The attrition milled and ball milled samples were subjected to thermal analysis using SEIKO simultaneous TG/DTA (Model: 320; sensitivity = 1 μg). To get the CA_2, the attrition-milled sample was calcined at 1000 °C for 120 min in oxidising atmosphere using an electric furnace. The rate of heating was maintained at 5 °C/min. The phases formed after calcination and particle size distribution of the calcined powder was determined. Morphological studies were carried using a scanning electron microscopy (Model: JEOL-840).

The compressive strength was tested on 25 × 25 × 25 mm^3 cubes after 1, 3, 7, 14 and 28 days. For each value, six numbers of cubes were tested. The cement to aggregate ratio was kept 3 and water to cement ratio 0.5. To identify the hydration products, XRD and TG/DTA techniques were applied. For comparison, same mixture of AH_3 and CH was ball-milled for 30 min, then dried, palletised and fired at 1500 °C for 4 h in air. The sintered pellets were then air-cooled and ground to cement fineness (sp. surface area 3.2 m^2/g) to use as reference material for compressive strength studies.

3. Results and discussion

3.1. Effect of milling

Fig. 1 shows the XRD patterns of AH_3, CH and attrition-milled samples. It is observed that AH_3 and CH is not amorphous in nature and characterized by the sharp peaks. After attrition milling, the mixture of AH_3 and CH become more amorphous in nature. Presence of a new phase corresponding to CAH_{10} indicate the reaction between AH_3 and CH during milling and the resulting precursor in not merely the physical mixture but compound.

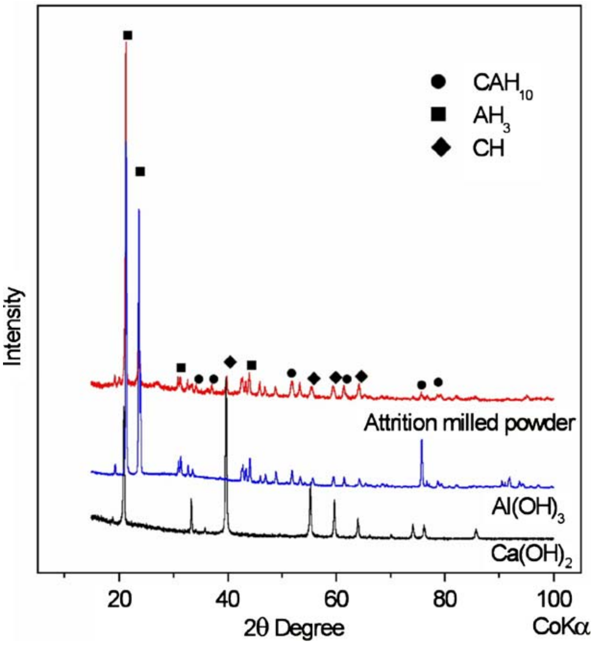


Fig. 1. XRD patterns of AH_3, CH, attrition-milled and ball-milled samples.

Fig. 2 shows the DTA curve of ball-milled and attrition-milled sample. The DTA plots vary significantly from each other. The following observations can be made:

1. The endothermic peak at 61 °C in ball-milled sample belongs to evaporation of physically combined water. In attrition milled sample, endothermic peak at 132 °C corresponds to the dehydration of CAH_{10} [17].
2. The strong endothermic peak in the region of 286–292 °C corresponds to the dehydration of AH_3 gel in both the samples [18]. The total observed weight loss of 25.02 and 25.65% up to 350 °C for attrition-milled and ball-milled samples are in reasonable agreement with the theoretical loss of 28.0% for the gibbsite component of this mixture.
3. The endotherm at 432 °C is probably due to the presence of a small amount of boehmite resulting from the decomposition of the gibbsite [18].
4. The endothermic peak at 532 °C in ball-milled sample corresponds to dehydroxylation of the CH with a weight loss of 4.01% (theoretical value 4.7%) [18]. Absence of this peak in attrition-milled sample suggests the consumption of CH during attrition milling.
5. The endothermic peak at 640 °C in attrition-milled sample is possibly due to decarbonation [18].
6. Small exothermic peaks in the region of 830–850 °C in case of attrition-milled sample may belong to the crystallization of CA_2. Based on this, the temperature

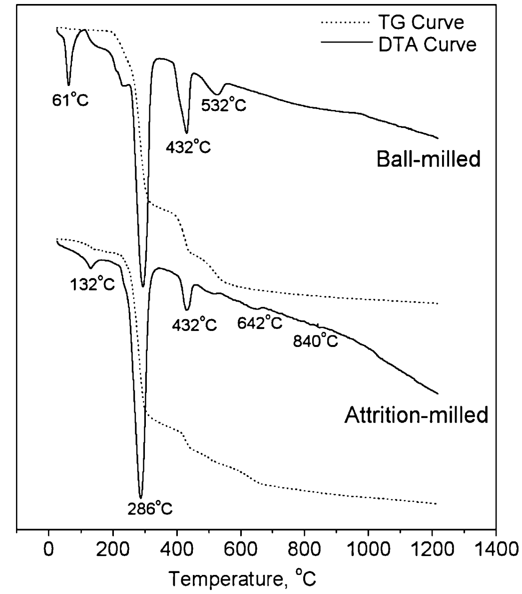


Fig. 2. DTA curve of ball-milled and attrition-milled sample.

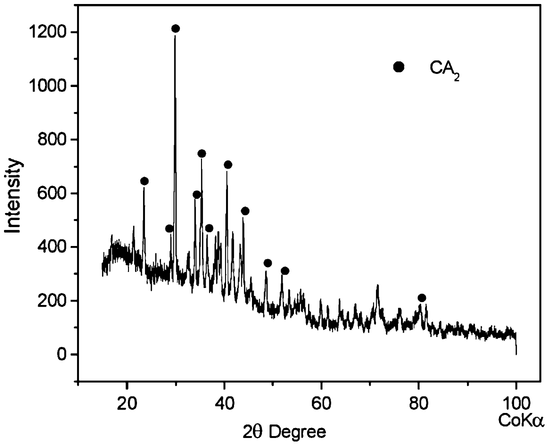
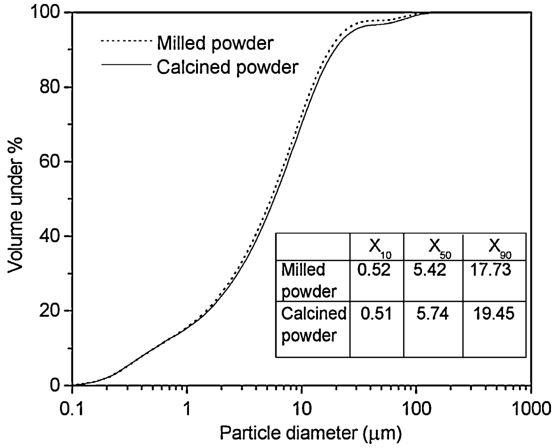


Fig. 3. XRD patterns of the milled mixtures heated for 2 h at 1000 °C.



	X_{10}	X_{50}	X_{90}
Milled powder	0.52	5.42	17.73
Calcined powder	0.51	5.74	19.45

Fig. 4. Particle size distribution of milled and calcined mixture.

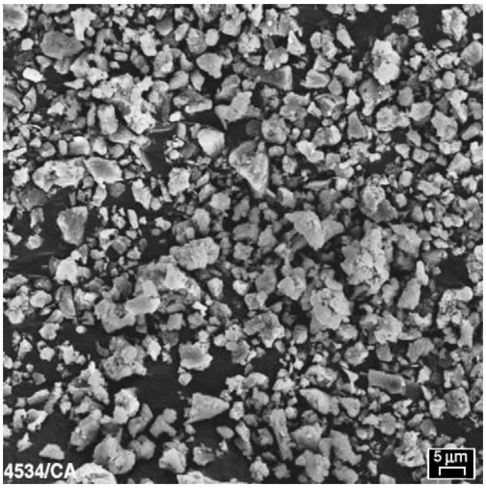


Fig. 5. Morphology of calcined powder.

for calcinations 1000 °C was selected to ensure the complete transformation to CA$_2$.

3.2. Characterization of calcined mixture

The XRD pattern of the attrition-milled mixture heated for 2 h is shown in Fig. 3. Heating to 1000 °C transforms the mechanically activated mixture into CA$_2$. Absence of any major peak belonging to CA or other phase suggests that transformation of CA$_2$ is complete. Fig. 4 shows the particle size distribution of milled mixture and calcined mixture. In milled sample, the particle size is ranging between 0 and 20 μm with a X_{50} value of 5.42 μm. No significant change in

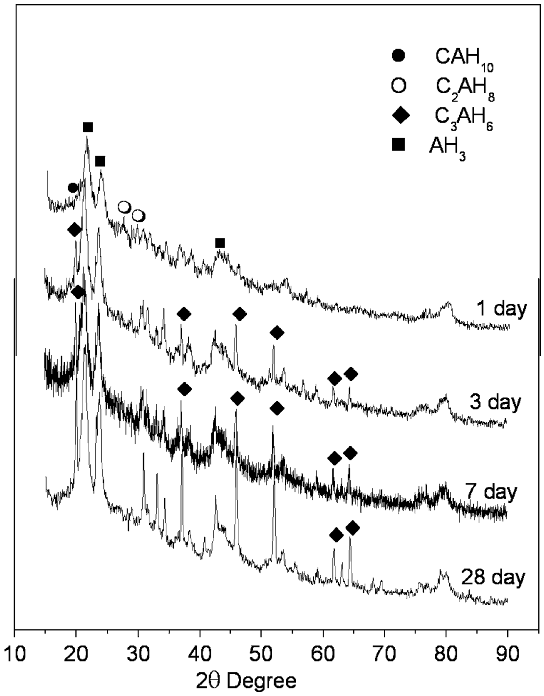


Fig. 6. XRD pattern of CA$_2$ hydrated for different periods.

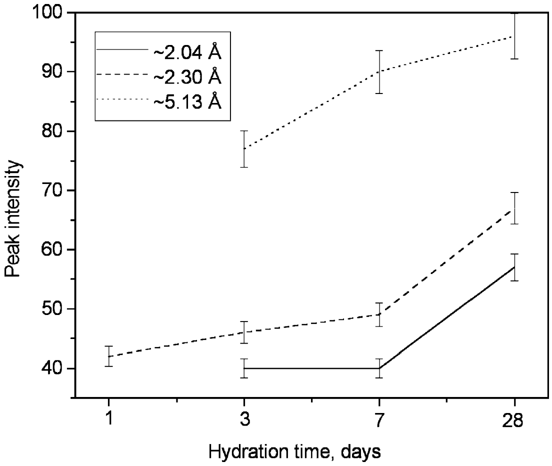


Fig. 7. Variation in XRD peak intensity of C_3AH_6 in relation to hydration time.

distribution pattern due to calcinations was observed. The morphology of the calcined particles is given in Fig. 5. Majority of the particles are semispherical to angular in shape and between 0 and 10 μm ranges. Also the particles are mostly free from aggregation.

3.3. Hydraulic activity

Hydration of calcium dialuminate is a slow process. No hydration products from pure CA_2 forms even after 1-day hydration [1]. In conventional CA_2, the initial hydration product CAH_{10} appears after 3 days followed by the formation of C_2AH_8 and its conversion to C_3AH_6 during 3–14 days [19]. Fig. 6 shows the analysis of XRD patterns of attrition-milled CA_2 hydrated for different period. Based on XRD data, it appears that most of the CAH_{10} was consumed in the early hydration reaction. Presence of C_2AH_8 phase and minor C_3AH_6 after 1-day hydration indicates the enhanced hydraulic activity. Consumption of C_2AH_8 peaks and appearance of C_3AH_6 peaks indicates the conversion of metastable C_2AH_8 to stable C_3AH_6 after 3-day hydration. The variation in the characteristic peaks of C_3AH_6 at ~2.30, 2.04, and 5.13 Å were examined in detail to monitor the progress of hydration. The intensity of the characteristic peak of C_3AH_6 is used as a measure of the progress of hydration reaction (Fig. 7). The higher peak intensity signifying increased formation of C_3AH_6.

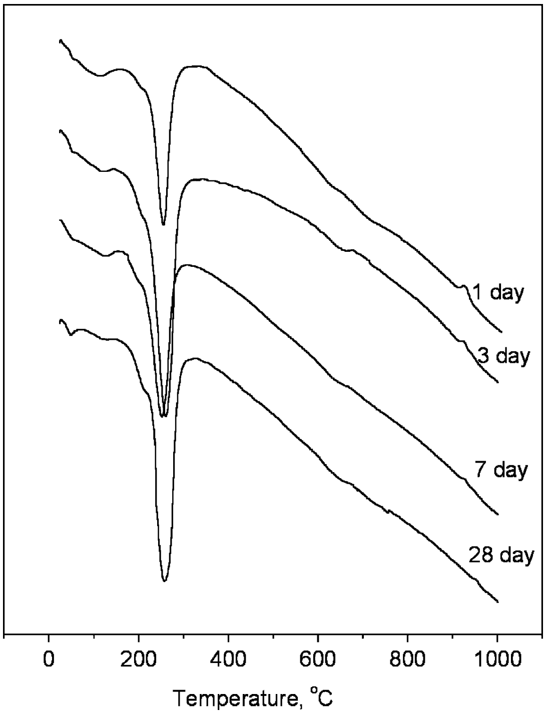


Fig. 8. DTA curve of CA_2 hydrated for different periods.

Fig. 8 shows the DTA curves of attrition-milled CA_2 hydrated for different periods. The DTA plots vary slightly in respect to hydration time, generally, six temperature regions for all samples are observed. The summary of temperature regions, their corresponding dehydration peak and peak temperature of attrition-milled CA_2 hydrated for different periods are given in Table 1. The peak temperature of conventional CA_2 obtained during our previous studies [19] is also included in Table 1 for comparison. In attrition-milled samples, most of the characteristic dehydration peaks were formed at relatively lower temperatures. The absence of CH dehydration peak indicates that all the free lime was consumed during milling and calcining.

Table 1
Peak temperature of attrition-milled and conventional CA_2 after different hydration period

Temperature region (°C)	Corresponding dehydration phase	Conventional CA_2				Attrition-milled CA_2			
		1[a]	3[a]	7[a]	28[a]	1[a]	3[a]	7[a]	28[a]
0–90	Dehydration of AH_3 gel [20,21]	80	81	81	81	51	52	52	54
90–160	Dehydration of CAH_{10} [20,21]	160	160	162	161	109	117	124	124
160–400	Dehydration of C_3AH_6 [20,21]. The broadening of peak with hydration time gives an indication of transformation of C_2AH_8 into C_3AH_6	270	290	294	300	254	254	254	254
400–600	Dehydration of CH [17,21–23]	–	505	502	–	–	–	–	–
600–750	Decomposition of carbonates [17,21–23]	705	702	712	706	634	660	646	651
750–1000	Recrystallization [23]	–	–	–	–	913	921	917	–

[a] Hydration time (days).

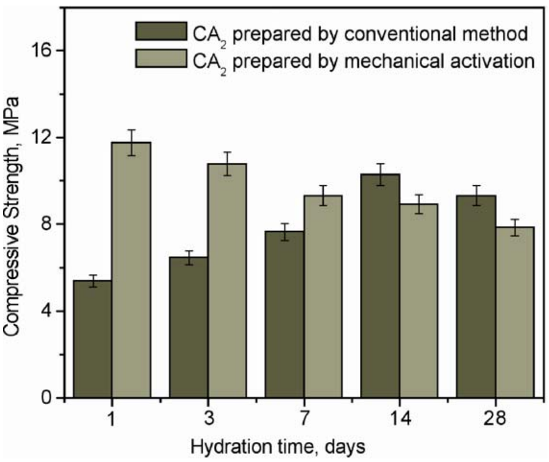


Fig. 9. Variation in compressive strength in relation to different hydration period.

Fig. 9 shows the variation of compressive strength of attritional-milled and conventional CA_2 based mortar hydrated for different time. In conventional CA_2, the maximum strength was achieved after 14-day hydration and then decreased. Whereas, the maximum strength in the CA_2 synthesised from the mechanically activated mixture was achieved on the first day itself and then decreased with the hydration period. Also the strength values are much higher than the conventional cement up to 7 days. The deterioration in hydraulic strength after 7 days is not critical because for castable or high temperature application, calcium aluminates are subjected to heat treatment during 3–7 days and further strength development is due to ceramic bond formation. Possible explanation for early strength development is linked with reactivity of the CA_2. The higher reactivity of CA_2 may be ascribed to a combined effect of lower particle size ($X_{50} = 5.74$ μm) and angular to semi-spherical shape. Other important variables affecting solid reactivity include surface area, state of aggregation, defects etc. Further investigations are on to elucidate some of these issues.

4. Conclusion

Following three are the conclusions from the present study:

1. Attrition milling of a mixture of $Al(OH)_3$ and $Ca(OH)_2$ in the molar proportions of CA_2 produces an mechanically activated mixture with an intermediate compound CAH_{10}, which on calcinations at 1000 °C converts into CA_2.
2. Formation of stable C_3AH_6 on 3-day hydration indicates the faster conversion of CAH_{10}–C_2AH_8–C_3AH_6 during hydration reactions of CA_2 obtained from attrition milled powders.
3. The early strength development in CA_2 was very fast and the maximum strength was achieved during first day itself. Also, the compressive strength values were higher than the conventional CA_2 based mortars.

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