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DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS OF $Ca(OH)_2$: SOME ANOMALOUS THERMAL EFFECTS

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ABSTRACT

An examination of the thermal characteristics of moist $Ca(OH)_2$ showed three peaks at 100, 400–450 and 250–300°C. The effect at 250–300°C was caused by calcium aluminate hydrate formed from the reaction of $Ca(OH)_2$ with the aluminum sample holder. This effect could be eliminated by using a sample holder made of gold.

INTRODUCTION

Thermal analysis techniques such as TG, DTA, DMA and DSC are used extensively in cement chemistry [1]. In the hydration of portland cement, depending on its chemical composition and the method and time of hydration, up to 25% calcium hydroxide ($Ca(OH)_2$) is formed. In the hydration of tricalcium silicate, a major component of cement, the hydration product may contain as much as 40% $Ca(OH)_2$. Quantitative estimation of $Ca(OH)_2$ is useful to follow the kinetics and the mechanism of hydration, and to determine the composition of calcium silicate hydrate products, as well as the influence of the admixtures and the durability of cements [2].

The differential scanning calorimetric analysis of $Ca(OH)_2$ produces a single endothermal peak at about 450–520°C that can be attributed to the decomposition of $Ca(OH)_2$ to CaO and H_2O. In our study of $Ca(OH)_2$ and tricalcium silicate pastes, under certain conditions, additional endothermal effects occurred. These anomalous effects could not be ascribed directly to $Ca(OH)_2$. This paper reports the conditions under which these peaks occur and the components causing them.

EXPERIMENTAL

Materials

Calcium hydroxide ($Ca(OH)_2$) was of reagent quality supplied by Fischer Scientific Co. Tricalcium aluminate hexahydrate ($3CaO \cdot Al_2O_3 \cdot 6H_2O$) was obtained by autoclaving laboratory-made $3CaO \cdot Al_2O_3$ at a steam pressure of 300 lb/sq in. (2.1 MPa) for 3 h.

The following samples were subjected to examination by DSC, XRD and SEM:

(a) Dry $Ca(OH)_2$ powder.

(b) Mixtures of $Ca(OH)_2$ and calcium silicate hydrate (dry or wet) containing 10, 20 and 40% $Ca(OH)_2$.

(c) 4 mg $Ca(OH)_2$ exposed to 40 mg of water for 1 min.

(d) 4 mg $Ca(OH)_2$ treated with 40 mg of water, kept for 3 days at 100% RH and then vacuum-dried for 3 h.

(e) 4 mg $Ca(OH)_2$ containing 40 mg of water, heated to 180°C in the DSC and cooled to room temperature.

(f) Tricalcium aluminate autoclaved for 3 h at 300 lb/sq in. (2.1 MPa).

Methods

The differential scanning calorimetric cell was a module of the Du Pont 1090 system. In each experiment 4 mg of the sample was placed in an aluminum or gold pan (sample holder) and heated at a uniform rate of 20°C min^{-1}.

XRD powder photographs were obtained with a Phillips camera using a Cu K_α source. The relative intensities of the lines were obtained by densitometer traces of the powder photographs.

The specimens were examined by a scanning electron microscope supplied by Cambridge Instruments Ltd.

RESULTS AND DISCUSSION

Figure 1 represents the DSC curves of the mixture of $Ca(OH)_2$ and synthetically prepared calcium silicate hydrate, containing 10, 20 and 40% $Ca(OH)_2$. Figure 1a refers to the dry mixtures. A typical endothermic effect occurring at 400–450°C is caused by the decomposition of $Ca(OH)_2$. The intensity of the peak increases as the percentage of $Ca(OH)_2$ in the mixture is increased.

Samples used in Fig. 1b are similar to those in Fig. 1a, except that they were all treated with water. Three endothermal peaks are observed at about 100°C, 250–300°C and 400–450°C. The peak at 100°C is due to the heat absorbed during the expulsion of water, and the peak at 400–450°C is caused by the dissociation of $Ca(OH)_2$. In addition, an unexpected endothermal effect occurring at 250–300°C increased in intensity as the amount of added $Ca(OH)_2$ was increased in the mixture. There was also a corresponding decrease in the endothermal peak of $Ca(OH)_2$. These results suggest that the new peak is caused by some reaction involving $Ca(OH)_2$.

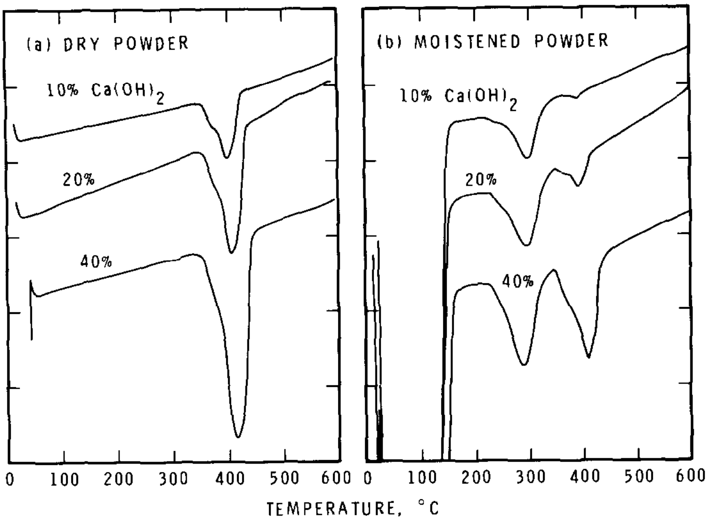

Fig. 1. DSC curves of calcium silicate hydrate and calcium hydroxide.

It was thought that the anomalous peak resulted from a reaction involving $Ca(OH)_2$ during the heating in the DSC apparatus. A few samples were therefore withdrawn after they had been heated to 180°C in the DSC

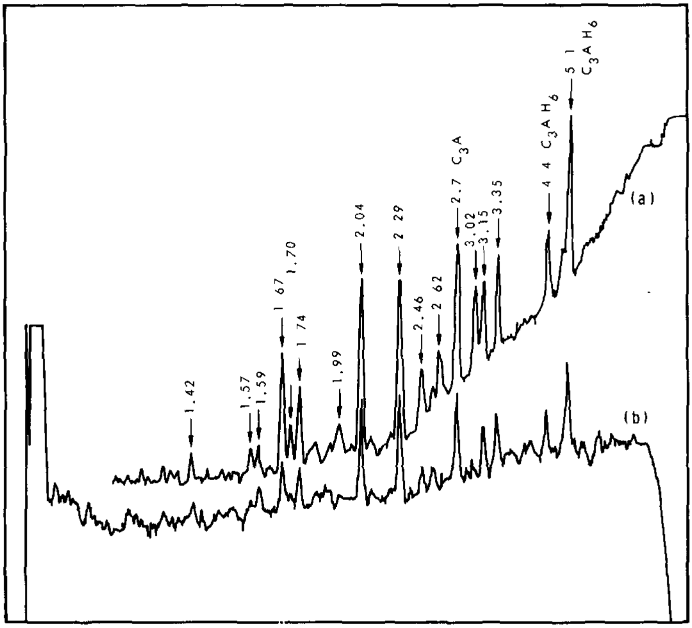

Fig. 2. XRD tracings of (a) $Ca(OH)_2$ moistened, heated to 180°C and cooled; and (b) of the autoclaved $3CaO \cdot Al_2O_3$ sample.

apparatus. The XRD data for these samples are presented in Fig. 2a. In Fig. 2b, which represents an autoclaved sample of C_3A, the strong *d* lines at 0.51, 0.44 nm and some other peak values were caused by the presence of

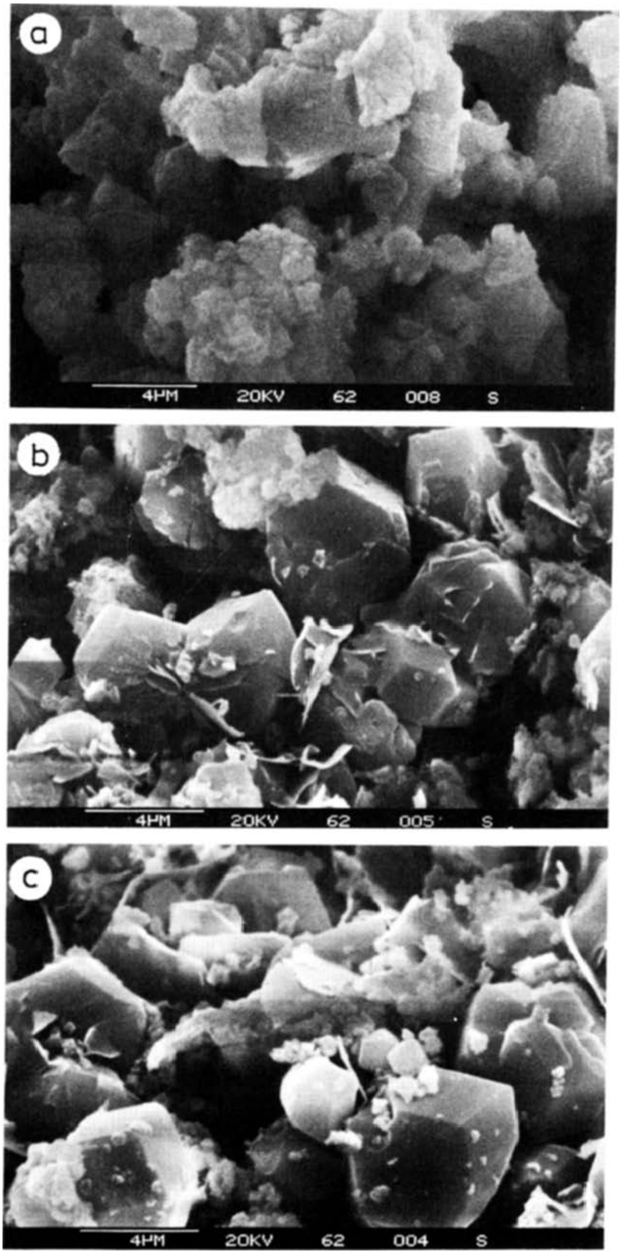

Fig. 3. Electron micrographs of $Ca(OH)_2$: (a) dry $Ca(OH)_2$; (b) and (c) moistened $Ca(OH)_2$ heated in Al pans to 180°C and cooled.

$3CaO \cdot Al_2O_3 \cdot 6H_2O$ [3]. A comparison of the lines for samples A and B shows them to be essentially similar. These results established that $Ca(OH)_2$ reacted with an aluminous material to form $3CaO \cdot Al_2O_3 \cdot 6H_2O$. After eliminating all possibilities, the Al component in the hydrate was traced to the aluminum sample holder used in this experiment. That cubic aluminate had formed was also confirmed by electron micrographs. In Fig. 3, micrograph (a), which is that of $Ca(OH)_2$, is composed of plates of $Ca(OH)_2$. Figures 3b and 3c show micrographs of moistened $Ca(OH)_2$-calcium silicate hydrate that was initially heated to 180°C and cooled. A clear indication of large cubic crystals, typical of $3CaO \cdot Al_2O_3 \cdot 6H_2O$, can be seen.

If the aluminum sample holder was responsible for the reaction of $Ca(OH)_2 + Al + H_2O$ which formed $3CaO \cdot Al_2O_3 \cdot 6H_2O$, then the formation of this compound could be eliminated by using a non-aluminum sample holder. A few experiments were performed using a gold sample holder. Curve (a) in Fig. 4 obtained for the moist $Ca(OH)_2$ heated in a gold sample holder exhibits only two endothermal effects at about 100°C and 400–450°C. The absence of an anomalous peak at about 250–300°C obtained when an aluminum holder was used (Fig. 1b), clearly shows that the interaction of the Al sample holder with $Ca(OH)_2$ in the presence of moisture develops a new calcium aluminate hydrate compound.

A few more experiments were conducted to examine if $Ca(OH)_2$ reacts with the aluminum sample holder at ambient temperatures. A moistened $Ca(OH)_2$ sample was left in the aluminum holder for 1 h at 100% RH and then vacuum dried for 3 h. This sample (Fig. 4b) showed two peaks at about

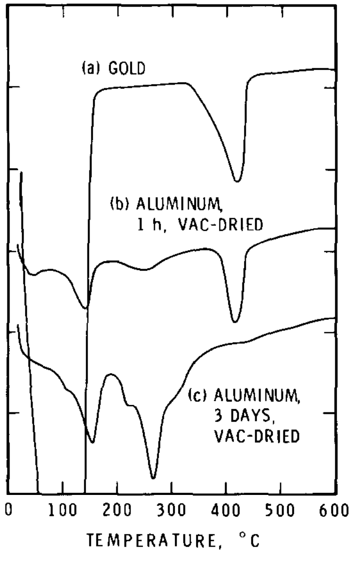

Fig. 4. DSC curves of moistened $Ca(OH)_2$ using aluminum or gold sample holders.

150 and 250°C, which are typical of the hexagonal aluminate hydrates of composition $4CaO \cdot Al_2O_3 \cdot 13H_2O$ and $2CaO \cdot Al_2O_3 \cdot 7\text{–}8H_2O$. This hexagonal phase is formed as a metastable product in the hydration of $3CaO \cdot Al_2O_3$. The $Ca(OH)_2$ sample exposed for 3 days at 100% RH developed a curve (Fig. 4c) different from Fig. 4b. This sample showed that cubic aluminate had formed (peak at about 275°C), in addition to the hexagonal aluminate hydrate, and that all the lime had disappeared.

CONCLUSIONS

Caution should be exercised in choosing the proper sample holder for the thermal analysis of cement pastes and $Ca(OH)_2$. The aluminum sample holder interacts with lime, especially in the presence of moisture, forming new compounds. New compounds may also form when thermal analysis of dry samples is carried out at different humidities. In the preparation of cement pastes, aluminum-containing materials should not be used.

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