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INHIBITION OF THE CALCINATION OF CALCIUM CARBONATE

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ABSTRACT

Aluminum oxide (Al_2O_3), calcium oxide (CaO), vanadium pentoxide (V_2O_5), and fly ash were respectively mixed with calcium carbonate (calcite, $CaCO_3$) in a ratio of 1:20 (w/w) and the mixtures were studied at a constant temperature of 700 ° C in a DTA–TGA analyzer. The results of calcination rate (wt% h^{-1}) have shown that Al_2O_3 and CaO do not have any effect on the calcination rate of $CaCO_3$, while V_2O_5 and fly ash inhibit the calcination rate of $CaCO_3$. An explanation is proposed.

INTRODUCTION

In a previous paper [1], the extended shell model has been developed to explain the calcination reaction of calcium carbonate ($CaCO_3$)

$$CaCO_3(s) \overset{\Delta}{\rightleftharpoons} CaO(s) + CO_2(g)$$

From this model, heat transfer and mass transfer are two main factors for predicting the calcination rate of $CaCO_3$.

A previous study [2] showed that lithium carbonate (Li_2CO_3), with a melting point of 723°C, was the best catalyst among alkali carbonates to enhance the calcination of $CaCO_3$. In the present study, aluminum oxide (Al_2O_3), calcium oxide (CaO), and fly ash with a melting point higher than that of Li_2CO_3, and vanadium oxide (V_2O_5) with a melting point lower than that of Li_2CO_3 were chosen to mix with pure $CaCO_3$ in an effort to test the model [1]. The mixtures were analyzed by DTA–TGA, and conclusions reached concerning the extended shell model.

EXPERIMENTAL

The additives used in this study were Al_2CO_3 (certified grade from Fisher Scientific Company), CaO (certified grade from Scientific Company), V_2O_5 (chemical pure grade from Vanadium Corporation of America), and fly ash

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(obtained from Raba-Kistner Consultants, Incorporated, San Antonio, TX). They were mixed each manually to a homogeneous mixture with reagent grade $CaCO_3$ in a ratio of 1 : 20 (w/w).

The DTA–TGA system employed in this study is a Mettler thermal analyzer with a Mettler BE 20 balance controller and a Mettler HE balance. The conditions for running the DTA–TGA included a heating rate of 10 ° C min^{-1}, a chart speed of 10 cm h^{-1}, and a 2 mV range for the DTA. The sample amount for each run was carefully controlled at 90.0 ± 0.5 mg.

Two different thermograms were obtained. One was obtained by programming the temperature to 700 ° C then keeping it there for about 50 min. From the TGA curve, the calcination rate could be calculated. The calcination rate was expressed as

$$\%\ \text{calcination rate} = \frac{\text{weight loss (mg)}}{\text{sample weight (mg)} \times \text{time (h)}} \times 100\%$$

The other thermogram was obtained by running the instrument to 1000 ° C. The transition temperature could then be found from the DTA curve.

The contracting test for additives was run by weighing about 3.00 g of each of the additives into casseroles, with the casseroles then placed in a Lindberg furnace at a known temperature for 1 h. After that, the additives in the casseroles were thoroughly examined and compared.

RESULTS AND DISCUSSION

Table 1 summarizes the data of calcination rate calculated from the TGA curve of DTA–TGA analyzer programmed to 700 ° C. All of the calcination rates of the mixtures are lower than that of pure $CaCO_3$. Because the weight ratio of each additive and pure $CaCO_3$ is 1 : 20, the effective weight of $CaCO_3$ in the mixture must be taken into account in order to do precise comparisons. The corrected average rate is obtained by multiplying the average calcination rate by a corrected factor of 21/20 for the effective

TABLE 1

Calcination rate of the additive–$CaCO_3$ mixtures (from the DTA–TGA analyzer at 700 ° C)

Composition (1 : 20)	Calcination rate ($wt\%\ h^{-1}$)	Average calcination rate ($wt\%\ h^{-1}$)	Corrected average, rate ($wt\%\ h^{-1}$)
$Al_2O_3 + CaCO_3$	25.39, 25.50	25.44	26.71
$CaO + CaCO_3$	25.87, 25.70	25.78	27.07
$V_2O_5 + CaCO_3$	19.62, 20.48	20.05	21.05
Fly ash + $CaCO_3$	22.47, 21.67	22.07	23.17
Pure $CaCO_3$	26.16, 26.62	26.39	26.39

TABLE 2

Transition temperatures of the additive–$CaCO_3$ mixtures (from the DTA curve)

Composition (1 : 20)	Transition temperature (° C)	Average transition temperature (° C)
$Al_2O_3 + CaCO_3$	839, 837, 838	838
$CaO + CaCO_3$	838, 839	838
$V_2O_5 + CaCO_3$	843, 842	842
Fly ash + $CaCO_3$	840, 841, 841	841
Pure $CaCO_3$	837, 838, 838	838

weight of $CaCO_3$ in the mixture. It is apparent from Table 1 that Al_2O_3 and CaO do not have a significant catalytic or inhibitive effect on the calcination rate of $CaCO_3$, while V_2O_5 and fly ash demonstrate an inhibitive effect on the calcination rate of $CaCO_3$.

In the DTA–TGA thermogram the transition temperature (the peak of the DTA curve) corresponds to the temperature of completion of calcination. Table 2 shows the transition temperatures of the mixtures. Again, Al_2O_3 and CaO do not change the transition temperature of $CaCO_3$, so they do not have any effect on the calcination rate of $CaCO_3$. Vanadium pentoxide and fly ash have an inhibitive effect, causing the calcination of $CaCO_3$ to be completed at a higher temperature.

Table 3 shows the melting points of Al_2O_3, CaO, V_2O_5 [3], and fly ash [4]. Because the melting points of Al_2O_3, CaO, and fly ash are relatively high, they are expected to be thermally inert at 700 ° C. This was tested by placing them in a 700 ° C Lindberg furnace for 1 h, after which none of them showed any significant contraction. Although the melting point of V_2O_5 is only 690 ° C, it does not contract after heating in a 680 ° C Lindberg furnace for 1 h. It starts to melt at 690 ° C and is completely liquefied at 700 ° C.

The extended shell model [1] can be used to explain the above calcining results. From the argument of heat transfer, Al_2O_3, CaO, V_2O_5, and fly ash do not contract around 700 ° C, so they cannot enhance the heat transfer by increasing the contacting area among $CaCO_3$ particles. As a result, the calcination rate cannot be increased by adding these additives to pure

TABLE 3

Melting points of the additives

Additive	Melting point (° C)
Al_2O_3	2072
CaO	2614
V_2O_5	690
Fly ash	~ 1245

$CaCO_3$. With regard to the mass transfer, Al_2O_3 and CaO are thermally inert; they can neither promote nor hinder the escape of carbon dioxide during the calcination of $CaCO_3$. But this is not true for V_2O_5 and fly ash. Vanadium pentoxide melts at 690 °C and completely liquefies at 700 °C. The expanding liquid fills the interstitial space and hinders the CO_2 from escaping freely among the $CaCO_3$ particles. As a result, the temperature of completion of calcination is higher than that of pure $CaCO_3$, and the calcination rate is lower than that of pure $CaCO_3$ at 700 °C. Although the major components of fly ash are metallic oxides with very high melting points, some constituents [5] with relatively low melting points are present, such as phophorous pentoxide which has a melting point of 583 °C [3]. The low melting constituents melt at a temperature below 700 °C and hinder the escape of CO_2 produced from the calcination of $CaCO_3$. That is why fly ash shows an inhibitive effect on the calcination of $CaCO_3$. This has been shown by study of the calcination rate of a P_2O_5–$CaCO_3$ (1 : 20) mixture. The measured calcination rate is only 21.21 wt% h^{-1}, which is lower than the value of 26.39 wt% h^{-1} for pure $CaCO_3$.

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