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Publication Date
1983-08-01
To be presented at the 6th International Symposium on Ceramics, Bologna, Italy, September 26-29, 1983; and to be submitted to the Journal of the American Ceramic Society

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The Effect of Lithium Carbonate on the Reaction of CaO Powders with CO₂

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August 1983

Abstract

Reaction between CaO powders and CO₂(g) is often limited by slow diffusion of CO₂ through the CaCO₃ product. Additions of Li₂CO₃ are shown to increase the reaction rate. At temperatures near or higher than the Li₂CO₃-CaCO₃ eutectic temperature, 935 K, complete reaction of the CaO can be achieved when the heating rate and Li₂CO₃ content are optimized. At lower temperatures Li₂CO₃ causes less but measurable increases in reaction rates. SEM and surface area observations suggest different reaction paths when Li₂CO₃ is present, when Li₂CO₃ and eutectic are present, and when eutectic alone is present.

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INTRODUCTION

Reactions between a solid reagent and a gaseous phase to form a nonporous solid product are often limited by a slow step controlled by the diffusion of the gaseous phase through the newly formed polycrystalline phase. For the reaction:

\[ \text{CaO}(s) + \text{CO}_2(g) = \text{CaCO}_3(s, \text{nonporous}) \quad (1) \]

Barker [1] found that CaO samples with a large number of very small pores (<4 nm) react with CO\textsubscript{2} initially very quickly, and then at a much slower rate due to the diffusion of the gaseous phase through the nonporous CaCO\textsubscript{3} layer. The critical CaCO\textsubscript{3} layer thickness where this change takes place was 22 nm. Oakeson and Cuttler [2], working with CaO nonporous samples, studied the same reaction as a function of the CO\textsubscript{2} pressure. Their conclusion was that the reaction rapidly becomes diffusion controlled and that the pressure dependence of the diffusion-controlled reaction approximates that expected for a Langmuir adsorption isotherm. Unless it is possible to minimize the influence of the diffusion-controlled regime [3], it appears that the reaction of low surface area commercial CaO with CO\textsubscript{2} would take a long time before reaching an industrially acceptable degree of carbonation. Studies carried out in these laboratories have dealt with the influence of LiCl [4], LiBr [5], and NaCl, Li\textsubscript{2}CO\textsubscript{3}, CaCl\textsubscript{2} [6] on the kinetics of calcite decomposition. At high CO\textsubscript{2} pressure, the additives increase the initial decomposition rate by 2-5 times, presumably because liquid phase reaction paths are provided by the additives. It can be hoped that a liquid phase may have an even greater influence on the CaO-CO\textsubscript{2}
recombination rate if the liquid prevents formation of a protective calcite coating on the CaO.

This paper reports the effects of Li$_2$CO$_3$ on the rate of reaction of CO$_2$ with low surface area CaO at temperatures below, near, and above the Li$_2$CO$_3$-CaCO$_3$ eutectic (935 K) [7]. The kinetic measurements were supplemented by observation of morphologies, BET surface area measurements, and measurements of heat effects in a differential thermal analysis (DTA) apparatus.

EXPERIMENTAL

Mallinckrodt reagent grade CaO powders of about 3 μm particle size were used throughout the experiments. The powders were found to be about 30% hydrated and dehydration at 673 K was carried out with or without the additive before any carbonation experiments were made. After the dehydration, the surface area of the powder was found to be ~6 m$^2$/g by the BET method using an N$_2$-He gas mixture.

For some runs, the samples were heated in air to 1473 K before they were mixed with Li$_2$CO$_3$. Li$_2$CO$_3$ powders were intimately mixed with the CaO particles in different percentages.

Differential thermal analysis and thermogravimetric experiments were done simultaneously using alumina crucibles in a Neztchs apparatus. The thermogravimetric system was evacuated initially and then CO$_2$ gas was introduced. Pressure was controlled using a single side absolute sensor head plus a control system placed at the top of the microbalance. Constant heating rates of 0.2°C/min, 2°C/min, 5°C/min, and 10°C/min were used in different experiments. The sensitivity of the microbalance was set at 2.5x10$^{-3}$ gram/cm and that of the DTA was 0.1 mV at full scale.
Isothermal weight changes were measured in the same apparatus. CO₂ gas was introduced as soon as the temperature reached the preselected value. The Pt-Pt/Rd thermocouple tip projected upward into a 5 mm long recess in the bottom of the crucible. Differential thermal analyses were made on mixtures of Li₂CO₃-CaCO₃, Li₂CO₃-CaO, and Li₂CO₃-CaCO₃-CaO in dry N₂.

Morphological observations on starting materials and products were made with an ISI-130 scanning electron microscope (SEM) which can resolve to ~3 nm. The samples were coated with a ~2 nm layer of gold to prevent electron charging in the specimen.

RESULTS AND DISCUSSION

Figure 1 illustrates the typical data obtained from the microbalance when the heating rate was set at 5°C/min. The CO₂ pressure was about 4000 Pa and the Li₂CO₃ content was 7 wt% of the mixture of Li₂CO₃ and CaO. In the same figure, for comparison, the behavior of the same quantity of pure CaO has been plotted. The degree of carbonation of CaO is always increased by the presence of Li₂CO₃. At 913 K, where the DTA shows a marked exothermic effect, the rate of reaction increases rapidly. This run was terminated when the sample reached 973 K, where calcite becomes unstable in CO₂ at 4000 Pa pressure [9]. The same kind of experiments carried out at higher CO₂ pressure (26,664 Pa), however, proved that the degree of carbonation reaches a limit dependent upon the heating rate (Table I); namely, the faster the heating rate, the lower the recorded final degree of carbonation. Heating at the same rates for more than 150°C higher than the temperature of the exothermic DTA peak caused negligible increases in the degree of reaction.
According to the literature [7], Li$_2$CO$_3$ and CaCO$_3$ form a eutectic phase which melts at 935 K. The maximum rate of carbonation is at measured temperatures which, depending on heating rates, lie 10 to 30°C below this eutectic (Table I). The reaction is exothermic, and the true temperatures at the reaction interface must be higher than the temperature recorded at the bottom of the crucible with the thermocouple. Probably the highest reaction rates reflect the formation of the Li$_2$CO$_3$-CaCO$_3$ eutectic liquid phase.

To explore this possibility, CaO particles were first carbonated to 21%. Then they were mixed with Li$_2$CO$_3$ (24 wt%) and treated again in CO$_2$ with a heating rate of 10°C/min. The results (Table I) show that the rapid gain in weight occurred at 923 K, very near indeed to the carbonate eutectic temperature.

The CaCO$_3$-Li$_2$CO$_3$ eutectic was heated in CO$_2$ in the absence of CaO. Negligible reaction between CO$_2$ and the eutectic liquid phase was observed. Furthermore, DTA analysis on the ternary system Li$_2$CO$_3$-CaCO$_3$-CaO in the absence of CO$_2$ and in the same range of temperature showed no thermal effects that might be connected with a ternary liquid phase.

As a step in gaining more insight into the reaction mechanism, the effects of different amounts of additive were studied. Figure 2 shows the results of isothermal thermogravimetric experiments carried out at 963 K and at CO$_2$ pressure equal to 4000 Pa. The isotherms show very rapid initial rates, almost independent of the amount of Li$_2$CO$_3$ added, followed by slower rates. These experiments (Fig. 2) and others [6] showed that the maximum carbonate formation produced when almost 10% Li$_2$CO$_3$ was present.
Insights into the influence of Li$_2$CO$_3$ on the CaO-CO$_2$ reaction can be obtained by taking into account the phase diagram (Fig. 3), although it must be remembered that sample compositions are not perfectly homogeneous so that local regions may be closer in composition than the averages are to the eutectic composition, 43 wt% CaCO$_3$. An important fact to note is that as the amount of Li$_2$CO$_3$ is increased, an increased quantity of CaCO$_3$ must be formed before the eutectic composition is reached. For instance, the 7% Li$_2$CO$_3$ mixture needs only 3.2% reaction of CaO, while the 50% Li$_2$CO$_3$ mixture requires 22.7% reaction. Consequently, when lower percentages of Li$_2$CO$_3$ are present, most of the CaO-CO$_2$ reaction occurs in the presence of CaCO$_3$(s) and a carbonate liquid phase (region A in Fig. 3), with more Li$_2$CO$_3$ present, reaction occurs largely in the presence of Li$_2$CO$_3$(s) and the Li$_2$CO$_3$-saturated liquid phase (region B in Fig. 3).

Under the experimental conditions adopted, the additive does not undergo significant vaporization. For reactions that occur in the CaCO$_3$-rich region, all the Li$_2$CO$_3$ initially added will be liquid and CaCO$_3$ will be precipitated from a Li$_2$CO$_3$-CaCO$_3$ liquid phase (point C in Fig. 3) from the beginning of the reaction to the end. Figure 4(a&b) show SEM observations of samples reacted up to 20% from a starting specimen prepared with 10 wt% of Li$_2$CO$_3$. Since these pictures were taken at room temperature, a definite conclusion that calcite precipitates at high temperatures from the liquid phase cannot be made; but the large calcite crystals seen in the pictures strongly suggest the recrystallization of the calcite.

Figure 5 shows a sample prepared from 57% Li$_2$CO$_3$ and reacted until 21% of the CaO formed calcite. No large calcite crystals are
present. When reaction is carried out in the Li$_2$CO$_3$-rich region, all
the CaCO$_3$ is liquid and the amount of the liquid phase (Li$_2$CO$_3$-CaCO$_3$)
increases from the beginning to the end of the reaction (point D in
Fig. 3). Up to 63% of the CaO must react before the CaCO$_3$ starts to
precipitate from the liquid phase. Therefore, no high-temperature
recrystallization of calcite should occur.

It is possible to correlate the lower final degree of CaO-CO$_2$
reaction with a greater amount of liquid phase formed during the
reaction. The observation that the mass of a Li$_2$CO$_3$-CaCO$_3$ sample did
not change when CO$_2$ was introduced into the system at 959 K indicates
the solubility of CO$_2$ in the carbonate eutectic is very low.

Consequently, although the liquid probably removes the CaCO$_3$ solid
layers from the CaO surfaces, the liquid may itself act as a protective
barrier to CO$_2$ transport to the CaO surface.

For a possible explanation of the data one might assume a
multistep process for the reaction. The first step is the formation of
a CaCO$_3$ layer on the CaO particles. As soon as CaCO$_3$ has reached the
amount required at the local temperature for the formation of the liquid
phase, the calcite formed on the CaO surface will dissolve as it forms
and recrystallize as more stable larger calcite crystals, as long as the
reaction occurs in the CaCO$_3$-rich region. If the rate-limiting step is
the diffusion of CaCO$_3$ or of CO$_2$ through the liquid phase, then the
reaction rate would decrease as the liquid layer grows, although the
rate would remain higher than that when a protective calcite layer is
formed.

Figure 6b shows the typical morphology of samples carbonated in
the CaCO$_3$-rich region. The initial CaO particles (Fig. 6a) were about
3 μm size as irregular block-like shapes. These blocks were well separated but the carbonated particles show small blocks interconnected in the phase of viscous appearance. Within the viscous regions well-defined crystalline planes are visible as are a finer structure made up of what appear to be small regular cracks. Surface areas of these samples are less than 1 m²/g. It is therefore concluded that the apparent fine cracks of those samples do not indicate a porous structure but rather a surface roughness.

The proposed mechanism would give an initial rate of isothermal reaction with Li₂CO₃ present that is equal to that without additive. Unfortunately, it is not easy to measure this value because a certain amount of CaCO₃ may be already formed on the CaO particles before isothermal conditions are reached. If so, the initial data plotted at 963 K (Fig. 2) could reflect a state where the Li₂CO₃-CaCO₃ liquid phase is already active.

To overcome this difficulty, a "quasi-isothermal" experiment was designed. The heating rate was set equal to 0.2°C/min, and the CO₂ pressure was 26,664 Pa. This would allow observation of the relative reaction rates at low temperatures. In Fig. 7 the results are illustrated for the CaO particles with and without Li₂CO₃ (15%). Both samples behave similarly up to 633 K. Then the one with Li₂CO₃ starts to pick up CO₂ at a rapidly increasing rate and reaches 100% reaction. From the evidence that both samples initially have the same reaction rate, it follows that the formation of a certain quantity of CaCO₃ on the CaO particles is required before the additive effect is observed.

It is interesting to note that some enhancement of the rate of the CaO-CO₂ reaction is caused by Li₂CO₃ as much as 250°C below the
Li$_2$CO$_3$-CaCO$_3$ eutectic melting point. Since DTA analysis on the CaO-Li$_2$CO$_3$ systems in dry N$_2$ and in the same range of temperature showed no thermal effects that might be connected with a liquid phase, this enhancement must be due to a solid-state or surface phenomenon.

The microstructural features of samples carbonated in this temperature regime strongly support a different reaction path. Fig. 8(c&d), taken on CaO particles containing 12.6% Li$_2$CO$_3$ and carbonated at 779 K up to 19.5% under a CO$_2$ pressure of 12132 Pa, shows that the particles are sintered and the grain boundaries are well developed. The grain surface shows fine cracks similar to those observed in higher-temperature samples. The low specific surface area, less than 1 m$^2$/g, implies that the CaCO$_3$ coating layer is not porous.

As shown in Fig. 8(a&b), the coating on CaO particles with Li$_2$CO$_3$ seems to have much smaller crystallites than coatings obtained without Li$_2$CO$_3$. Similar grain size decreases are produced in MgF$_2$ by small additions of CaF$_2$ [8]. In this low-temperature regime, the increase in reaction rate when Li$_2$CO$_3$ is present may be a consequence of increased CO$_2$ permeation along an intergranular path. Experiments are currently underway to test this hypothesis.

CONCLUSIONS

The effect of Li$_2$CO$_3$ on the rate of reaction of CO$_2$ with low surface area CaO powders has been found to be strongly influenced by the eutectic phase between CaCO$_3$ and Li$_2$CO$_3$. The reaction rates and product morphologies are different in three regimes: At temperatures where the Li$_2$CO$_3$-CaCO$_3$ eutectic phase can form, the CaCO$_3$, which forms a protective coating on CaO, is dissolved and reprecipitated as large
CaCO₃ crystals, and the reaction proceeds on the CaO surface with a high rate. If enough Li₂CO₃ is present so that the liquid does not become saturated with CaCO₃, the liquid content of the sample increases as reaction proceeds and the liquid phase itself acts as a protective coating. Below the eutectic temperature, Li₂CO₃ additions decrease the grain size of the polycrystalline CaCO₃ coating layer, and an increase in reaction rate occurs, probably because the increased number of grain boundaries provide additional paths for intergranular diffusion to the CaO.

ACKNOWLEDGMENTS

Valuable advice on this manuscript was provided by A.W. Searcy, L.C. De Jonghe, and D.J. Meschi.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
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Table I. Influence of heating rate on maximum reaction rate and on final degree of carbonation.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Heating rate (°C/min)</th>
<th>CO₂ pressures (Pa)</th>
<th>Temperature corresponding to maximum in the DTA traces (K)</th>
<th>Degree of carbonation when rate became negligible (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO-Li₂CO₃ (7%)</td>
<td>5</td>
<td>4,000</td>
<td>913</td>
<td>65</td>
</tr>
<tr>
<td>CaO-Li₂CO₃ (15%)</td>
<td>10</td>
<td>26,664</td>
<td>893</td>
<td>70</td>
</tr>
<tr>
<td>CaO-Li₂CO₃ (15%)</td>
<td>2</td>
<td>26,664</td>
<td>903</td>
<td>81</td>
</tr>
<tr>
<td>CaO-Li₂CO₃ (15%)</td>
<td>0.2</td>
<td>26,664</td>
<td>913</td>
<td>100</td>
</tr>
<tr>
<td>CaO-Li₂CO₃ (53%)</td>
<td>10</td>
<td>26,664</td>
<td>923</td>
<td>60</td>
</tr>
<tr>
<td>CaO-CaCO₃-Li₂CO₃ (21%) (24%)</td>
<td>10</td>
<td>26,664</td>
<td>923</td>
<td>34</td>
</tr>
</tbody>
</table>
Figure Captions

Fig. 1 The dynamic carbonation of CaO with 7% Li₂CO₃ and without Li₂CO₃.

Fig. 2 The isothermal carbonation of CaO with various compositions of Li₂CO₃ at 963 K.

Fig. 3 The phase diagram of Li₂CO₃-CaCO₃ system from Ref. 7. The line ---- indicates the experimental temperature.

Fig. 4 20% carbonated sample with 10% Li₂CO₃ heated at 963 K in 4000 Pa of CO₂.

Fig. 5 CaO carbonated with 57% Li₂CO₃ at 963 K and 4000 Pa of CO₂.

Fig. 6 (a) The vacuum dehydrated initial CaO particles.
   (b) The carbonated CaO with 9.5% Li₂CO₃ at 963°K and 4000 Pa of CO₂.

Fig. 7 The dynamic carbonation of CaO with 15% Li₂CO₃ and without Li₂CO₃.

Fig. 8 CaO carbonated without Li₂CO₃ (a&b) and with 12.6% Li₂CO₃ (c&d) at 779 K and 12132 Pa of CO₂.
$W_{\text{CaO}} = 50 \text{ mg}$

$P_{\text{CO}_2} = 4000 \text{ Pa}$

Heating rate $\approx 5^\circ\text{C/min.}$

Figure 1
Figure 2

\[ W_{CaO} = 50 \text{ mg} \]
\[ P_{CO_2} = 4000 \text{ Pa} \]
\[ T = 963 \text{ K} \]
Figure 3

```
Li2CO3 + CaCO3

973 K

1008 K

1073 K

1173 K

1273 K

1373 K

Temperature, K

0 20 40 60 80 100

Wt. %

CaCO3

Li2CO3

Liquid

CaCO3 + Liquid

50 Mol %

Figure 3
```
Figure 6
$W_{\text{CaO}} = 100 \text{ mg}$
$P_{\text{CO}_2} = 26,664 \text{ Pa}$
Heating rate $\approx 0.2^\circ\text{C/min}$

Curve
\begin{align*}
A & : \text{CaO + Li}_2\text{CO}_3 (15\%) \\
B & : \text{CaO} \\
C & : \text{DTA Trace of CaO-Li}_2\text{CO}_3 (15\%)
\end{align*}

Figure 7
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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