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Steam Calcination of Magnesium Carbonate: A Kinetic Study

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Extended Abstract

Magnesium carbonate mineral (MgCO₃), in the form of magnesite, and dolomite ((Mg,Ca)(CO₃)₂) constitute the primary sources for global magnesium metal production ¹. Magnesium and magnesia (MgO) are utilized in many sectors, including those that produce refractory and insulating materials, paper, printing inks, and medicines, as well as in the automotive, aerospace, aircraft, building, and electrical industries ². The global magnesite market is poised for growth, propelled by increasing demand from steel, fertilizer, and refractory sectors.

The calcination reaction of magnesite is the loss of $CO₂$ and the formation of magnesia (MgO); see reaction (1):

$$
MgCO_3 \to MgO + CO_2 \qquad \Delta H_r^{\circ} = 67 \, kJ/mol \tag{1}
$$

Each kilogram of magnesite produces 0.48 kg of MgO when fully decomposed. There are three main factors controlling the calcination reaction kinetics $3, 4$;

1- Magnesite ore temperature must reach the decomposition temperature.

2. The ore has to be given enough time at high temperature to fully decomposed.

3. The CO2 produced during the calcination process must be removed to improve the rate and yield of decomposition reaction.

The decomposition temperature of pure magnesium carbonate is $350 \degree C$, however the process requires higher temperature to fully decompose (up to 900 °C)⁵. The main two products of the calcination process of magnesite are; Caustic calcined magnesia (CCM), which is calcined at temperatures below 900°C, and dead-burned magnesia (DBM), also known as sintered magnesia. produced through the calcination of magnesite at temperatures exceeding 1500 °C. This high temperature facilitates the completion of the sintering process.

Steam calcination is a process that involves the decomposition of a solid material, typically a carbonate or hydroxide, into its oxide form using steam as a reaction medium ⁶. The steam calcination process has number of advantages, namely; a catalytic effect that is yet to be fully understood ⁷⁻⁹, and the ability to capture the process produced $CO₂$ by simply condensing the steam in the exhaust. Though previously considered for limestone, steam calcination remains unexplored for other minerals $6, 7, 9, 10$. Silakhori et al. 9 study, investigated CaCO3 decomposition in a steam-rich environment, revealing steam's catalytic impact on calcium carbonate calcination. In a mixture of 90% steam and 10% carbon dioxide, the decomposition temperature dropped by 40°C, with the activation energy reducing from 194.1 kJ/mol to 161.7 kJ/mol as the steam ratio increased from 10% to 90%.

To the best of our knowledge, there is no published research on the use of steam to calcine magnesite in the literature. The use of steam to calcine magnesite and later to create the CCM or DBM is yet to be explored and be fully understood.

Figure 1 shows the setup used to test the steam calcination of $MgCO₃$. The setup consists of different gas cylinders (Nitrogen, oxygen, and carbon dioxide) and a steam generator. The gas cylinders are connected to mass flow controllers (MFCs) used to control the flow rate of the gas. The three gas streams are preheated before being mixed with steam in order to avoid steam condensation. The mixed gases are fed into a horizontal tube furnace where their temperature is raised to the required calcination temperature (for example 500 °C), before being supplied to the fluidized bed where a weighted sample of $MgCO₃$ is present. The fluidized bed is installed inside a vertical electric furnace, used to keep the fluidized bed reaction temperature at the set temperature needed for the reaction. The fluidized bed is designed in a way that is possible to insert it or take out of the vertical furnace while being hot and in operation, therefore, exposing the sample to a sudden temperature change, instead of the gradual raise temperature typically found in TGA instruments. The fluidized bed tube is kept for a

specified time, after which it is taken out and weighted again, and the change in weight of the sample represent the conversion of the $MgCO₃$ to MgO .

Figure 1: Experimental setup used to study steam calcination of calcium carbonate.

Results and Findings

The calcination of pure MgCO₃ (CAS NO 39409-82-0) was studied in two different environments; the first is pure steam, and the second is flue gas with the following composition: 72.8% N₂, 16% H₂O, 8% CO₂, and 3.3% O₂ (molar basis). The flow rate of the gas was the same in both cases at 17.5 SLM. The results are shown in Figure 2. In each run 3 ± 0.05 grams of the MgCO3 were placed in the fluidized bed, with bed thickness of about 2 cm.

From Figure 2 it could be noticed that the reaction rate at 400 $^{\circ}$ C in steam is almost the same as the reaction rate in flue gas at 500 °C, and almost double the reaction rate in flue gas at the same temperature. The results also indicate that reaction in steam is following the first-order reaction model.

The results obtained from using steam as a medium for the calcination of pure $MgCO₃$ are encouraging and warrant further research and development.

Figure 2: Isothermal Conversion of pure $MgCO₃$ in steam and flue gas at different temperatures.

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