

Effect of CO₂-rich Atmosphere on the Thermal Decomposition of Natural Limestone Destined to Cement Production

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Abstract

Cement production is a major contributor to global carbon dioxide (CO₂) emissions, accounting for approximately 7% of anthropogenic CO₂ emissions worldwide. The vast majority of these emissions arise from the calcination of limestone, a key component of the cement production process. During calcination, limestone is heated to high temperatures, causing it to decompose into calcium oxide (CaO) and CO₂. Roughly two-thirds of the CO₂ emissions during cement production arise from this process, which releases large amounts of CO₂ into the atmosphere. One way to mitigate the CO₂ footprint of cement production is through the capture and utilization of CO₂ emissions during the calcination of limestone. By capturing CO₂ during the decomposition of limestone, cement producers can reduce their overall emissions and contribute to global efforts to combat climate change. However, the effectiveness of this approach depends on a number of factors, including the partial pressure of CO₂ during the calcination process. In recent years, a new technology has emerged for the separate calcination of limestone, which involves calcining limestone in a CO₂-rich atmosphere. This approach helps to avoid the dilution of CO₂ by combustion flue gas, enabling more efficient capture and utilization of CO₂ emissions. However, the use of a CO₂-rich atmosphere may also have an impact on the thermal decomposition of limestone, affecting the energy balance of the process. The aim of this paper is to investigate the influence of CO₂ partial pressure on the thermal decomposition of natural limestone used in cement production. A series of experiments were conducted to measure the thermal decomposition of limestone at different CO₂ partial pressures, and thermodynamic calculations were used to model the behaviour of the system. The results showed that CO₂ shifts the onset decomposition temperature of limestone to higher values, which can have a significant impact on the energy balance of the separate calcination technology.

Keywords

Cement, Limestone, Calcination, Carbon dioxide capture, Thermodynamic

Introduction

Cement production is a major contributor to global CO₂ emissions [1]. Almost two-thirds of CO₂ emissions come from the decomposition of the calcium carbonate (CaCO₃) into CaO [2]. The thermal decomposition of limestone present in the cement raw meal has been extensively studied [3-6]. In many modern cement plants, calcination takes place in a combustion chamber called the 'pre-heater'. According to literature, the onset decomposition temperature of limestone ranges between 750 and 900 °C [7]. However, the rate and temperature of CaCO₃ decomposition are not fixed values, as they depend on the CO₂ partial pressure [6, 8].

The motivation behind this study lies in the urgent need to address the environmental impact of cement production, particularly its significant contribution to global CO₂ emissions [9]. By focusing on the calcination process and exploring the effects of a CO₂-rich atmosphere. Understanding the influence of CO₂ partial pressure on limestone decomposition is crucial for optimizing the process and implementing CO₂ capture strategies effectively [10].

One way to reduce the CO₂ footprint of cement production is through CO₂ capture during limestone decomposition. To achieve this, limestone can be calcined separately to avoid dilution of CO₂ by combustion flue gas [11]. This process is called Direct Separation Calcination Technology [12, 13], in which partial pressure of CO₂ in the decomposition atmosphere can reach high values near 1 atm. The current paper investigates how a CO₂-rich atmosphere can affect the decomposition of natural limestone destined to cement production.

Materials and Method

The material used in this work is a natural limestone (Called NL4) provided by Holcim France. To conduct experiments, the NL4 sample was milled and then sieved using a 40 μm sieve. All used materials are nanoscale materials.

X-ray diffraction data were collected at room temperature in the Bragg-Brentano geometry using a Bruker D8 Advance X-ray diffractometer with CuKα radiation (λ_{Cu} = 1.54056 Å), without monochromator. Thermogravimetric analysis (TGA) was carried out on 50 mg of sample using a SETARAM Lab-sys TG-DTA/DSC thermal analyzer. The sample was heated in an alumina crucible from ambient temperature to 1100 °C at the heating rate of 10 °C/min (ramp) under atmospheric air. For measurements under CO₂ atmosphere, the equipment was connected to a gas bottle containing CO₂ gas. Changes in standard Gibbs free energy help to predict whether a reaction will be spontaneous in the forward or reverse direction under standard conditions (solids are considered pure and pure gases pressure equal to 1 atm). Thermodynamic calculations of the Gibbs energy of the decomposition of CaCO₃ into CaO and CO₂ were performed using suitable thermochemical data [14] (Table 1). Thermochemical data include standard enthalpy (ΔH_f⁰), standard entropy (ΔS⁰) and heat capacity (C_p) for the different compounds.

In the calculation, the standard enthalpy of each compound was given by Eq. 1 [15]:

$$\Delta H^0(T) = \Delta H_f^0(298) + \int_{298}^T C_p(T) dT \quad (1)$$

Where ΔH_f⁰(298) is the standard enthalpy of formation at

298 K, T is the temperature and C_p(T) is the heat capacity at constant pressure (Eq. 2):

$$C_p(T) = a + bT + cT^2 + dT^3 \quad (2)$$

Where a, b, c and d are the corresponding parameters taken from thermodynamic data (Table 1).

Standard entropy values can be calculated from Eq. 3:

$$\Delta S^0(T) = \Delta S_f^0(298) + \int_{298}^T \frac{C_p(T)}{T} dT \quad (3)$$

Where ΔS_f⁰(298) is the standard entropy of formation at 298 K.

The equilibrium conditions can be examined by calculating the Gibbs free energy change (ΔH_f⁰(T)) for the reaction of CaCO₃ thermal decomposition (CaCO₃ → CaO + CO₂):

$$\Delta G_f^0(T) = \Delta H_f^0(T) - T\Delta S_f^0(T) \quad (4)$$

Where ΔH_f⁰(T) is the standard enthalpy change of the reaction and ΔS_f⁰(T) is the corresponding standard entropy change.

The equilibrium stability of CaCO₃ can be evaluated through the calculation of the equilibrium constant, K^{eq}:

$$K^{eq} = e^{\frac{\Delta G_f^0(T)}{RT}} = \frac{a_{CaO} \cdot P_{CO_2}}{a_{CaCO_3}} \quad (5)$$

Eq. 5 relates the activities of the products and reactants at equilibrium, R is the gas constant and T is the absolute temperature. Considering calcium carbonate and calcium oxide as nearly pure solids, their activities, to a good approximation, are equal to 1 (a_{CaO} = a_{CaCO₃} = 1). The equilibrium constant is then equal to the partial pressure of the CO₂:

$$P_{CO_2} = K^{eq} = e^{\frac{\Delta G_f^0(T)}{RT}} \quad (6)$$

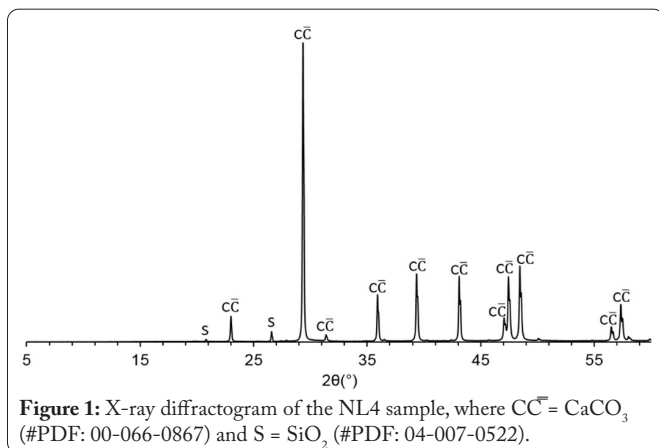
Results and Discussion

Mineralogical characterization of the natural limestone

Figure 1 shows the X-ray diffractogram of the NL4 sample. The X-ray diffractogram of limestone exhibits sharp diffraction peaks that can be attributed to the presence of calcite mineral [16]. Some characteristic peaks of quartz at 2θ angles of 20.96 and 26.50° are also present. The presence of quartz in natural limestone was previously confirmed by other authors [17].

Table 1: Thermochemical data of the compounds involved during CaCO₃ thermal decomposition.

Compound	ΔH _f ⁰ (298) (kJ.mol ⁻¹)	ΔS _f ⁰ (298) (J.mol ⁻¹ .K ⁻¹)	A (J.mol ⁻¹ .K ⁻¹)	b x 10 ⁻³ (J.mol ⁻¹ .K ⁻¹)	c x 10 ⁵ (J.mol ⁻¹ .K ⁻¹)	d x 10 ⁻⁶ (J.mol ⁻¹ .K ⁻¹)	Ref.
CaO	0	0	57.753	-10.779	-11.51	5.328	[22]
CaCO ₃	-1206.600	91.710	99.544	27.136	-21.479	0.002	[14]
CO ₂	0	0	29.314	39.970	-2.484	-14.783	[22]



Effect of CO₂ partial pressure on NL thermal decomposition

Figure 2 presents the TGA thermograms of the NL4 sample decomposition under air (grey curve) or under CO₂ atmosphere (black dotted curve). As the CO₂ partial pressure increases, the decomposition shifts to higher temperatures. Higher CO₂ partial pressure leads to an increase in the onset temperature of natural limestone decomposition from 640 °C under air to 920 °C under CO₂ atmosphere (Figure 2). Galan et al. [18] found that changing the x-axis from temperature to time does not alter the shape of the decomposition curve. The higher the CO₂ concentration in the atmosphere, the longer it takes to complete the decomposition. Additionally, a slight weight loss is observed between 400 and 700 °C (Figure 2). This may be due to the presence of small quantities of clay in the NL4 sample [19].

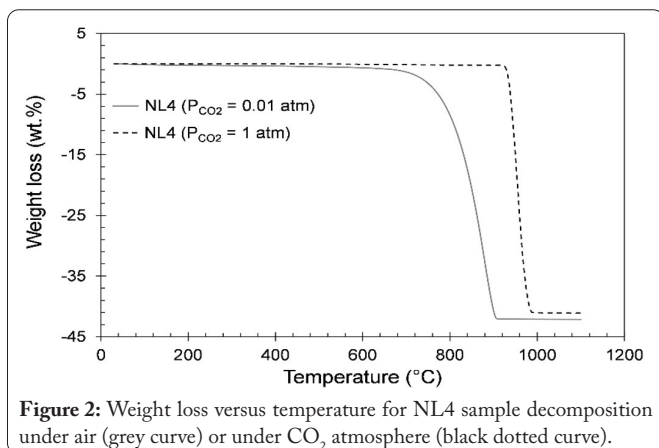
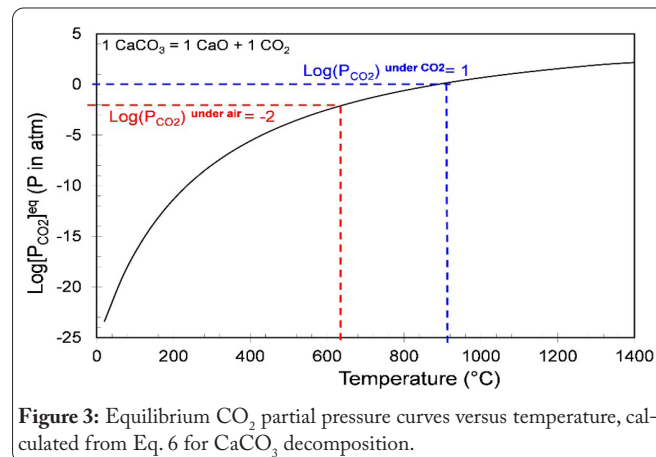


Figure 3 presents the calculated equilibrium partial pressure of CO₂ versus temperature (Eq. 6). For a CO₂ partial pressure of 0.01 atm (conditions of an air atmosphere), the decomposition of CaCO₃ occurs at 639 °C (Figure 3). This value is in accordance with the literature-reported value, which was found to be 641 °C [20]. This equilibrium temperature is close to the onset temperature (640 °C) measured by TGA of the NL4 sample decomposition under an air atmosphere (Figure 2). For a CO₂ partial pressure of 1 atm, corresponding to the conditions of a CO₂-rich atmosphere in TGA experiments, the equilibrium is reached at 919 °C (Figure 3). This value cor-

responds to the onset temperature (920 °C) of the NL4 sample decomposition under a CO₂ atmosphere (Figure 2). The agreement between thermodynamic calculations and TGA experiments regarding the onset temperature of decomposition can be attributed to the high kinetics of the sample decomposition during TGA experiments under the conditions of a 10 °C/min heating rate, 50 mg sample weight, and below 40 μm sample fineness [8, 21].



Conclusion

This paper provides insights into how CO₂ partial pressure can shift the decomposition temperature of limestone. The onset temperature of decomposition of natural limestone can be expressed as a function of CO₂ partial pressure. The results show that the onset temperature of natural limestone decomposition increases from 640 °C under air to 920 °C under CO₂ atmosphere. The experimental results from TGA were confirmed by thermodynamic calculations, and this agreement was attributed to the high kinetics of carbonate decomposition. Furthermore, as the decomposition of limestone requires higher temperatures in a CO₂-rich atmosphere, more energy is needed for calcination and should be considered when considering the use of Direct Separation Calcination Technology.

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Conflict of Interest

The authors declare that they have no conflict of interest regarding the subject matter of this publication.

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