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Effect of pressure and gas concentration on CO_2 and SO_2 capture performance of limestones

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HIGHLIGHTS

- The pressurized CO_2 and SO_2 capture ability of Ca-sorbents was investigated.
- Pressure increment resulted in reduced CO_2 capture and increased SO_2 retention.
- Sulphation via unreacted core mode utilized higher proportions of calcium.
- Changing CO_2 p. pressure slightly influenced SO_2 retention at elevated pressure.
- Increased total and SO_2 p. pressure strongly deteriorates reversibility.

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ABSTRACT

Two Greek limestones with different properties were tested to determine their CO_2 and SO_2 capture performance. The reversibility of the sorbents for CO_2 capture was investigated by performing looping cycles in atmospheric and pressurized thermogravimetric reactors, with synthetic gas mixtures containing different partial pressures of CO_2 and SO_2 to simulate flue gases. The morphological and porosity characteristics of the original and spent sorbent were examined by Scanning Electron Microscopy and Pore Sized Distribution analyses.

Increasing pressure from atmospheric to 10 bar led to deterioration in CO_2 capture performance. Further pressure increment had negligible effect on the CO_2 capture performance. SO_2 retention, however, improved with increasing pressure. For calcium looping with repeated cycles, sorbents sulphated via the unreacted-core mode converted more available calcium, but this adversely affected the reversibility of cyclic CO_2 capture. The reversibility strongly deteriorated when higher total pressure was combined with increased SO_2 partial pressure. The CO_2 uptake of an unreacted-core sulphated sorbent, previously used for SO_2 retention, was mainly affected, apart from pore blockage or sintering, by the occupation of calcium. Sulphation during simultaneous capture resulted in higher CO_2 removal efficiency for uniformly and network sulphated particles compared to the sulphur capture via direct sulphation.

1. Introduction

Fossil fuel power plants are responsible for meeting over 85% of worldwide electrical energy production demands, with over 40% of the total manmade CO_2 emissions originating from power stations which burn fossil fuels [1]. Carbon dioxide has been identified as the most important greenhouse gas contributing to global warming effects. The most common CO_2 capture processes in industry include liquid absorption with amine solvents, especially mono-ethanolamine (MEA) [2]. In recent years, solid sorbents, in particular calcium-based sorbents, have attracted considerable attention for capturing CO_2 from flue gas. Limestone is one of the most promising candidates to act as CO_2 carrier because of its abundance and its relatively low cost. Recently, the economics of CO_2 capture projects involving chemical looping cycles have been extensively investigated [3–6]. These studies suggest that these Ca-based CO_2 capture systems can be economically feasible and comparable to amine scrubbing. Thus, calcium sorbents constitute a potentially attractive option for CO_2 capture. Furthermore, electricity production from coal combustion produces further harmful environmental consequences due to the release of other gaseous

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compounds such as SO_2. Calcium-based sorbents, namely limestones and dolomites have also been extensively explored as candidates for removing SO_2 from combustion flue gases [7]. Their main disadvantage is the rather low overall calcium utilization achieved during the process. Simultaneous capture of both gaseous emissions has also been examined as an alternative to improve utilization of available calcium [8,9]. In this case, the reduced calcium utilization is accompanied by low sorbent reversibility and low long term capture efficiency. The low calcium utilization suggests that the overall process could be significantly improved.

Limestones have low surface areas. Under the appropriate temperature conditions and CO_2 partial pressures, $CaCO_3$ decomposes to produce porous solid CaO and gaseous CO_2 according to the calcination reaction:

$$CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2(g)} \tag{1}$$

Calcination is an endothermic reaction and hence is favoured at high temperatures. In practice, temperatures must exceed 900 °C at atmospheric pressure to ensure a sufficient reaction rate for practical systems [10]. The separation of CO_2 from flue gases depends on the reversible reaction, i.e. carbonation. The calcined product (CaO) has a well-developed porous structure and enhanced surface area, allowing the gaseous CO_2 to permeate into the interior of the particles and react at active CaO sites, according to the exothermic carbonation reaction:

$$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} \tag{2}$$

In CO_2 capture systems carbonation occurs at temperatures of 650–750 °C at atmospheric pressure [10,11]. The carbonation process occurs in two stages – an initial rapid reaction stage and a much slower diffusion-controlled stage. The fast stage is most important for CO_2 capture systems [12,13] and is governed by the gas–solid chemical reaction on the surface of the reacting particles. In this phase the reaction rate is dependent on the surface area of the sorbent particles [14]. As the reaction proceeds, the rate gradually decreases as a consequence of the calcium carbonate formation on the surface. The CO_2 diffusion resistance increases as a result of the greater molar volume of the product $CaCO_3$ ($36.9\ cm^3/g$) compared with CaO ($16.9\ cm^3/g$). This provokes significant changes in the internal structure of the lime particles, such as pore shrinkage and plugging. The transition from fast to slow carbonation is normally quite distinct and appears to be associated with the formation of a given thickness of product layer [12]. The second stage of carbonation is governed by product layer diffusion and can continue for long periods [12,15–18]. With repeated carbonation/calcination, the CO_2 capture ability of the sorbent progressively declines. Various empirical equations have been proposed e.g. [15,17,19] to predict the CO_2 capture of the sorbents over a large number of cycles. Abanades and Alvarez [12] noticed that the cyclic CO_2 capability of the sorbents decreases sharply when strong sintering conditions are applied during calcination. Anthony [13] underlined the need for mild calcination conditions to maintain the high reversibility of the sorbent, whereas Sun et al. [18] attributed the increased failure of calcium carbonate to capture CO_2 to sintering effects during carbonation. In essence, sintering causes the loss of small pores and growth of larger pores, resulting in the reduction of internal surface area. These textural changes provoke deterioration in limestone performance during cycling since carbonation conversion is strongly dependent on the porosity, especially the small pores [20].

In addition to their ability to capture CO_2, limestones have great potential for capturing sulphur dioxide, despite SO_2 concentrations being two orders of magnitude lower than that of CO_2. The desulphurisation of the combustion flue gases is achieved via the following reaction under atmospheric conditions:

$$CaO_{(s)} + SO_{2(g)} + 1/2O_{2(g)} \rightarrow CaSO_{4(s)} \tag{3}$$

Sulphation is irreversible under typical FBC conditions, although it proceeds at a much lower rate than carbonation. However, high total conversions, of even up to 95%, can be achieved over extended reaction times [21].

Sulphation constitutes a complex reaction process, which like carbonation, occurs in two stages [22]. The first stage includes diffusion of gaseous SO_2 and O_2 through the gas mixture to the particle surface, diffusion of these components through the pores to the active sites of the CaO, absorption onto the surface, and finally the above gas–solid chemical reaction, which constitutes the rate-limiting step [7]. As sulphation proceeds, however, the $CaSO_4$ formed leads to pore blockage, due to the higher volume per unit mass occupied by the primary sulphation product ($46\ cm^3/g$) compared to the calcine ($16\ cm^3/g$) [23]. Pore closure mainly occurs on the surface of the particles, obstructing direct contact of the interior calcine [21,22,24–26]. Theoretically, 1 mol of SO_2 should be captured by 1 mol of Ca, but actual utilization of calcium is significantly lower.

As for carbonation, the second stage is much slower and is rate-limited by the diffusion of the reactant gases through the product layer to reach the interior active sites where reaction occurs. Recent studies on the sulphation of Ca-based sorbents [26,27] have reported three different sulphation modes: unreacted core, uniform and network. The mode followed can be recognized by the morphological characteristics of the spent sorbent, and depends on the structure and porosity of the calcine. From Laursen et al. [26], uniformly sulphated particles are characterized by homogeneous sulphation throughout the particle, network particles by highly sulphated peripheries of microparticle clusters and slightly sulphated cores of the microparticle clusters, and unreacted-core particles by highly sulphated layers around the periphery and almost no sulphur in the core. Unreacted-core sulphated particles exhibit lower SO_2 retention than their uniform and network sulphated counterparts, while the $CaSO_4$ layer produced at the particle rim is thicker than for uniformly sulphated particles. Previous research [26] reported that unreacted-core sulphated particles tend to be regenerated when exposed to steam hydration, whereas uniformly sulphated particles show very little regeneration.

In combustion systems where the partial pressure of CO_2 is high enough that $CaCO_3$ does not calcine, the removal of SO_2 can be realized via direct sulphation, i.e. direct reaction of the gaseous SO_2 with calcium carbonate in the presence of O_2:

$$CaCO_{3(s)} + SO_{2(g)} + 1/2O_{2(g)} \rightarrow CaSO_{4(s)} + CO_{2(g)} \tag{4}$$

This direct sulphation reaction leads to higher calcium conversion than the reaction of calcine with SO_2. However, in most cases reaction rates are lower [28]. The increased calcium utilization is attributed to enhanced porosity attained by the outward flow of CO_2 through the product $CaSO_4$, enabling permeation of the reacting gases to $CaCO_3$ active sites. There are contrasting opinions about the effect of pressure on direct sulphation. According to Iisa and Hupa [29], increased pressure favours calcium conversion, which can be enhanced by up to 50% with pressures of ~25 bar. On the other hand, Qiu and Lindqvist [28] report that increased pressure impedes direct sulphation and that conversion of $CaCO_3$ to $CaSO_4$ decreases at pressures between 6 and 13 bar. For a sorbent particle and given that the gas diffusivity is inversely proportional to total pressure, the reduced reaction rate is explained by the diffusion resistance of the ingress gas mixture and of the egress CO_2 product [30].

In fossil fuel combustion, both CO_2 and SO_2 are present in the flue gas. Although SO_2 appears at significantly lower concentrations, calcium-based cycling necessitates carbon and sulphur removal via simultaneous or successive steps. Under simultaneous