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Review

The calcium looping cycle for CO_2 capture from power generation, cement manufacture and hydrogen production

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ABSTRACT

Calcium looping is a CO_2 capture scheme using solid CaO-based sorbents to remove CO_2 from flue gases, e.g., from a power plant, producing a concentrated stream of CO_2 (~95%) suitable for storage. The scheme exploits the reversible gas–solid reaction between CO_2 and CaO(s) to form $CaCO_3$(s). Calcium looping has a number of advantages compared to closer-to-market capture schemes, including: the use of circulating fluidised bed reactors—a mature technology at large scale; sorbent derived from cheap, abundant and environmentally benign limestone and dolomite precursors; and the relatively small efficiency penalty that it imposes on the power/industrial process (i.e., estimated at 6–8 percentage points, compared to 9.5–12.5 from amine-based post-combustion capture). A further advantage is the synergy with cement manufacture, which potentially allows for decarbonisation of both cement manufacture and power production. In addition, a number of advanced applications offer the potential for significant cost reductions in the production of hydrogen from fossil fuels coupled with CO_2 capture. The range of applications of calcium looping are discussed here, including the progress made towards demonstrating this technology as a viable post-combustion capture technology using small-pilot scale rigs, and the early progress towards a 2 MW scale demonstrator.

Keywords: Calcium looping; CCS; CO_2 capture; Power generation; Cement manufacture

Contents

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1. Introduction

Carbon Capture and Storage (CCS) is a range of technologies being developed to help mitigate climate change by isolating from the atmosphere a significant fraction of the CO_2 produced during fuel combustion (e.g., coal, gas and biomass). In the case of coal-fired power stations, the technology could prevent up to ~90% of the CO_2 from being emitted to the atmosphere; greater net emission reduction may be possible if coal is co-fired with biomass by accounting for the CO_2 removed from the atmosphere during the biomass growth. CCS involves capture, purification and compression of the CO_2 ready for transportation to a permanent storage location. This review focuses on CO_2 capture, which is the most costly stage in the CCS process; for information on the topics of transport and storage please refer to Steeneveldt et al. (2006). The CO_2 capture technology closest to market is post-combustion 'scrubbing' using amine-based solvents, which has been used for industrial-scale separation of CO_2 for several decades. However, there are issues associated with amine-scrubbing for CO_2 capture from a combustion flue-gas, including the high cost of manufacturing the solvent (e.g., MEA at ~USD 1250/tonne) (Rao and Rubin, 2002), the high efficiency penalty (~9.5–12.5 percentage points) (Xu et al., 2010), degradation of the solvent due to reactions with O_2 and SO_2 (frequently present in industrial flue gases), and the handling and disposal of large quantities of degradation products/waste solvent (which raises both environmental and health and safety concerns).

Research into a range of alternative CO_2 capture technologies, which aim to address such issues, are being pursued all over the world and one promising technology involves the use of a solid CO_2 sorbent using calcium-based materials, known as 'The Calcium Looping Cycle' or 'Ca-looping'. This process offers a number of advantages, including; the use of well established fluidised bed technology; it is a high-temperature process and so high-grade excess heat can be recovered to provide additional energy to drive a steam cycle, thus reducing the overall efficiency penalty of the process; the materials used to perform the CO_2 capture are widely available and environmentally benign (derived from limestones/dolomites); the affinity of the materials to SO_2 provides simultaneous partial desulphurisation of the industrial flue gas; and, the waste material from the process has potential uses elsewhere in industry, most notably the cement industry. These advantages are discussed in detail herein.

2. Basics of the cycle

An extensive review of the Ca-looping cycle for CO_2 capture has recently been published (Blamey et al., 2010); the main features of which are summarised herein. For further information, see also reviews by Stanmore and Gilot amongst others (Stanmore and Gilot, 2005; Harrison, 2008; Anthony, 2008; Florin and Harris, 2008a; Li and Fan, 2008), and the IEA GHG High Temperatures Solid Looping Cycles Network (IEA, 2010).

The Ca-looping process uses a CaO-based sorbent, typically derived from limestone, reacting via the reversible reaction described in Eq. (1). The forwards step is known as calcination and is an endothermic process which readily goes to completion under a wide range of conditions. The backwards step is known as carbonation:

$$CaCO_{3(s)} = CaO_{(s)} + CO_{2(g)} \quad \Delta H^\circ = +178\,kJ/mol \tag{1}$$

$$CO_{(g)} + H_2O_{(g)} = CO_{2(g)} + H_{2(g)} \quad \Delta H^\circ = -41\,kJ/mol \tag{2}$$

The equilibrium vapour pressure of CO_2 over CaO according to Eq. (1) can be calculated as a function of temperature; partial pressures of CO_2 greater than the equilibrium partial pressure at a given temperature will favour carbonation, while those lower than the equilibrium will favour calcination (see Fig. 1). As a result, if a sorbent is cycled between two vessels at suitable temperatures, carbonation of sorbent can be effected in one and calcination in the other. The objective of CO_2 capture is to obtain a pure stream of CO_2 suitable for storage; one method of achieving this is by separation of CO_2 (3–30% by volume) from an exhaust gas obtained from power stations or industry (i.e., post-combustion CO_2 capture). A typical Ca-looping process for CO_2 capture as proposed by Shimizu et al. (1999) is shown in Fig. 2. In this example, the heat necessary for calcination is provided by oxy-combustion of coal, how-

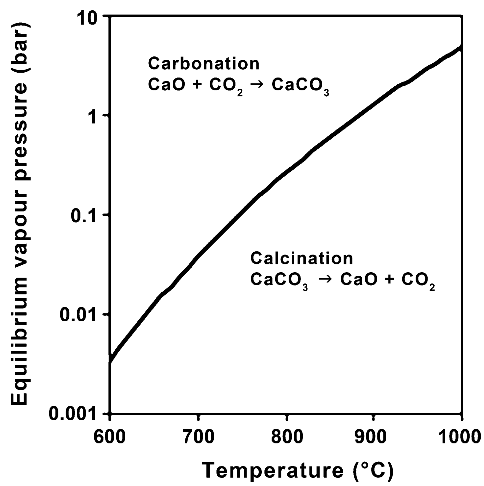

Fig. 1 – Equilibrium vapour pressure of CO_2 over CaO as a function of temperature (McBride et al., 2002).