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ScienceDirect

Energy Procedia 114 (2017) 250 – 258

Energy Procedia

13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland

Kinetics of CO_2 absorption by calcium looping in molten halide salts

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Abstract

Carbon Capture in Molten Salts (CCMS) is a high temperature method for extracting CO_2 from a variety of flue gases related to power generation and carbon-intensive industries. The chemical principles are similar to those in calcium looping in the solid state; a carbonation reaction of CaO with CO_2 to form $CaCO_3$ followed by regeneration of CO_2 through the reverse reaction. In CCMS, the active substances ($CaO/CaCO_3$) are dissolved or partly dissolved in molten salts, allowing fast reaction kinetics, high CO_2 sorption capacities, and avoiding solids attrition issues. In our previous studies, the focus has been on the total CO_2 sorption capacity and demonstration of cyclic absorption and desorption. Experiments have been performed with up to 20 wt% CaO in molten $CaCl_2$ and eutectic $CaF_2/CaCl_2$. It has been demonstrated that up to 85% of the CaO reacts during absorption, and ~100% of the $CaCO_3$ is decomposed during desorption. No degradation of the sorbent has been observed after 12 cycles. In the present study, the focus is turned to the reaction kinetics between CO_2 and CaO. The raw data from previous experiments are analyzed to obtain the sorption capacity (g CO_2 / 100 g sorbent) as a function of time, and the linear region of the capacity is further used to evaluate the reaction kinetics. The effect of absorption temperature, molten salt composition, CaO content and cyclic CO_2 capture is studied. The results show that $CaF_2/CaCl_2$ is more favorable for CCMS than pure $CaCl_2$; the kinetically controlled regime lasts longer and the total sorption capacity is higher. For both of the salt mixtures, the sorption capacities are stable during cyclic CO_2 capture, without any deterioration of the reaction kinetics.

Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: CO_2 capture; kinetics; calcium looping; molten salts

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doi:10.1016/j.egypro.2017.03.1167

1. Introduction

The emissions of greenhouse gases such as CO_2 have increased significantly the last decades. This trend is in pace with growing energy consumption based on fossil fuels, but also with considerably contributions from other carbon-intensive industries such as the manufacture of iron, steel and cement. Because of their established infrastructure for exploitation and distribution, it is likely that CO_2 emitting industries will continue to play dominant roles in the world's economy in the near future. According to the International Energy Agency (IEA), the 2°C scenario cannot be fulfilled without implementation of carbon capture and storage (CCS) [1]. The idea with CCS is to separate CO_2 from waste gases generated by stationary emission sources, followed by compression of the captured gas and transportation to a permanent storage site. The capture step represents the major part of the whole process, both in cost and complexity [2]. Many different capture technologies are pursued. Among these, three approaches are identified with greatest potential for commercial deployment; namely post-combustion CO_2 capture using amine solvents, oxy-fuel combustion, and calcium looping [3]. Calcium looping is an emerging technology that can be used for capturing CO_2 from post-combustion, pre-combustion, or industrial processes [4]. It is based on the reversible reaction between CO_2 and CaO to form $CaCO_3$ [5]:

$$CaO\ (s) + CO_2\ (g) \leftrightarrow CaCO_3\ (s) \qquad (1)$$

The turning point temperature for this reaction is around 900°C (atmospheric pressure), and cyclic absorption and desorption of CO_2 may be performed by a thermal swing [4]. Alternatively, pressure swing can be utilized, but this is less economically attractive due to more restrictions on reactor materials [6]. The CaO sorbent is usually derived from limestone / dolomite, which is an abundant, cheap and environmentally friendly material. Other advantages of the calcium looping technology are relatively low efficiency penalty on the power / industrial process and possible synergy with cement manufacture [4].

The main challenge for calcium looping in the solid state is that the particles' morphology change over time. This particle degradation is caused by physical / structural stresses and sintering, and leads to less reactive surface and a significant decrease in sorbent reactivity after several absorption – desorption cycles [4, 7]. For CaO derived from natural limestone, the residual sorption capacity falls down to approximately 8g CO_2 / 100g sorbent at long term use [8]. The active surface area could be preserved by modifying solid CaO sorbents and thus reduce the rapid decay in reactivity. Manovic and Anthony [9] have reviewed the research on sorbent modification methods for enhancing the sorbent performance over time. The most promising methods were identified as reactivation by steam/water, thermal pretreatment, and addition of supports or incorporation of CaO into inert solid matrices such as aluminate-based cements. The latter technique is very promising because the inert supports are believed to be able to separate CaO particles and prevent or delay them from sintering at high temperatures [10]. Inert materials that have been used for this purpose are for example Al_2O_3, $Ca_{12}Al_{14}O_{33}$, ZrO_2, and $CaTiO_3$. However, due to high preparation cost of the synthesis methods, the application of these materials at large scale is challenging [11].

Another approach is Carbon Capture in Molten Salts (CCMS) [12-14]. In this concept, molten salts are used as chemical solvents of the active substances in calcium looping, with the main idea of hindering particle degradation. A flue gas containing CO_2 enters an absorption chamber (absorber) where CaO is present in a molten salt matrix. $CaCO_3$ is formed through Eq. 1 and dissolves continuously in the melt, leaving highly reactive surfaces of CaO readily available. The molten salt containing $CaCO_3$ is transferred to a desorption chamber (desorber) operated at higher temperature. The reverse reaction takes place (calcination), and the CO_2 is removed from the desorber. This may for example be performed with superheated steam, which may be separated from the CO_2 by condensation at a later stage. The released CO_2 could further be compressed and transported to a storage site. The cycle is completed by transferring the regenerated CaO-rich molten salt back to the absorber. All the active substances are dissolved or in a supersaturated suspension in the molten salt medium which then acts as a solvent as well as a carrier. Variations of the method has shown to be able to absorb CO_2 down to < 100 ppm in the gas emitted in a small scale batch reactor, indicating a potential to capture CO_2 from very diluted gas mixtures [12]. Recent experimental work has shown CO_2 capture with up to 20 wt% CaO - corresponding to a theoretical sorption capacity of 15.7g CO_2 / 100 g sorbent, in the molten salts $CaCl_2$ and $CaF_2/CaCl_2$ [13-15]. In these systems, it has been demonstrated that up to 85%