

# Improving Performance of Regenerable CaO-based CO<sub>2</sub> Absorbent Using Novel Sintering-Resistant Formulations

Liyu Li\*, David L King, Xiangxin Yang, Chris Howard, Jun Liu  
Institute of Interfacial Catalysis, Pacific Northwest National Laboratory  
Richland, WA 99354 (USA)  
\*Liyu.Li@pnl.gov (corresponding author)

## Introduction

It is well accepted that CaO-containing materials are good candidate absorbents for regenerable CO<sub>2</sub> removal from various warm gasification streams due to their high reactivity, high CO<sub>2</sub> capacity, and low material cost. However, in practice, the carbonation and decarbonation reactions of these absorbents are far from complete and reversible. Rapid loss of CO<sub>2</sub> capacity is generally observed as a result of CaO particle sintering during the highly exothermic carbonation process and the high temperature decarbonation process. A thin non-porous carbonate product layer (20-50 nm) is formed on the surface of the sintered absorbent particles that hinders bulk CO<sub>2</sub> absorption. As a result, CaO conversion to CaCO<sub>3</sub> decreases as the number of reaction cycles increases. A specially designed high capacity absorbent that does not sinter and can maintain high surface area during multiple carbonation-decarbonation cycles is desired. In the past years, several systems have been developed which can partially prevent the sintering of metal oxide-based high temperature CO<sub>2</sub> absorbents, including the Li<sub>4</sub>SiO<sub>4</sub> system developed by Nakagawa et al. from Toshiba Corp, Japan [1], the special CaO absorbent obtained from calcination of precipitated calcium carbonate (PCC-CaO) by LS Fan's group from Ohio State University, USA [2], and the Al<sub>2</sub>O<sub>3</sub>-stabilized CaO system reported by NS Cai's group from Tsinghua University, China [3]. Among these systems, the CaO-Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (3:1 mass) absorbent developed by Cai et al. gives the best long term performance (~40 wt% after 50 cycles).

## Materials and Methods

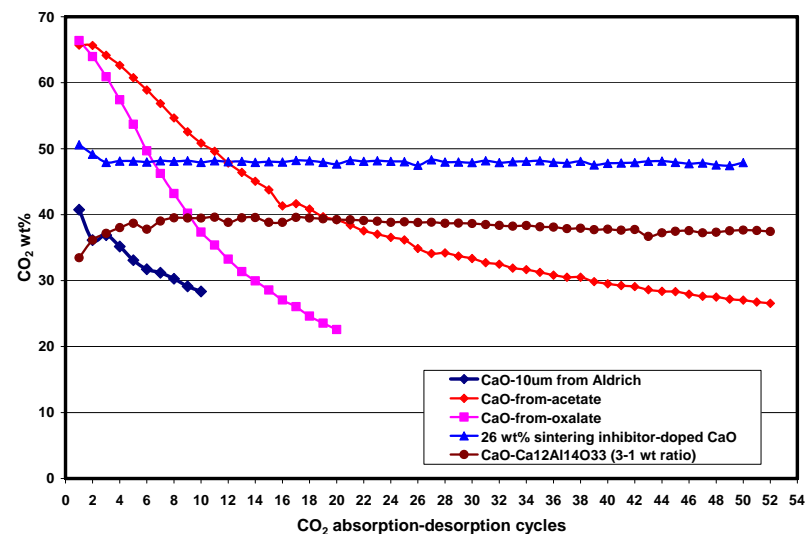
Sintering inhibitors were physically mixed with commercial CaO sources followed by calcination. The carbonation-decarbonation tests were first carried out by TGA-DSC at 758°C using 100% CO<sub>2</sub> (for carbonation), and pure He (for decarbonation). Absorption and desorption cycles alternated by actuating an automated switch valve every 30 minutes. Promising absorbents were further evaluated in a high pressure fixed bed reactor using a simulated pre-combustion coal gas stream.

Fresh and used absorbents were characterized using Powder X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission electron microscopy (TEM). Selected area energy dispersive X-ray spectroscopy (EDS) was performed on regions of interest using the EDS systems equipped on the microscopes. The nitrogen BET surface area was measured with degassed samples. Thermogravimetric analysis (TGA) was carried out in a Netzsch STA 409 system.

## Results and Discussion

We have found that the well-established sintering effect with CaO-based materials can be effectively prevented by doping with a modest amount of sintering inhibitors. With 26

wt% doping, a CaO-based absorbent gave almost constant 50 wt% CO<sub>2</sub> capacity for 50 carbonation-decarbonation cycles at 758°C. Without doping, the CO<sub>2</sub> capacity of best pure CaO absorbent decreased from 66 wt% for 1<sup>st</sup> cycle to 26 wt% for 50<sup>th</sup> cycle under the same test conditions. Also, pure CaO particles always agglomerated after carbonation-decarbonation cycling, whereas sintering inhibitor-doped CaO particles remained well dispersed. Figure 1 compares the performances of a 26wt% inhibitor-doped CaO absorbent, a CaO-Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> absorbent (synthesized according to Reference [3]), and two pure CaO absorbents. More results will be discussed.



**Figure 1.** CO<sub>2</sub> absorption-desorption performances of different CaO-based absorbents at 758°C. Operation consists of alternating steps of CO<sub>2</sub> absorption (from a pure CO<sub>2</sub> stream) and CO<sub>2</sub> desorption (into a pure He stream), consistent with a pressure swing process.

## Significance

Advantages of this absorbent include high regenerable CO<sub>2</sub> capacity, fast CO<sub>2</sub> absorption and desorption kinetics, and stable physical properties during long term high temperature operation. This material can be used for both pre-combustion and post-combustion CO<sub>2</sub> capture to reduce green house gas emission. It can also be used for CO<sub>2</sub> absorption-enhanced reforming for H<sub>2</sub> production from coal, biomass or natural gas.

## References

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