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Research group 03 CATHPRO

Attendance

May 30

May 31

Both days

Performance of CaO-based sorbents for Calcium-Looping CO₂ capture: waste resources, natural and synthetic materials

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Abstract:

Calcium-Looping Cycle (CaL) is one of the most promising processes for CO₂ capture based on the reversible chemical reaction between CaO-based sorbents and CO₂ to form CaCO₃. Comparatively with other technologies, the sorbent can be easily regenerated and additionally the initial CO₂ capture efficiency is especially high during the initial carbonation - calcination cycles. During the calcination step, CO₂ is selectively released from CaCO₃, and if this step is carried out under a higher CO₂ partial pressure, a pure stream of CO₂ can be generated suitable for storage or for conversion processes (e.g. fuel, chemicals).

The main drawback of this technology is the sorbents deactivation due to the sintering and pores blockage throughout the cycles, especially if natural limestone is used. To overcome this limitation, the replacement of limestone by waste materials like marble¹ powder (WMP) or natural dolomite as source of CaO and the addition of industrial wastes like coal fly ash (CFA) or spent fluidized catalytic cracking catalyst (SFCC) for hindering CaO particles sintering, are promising options. Additionally, the possible utilization of these exhausted sorbents as raw matter for the clinker production in cement industry can lead to development of eco-cements. Tailoring synthetic sol-gel CaO sorbents² with high reactivity and stability for CaL CO₂ capture is also an interesting option. However, the main advantage of CaL is the availability and use of inexpensive CaO-based sorbents, so for practical and industrial scalable applications, a compromise should be made between improving the sorbent performance and the cost, which means that the development of inexpensive and low energy intensive methods need to be a priority.

Innovative results obtained¹ show that WMP have potential to be an economically attractive option to be used as cheap CaO-based sorbents for CaL CO₂ capture, thus contributing to reduce the cost of the CaL process, as well as minimizing the adverse environmental impacts of the high volume of WMP generated in the marble producers.

The performance of sorbent samples of natural limestone, dolomite and WMP, was assessed in a laboratory scale fixed-bed quartz reactor unit along 20 carbonation-calcination cycles, using gas mixtures with a CO₂ concentration within the range of the industrial flue gas emissions (15-25% of CO₂). The CaO conversion obtained after 20 cycles was 28 %, 40 % and 78 % for limestone, WMP and dolomite, respectively. The MgO present in dolomite is inert at the Ca-looping temperatures (carbonation: 700 °C and calcination: 800 or 930 °C) and its blend with WMP (20% MgO) also allowed improving the WMP performance along 20 cycles.

The sintering resistance of a natural limestone and a commercial CaCO₃ can be improved by physically dry mixing with CFA and SFCC catalyst wastes that may act as CaO particles spacers. For both sorbents, the addition of 10 % of CFA and SFCC reduces the sorbents deactivation rate, but the more significant improvement on the carbonation conversion can be observed for the commercial CaCO₃.

Both wastes can be used as interesting options to improve the CO₂ capture technology efficiency, and their use will additionally allow reducing the landfill of industrial wastes and fulfil the circular economy concept by their introduction on the clinker production.

In the case of synthetic CaO, the influence of sol-gel synthesis calcination temperature (750 and 850 °C) and the amount of granular activated carbon (AC) introduced during the sol-gel synthesis of CaO sorbents (250 or 500 mg AC/2 g wet sol-gel) were evaluated. A higher initial CO₂ uptake was achieved for the sol-gel sorbents calcined at 750 °C than that for those calcined at 850 °C. For the calcination temperature of 750 °C the AC addition does not significantly influence the sorbent reactivity after 20 cycles, but at 850 °C, both the reactivity and stability strongly depend on the amount of AC incorporated during the sol-gel synthesis. For the 250 mg AC/2g wet sol-gel sorbent calcined at 850 °C, an opposite evolution of the profiles of the CaO conversion is observed for the first 6 cycles reaching a stabilized plateau of CaO conversion near 72% after 20 cycles². The textural and morphological changes along the cycles of all the sorbents were evaluated by N₂ sorption, scanning electron microscopy, Hg porosimetry and X-ray diffraction techniques.

Keywords: CaO-based sorbents, CO₂ capture, Calcium-Looping process

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References:

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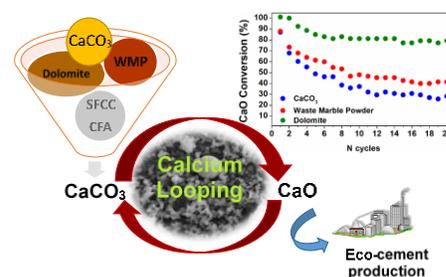


Fig. 1. CO₂ capture by Ca-looping cycles