

# Screening of the potential reuse of air pollution control residues from different industries as alternative CO<sub>2</sub> sorbents in the calcium looping process

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## Highlights

- Air pollution control (APC) residues are tested as CO<sub>2</sub> sorbents in the calcium looping process.
- The CO<sub>2</sub> uptake is determined by the Ca content and decreases with cycles due to sintering.
- Cl-, F-, and S-containing species influence the diffusion-controlled phase of the reaction.
- The CaL process using APC residues instead of limestone is preliminary modelled.

## 1. Introduction

The removal of acid pollutants (HCl, SO<sub>2</sub>, HF) represents a pivotal stage in the flue gas cleaning of several industrial processes. If conducted via dry sorbent injection, e.g., using powdered calcium hydroxide (Ca(OH)<sub>2</sub>), acid gas removal generates a stream of solid air pollution control (APC) residues, whose typical destination is currently landfilling, with a clear penalty for the overall sustainability of the flue gas cleaning operation. However, APC residues still contain a significant weight fraction of unreacted calcium, which could be exploited for its binding capacity towards carbon dioxide (CO<sub>2</sub>). Recent studies [1,2] proposed CO<sub>2</sub> mineralization as a valorization route for these residues. Here, we propose the direct use of these residues in CO<sub>2</sub> capture from flue gas with the calcium looping (CaL) approach, based on the reversible carbonation of calcium oxide (see Fig. 1a). Differently from CO<sub>2</sub> mineralization, in the CaL scheme residues are exposed to repeated carbonation/calcination cycles [3]. The present study explores the cyclic CO<sub>2</sub> uptake potential of APC residues from the flue gas cleaning of two relevant industrial sectors (waste-to-energy and ceramic industry). The objective is to quantify the CO<sub>2</sub> sorption performance of representative APC residues and to analyze how the gas-solid carbonation process is affected by the chemical nature of the residues.

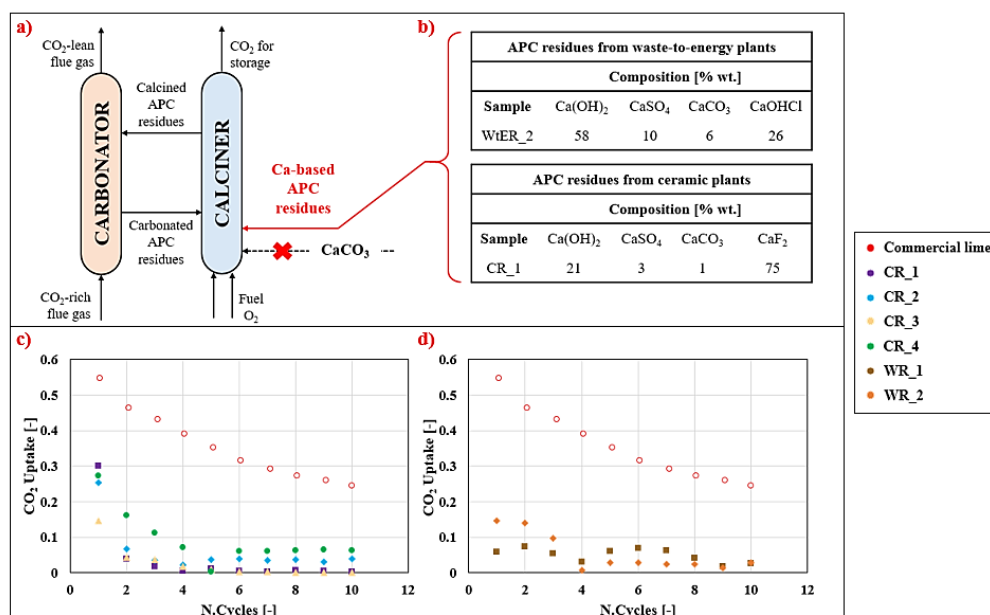
## 2. Methods

X-ray diffractometry (XRD), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA) were used to characterize a set of APC residues obtained from different industrial plants, determining the variability of composition in terms of available Ca for carbonation and Cl-, S- and F-containing species from flue gas cleaning (see Fig. 1b). TGA was used to quantify the cyclic CO<sub>2</sub> uptake performance of the samples.

## 3. Results and discussion

Fig. 1c and 1d report the CO<sub>2</sub> uptake capacity of APC residues from ceramic plants (CR) and WtE plants (WR), respectively. Although inferior compared to that of reference commercial lime, a non-negligible uptake potential of at least 0.05 g CO<sub>2</sub>/g sorbent can be still observed after 10 cycles. Samples with the highest CaO content exhibit the highest CO<sub>2</sub> uptake performance. Notably, the highest performance is concentrated in the first cycles, followed by a decrease and a stabilization. CR residues generally exhibit a monotonic decline in performance, while WR samples present a more complex behavior. An analysis of the kinetics of CO<sub>2</sub> sorption over time during cycles clarifies that the reaction involves a first kinetically-controlled phase, followed by a diffusion-controlled phase. While for CR samples CO<sub>2</sub> sorption in both phases decreases upon cycling, mainly because of the sintering of the solid induced by the high calcination temperature (> 900 °C), as shown by SEM, for WR samples CO<sub>2</sub> uptake in the diffusion-controlled phase does not exhibit a steep decline. This phenomenon may be ascribed to the different chemical compositions of the samples, and in particular to the presence of a chlorinated phase

in WR residues that might melt at the carbonation temperature (700 °C) promoting product layer diffusivity in the gas-solid reaction. The CO<sub>2</sub> uptake estimates obtained from the experimental campaign were used to set up a preliminary mass and energy balance considering the substitution of limestone with APC residues in a CaL scheme, demonstrating that the reduction in the specific CO<sub>2</sub> sorption capacity of residues compared to limestone can be offset by the economic advantage of guaranteeing a cascade reuse of such waste streams.



**Figure 1.** (a) Schematic representation of the CaL process with Ca-based APC residues as an alternative feedstock to limestone; (b) comparative analysis of a WtE and a ceramic sample composition expressed in weight percentage; (c) comprehensive CO<sub>2</sub> uptake of ceramic samples over a series of 10 cycles; (d) comprehensive CO<sub>2</sub> uptake of WtE samples over a series of 10 cycles.

## 4. Conclusions

The present study investigated the potential of APC residues as CO<sub>2</sub> sorbents for the CaL process. For the first time residues from different flue gas cleaning processes were analyzed and differences in their behavior were linked to differences in their chemical composition, pointing out the importance of the specific origin of APC residues in determining their suitability as CO<sub>2</sub> sorbents. The carbonation potential is associated with the CaO content in the residues. F- and S-containing species in the residues have only detrimental effects on CO<sub>2</sub> capture, while the presence of Cl-containing species might favor product layer diffusivity.

APC residues constitute a feedstock for the CaL process that comes at zero or even negative cost. Considering the CO<sub>2</sub> uptake potential shown in this study, their use as a partial substitution of limestone feed in a CaL scheme allows the cascade valorization of a waste stream without penalizing the economics of the process.

## References

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## Keywords

Flue gas cleaning; calcium looping; carbonation; thermogravimetric analysis.