

Calcium looping with air pollution control residues from municipal solid waste incinerators: a preliminary screening

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Abstract

Acid gases such as HCl and SO₂ are typical pollutants generated by waste combustion and their removal by means of dry neutralization processes generates so-called air pollution control (APC) residues, whose fate is to be sent to disposal, in absence of commercially viable valorization routes. When the reactant used in dry neutralization is slaked lime, the residues contain fly ash, unreacted calcium hydroxide and the products of its reaction with HCl and SO₂. Given the high Ca content of APC residues, the present study explored the possibility to use these waste materials as CO₂ sorbents in the calcium looping process. Samples collected in three waste-to-energy plants were tested in a thermogravimetric analyzer over multiple carbonation/calcination cycles, comparing their performance to that of virgin slaked lime. The CO₂ carrying capacity of residues resulted inferior to that of virgin lime, since the amount of calcium available for carbonation in the residues is lower than in the fresh material, but in terms of CaO conversion the carbonation performance over 20 cycles was comparable. Furthermore, the evolution of CO₂ uptake upon cycling showed a peculiar trend, with a temporary increase of performance occurring during cycling. This phenomenon was attributed to the possible role of the chlorinated phase in the residues in promoting CO₂ sorption during the diffusion-controlled stage of reaction. The findings of this preliminary screening provide a useful basis for the planning of further investigations on the suitability of APC residues for calcium looping applications.

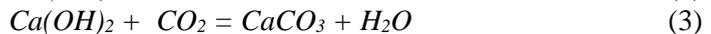
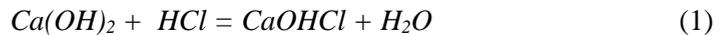
Introduction

CO₂ capture and storage is a technological option aimed at mitigating the emissions of carbon dioxide from large-scale sources, such as thermoelectric power stations, cement manufacturing sites and steelmaking plants. An emerging approach for CO₂ capture is the so-called calcium looping, CaL [1], based on the reversible reaction between calcium oxide (CaO) and carbon dioxide to form calcium carbonate (CaCO₃). The regenerable CaO is provided by natural materials, such as limestone

or dolomite. In the CaL process, the sorbent adsorbs CO₂ from a flue gas stream in a carbonator vessel operated at 650-700 °C and releases it in a calciner vessel operated at 950 °C, thus generating a CO₂-rich gas stream suitable for geological storage. Various bench scale and pilot scale investigation campaigns have already demonstrated the feasibility of the process [2].

In order to reduce the consumption of natural resources, several investigators have recently proposed the use of Ca-rich waste materials (*e.g.* lime mud [3] or carbide slag [4]) as feedstock for the process.

Air pollution control residues from dry acid gas removal are a class of waste materials containing a relevant calcium fraction. They are generated as solid products of the neutralization of acid gases (HCl, SO₂), characteristic pollutants emitted by waste incineration, by means of the injection of a powdered reactant such as slaked lime, Ca(OH)₂:



According to reactions 1-3, the residues, referenced in the following as calcium-based waste (CBW), contain CaOHCl and CaSO₃ derived from the abatement of acid gases, and CaCO₃ derived from the undesired reaction with the CO₂ present in the flue gas. In addition, a relevant fraction of the residues is still formed by unreacted Ca(OH)₂, because at the typical operating temperatures of dry acid gas removal (150-180 °C) the complete conversion of the reactant is hindered by diffusional limitations [5].

After the acid gas removal stage, CBWs are typically separated from the flue gas in the same fabric filter where also the fly ash generated by waste combustion are captured. Therefore, CBWs are mixed together with an ash fraction containing harmful micro-pollutants (*e.g.* heavy metals) and, as such, are generally classified as hazardous waste throughout Europe. To date, no commercial valorization option is available. “Once-through” gas-solid carbonation has been proposed as a stabilization method to reduce the leaching potential of CBWs [6]. Here, it is proposed to expose the CBWs to repeated carbonation/calcination cycles in order to valorize the residual sorption capacity of the residues in a CaL scheme. The results of a preliminary investigation of the CO₂ uptake potential of CBWs in TGA are presented.

Experimental section

CBW samples generated by the dry sorbent injection of slaked lime were collected at three Italian waste-to-energy plants. A sample of the commercial slaked lime before injection (provided by the same supplier to the three plants) was collected and used as reference of the virgin material before reaction with acid gases.

The elemental composition of the samples was determined according to the UNI

EN ISO 11885:2009 protocol, while scanning electron microscope (SEM) imaging was employed to visualize their morphology. Thermogravimetric runs, carried out in a TGA-Q500 (TA Instruments), were used to gather quantitative information on the relative abundance of $\text{Ca}(\text{OH})_2$, CaCO_3 and CaOHCl in the CBW samples, thanks to the different decomposition temperature of the compounds.

The carbonation performance of the CBW samples was also tested in TGA, following the subsequent thermal program: i) pre-calcination in N_2 by heating the sample up to $800\text{ }^\circ\text{C}$ at a rate of $50\text{ }^\circ\text{C}/\text{min}$; ii) 20 min carbonation in 60 vol.% CO_2 , after cooling the sample to $700\text{ }^\circ\text{C}$ at a rate of $50\text{ }^\circ\text{C}/\text{min}$; iii) 10 min regeneration of the sample via calcination in N_2 after heating the sample to $900\text{ }^\circ\text{C}$ at a rate of $50\text{ }^\circ\text{C}/\text{min}$. Steps ii) and iii) were repeated 20 times in order to test the cyclic performance of samples. A platinum pan and an amount of sample of $\sim 20\text{ mg}$ were used in the experiments.

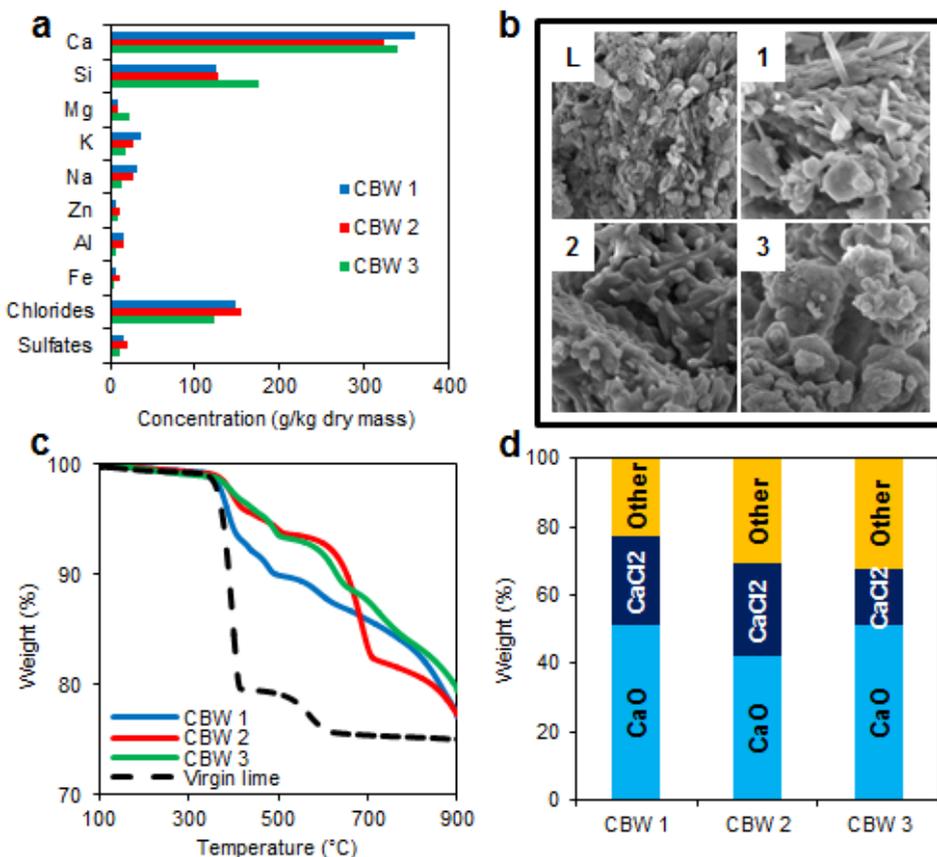


Figure 1. Characterization of the CBW samples. a) concentration of the main components in the “as received” samples; b) SEM micrographs of the virgin lime (L) and the three CBW samples; c) thermal decomposition of the samples; d) composition of the CBW samples after pre-calcination at $800\text{ }^\circ\text{C}$.

Results and discussion

The CBW samples analyzed in the study were characterized as summarized in Figure 1. Regarding their elemental composition (Fig. 1a), calcium is unsurprisingly the most abundant element in CBWs, but a variety of other elements, which are the major components of the fly ash fraction, are present. Chlorides and sulfates derive from the capture of HCl and SO₂. Chlorides are an order of magnitude more abundant than sulfates, as a consequence of the higher concentration of HCl in the flue gas of waste incinerators. The SEM images in Fig. 1b illustrate the morphology of the samples. The flat and roughly hexagonal nanograins of Ca(OH)₂ which populate the micrograph of the commercial virgin lime are visible also in the CBW samples, confirming the presence of unreacted Ca(OH)₂, although mixed with carbonate layers and laminar crystals of the chlorinated phase. TGA was employed to quantitatively investigate the composition of samples (Fig. 1c), since the main compounds in the CBWs decompose at different temperature ranges [7]:



Considering the occurrence of reactions 4-6 during heating, the composition of the calcined samples was estimated as shown in Fig. 1d, where the fraction labelled “other” includes the fly ash fraction and the sulfated phase.

Only the CaO fraction was assumed to take part in carbonation. Hence, the carbonation performance of the calcined CBW samples, exposed to repeated carbonation/calcination cycles, was expressed in terms of conversion of the CaO fraction (Fig. 2a). The absolute CO₂ uptake in terms of g of adsorbed CO₂ per g of sample is reported for selected cycles in Fig. 2b.

While, as expected, the CO₂ carrying capacity of the virgin lime declines monotonically upon cycling, the CBW samples exhibit a more complex evolution of CO₂ uptake over cycles. Although their uptake in absolute terms remains always lower than the virgin material (see Fig. 2b), the CBWs show an abrupt decline of CO₂ capture in the first 3 cycles and then a recovery of performance, which results in a conversion of CaO higher than that of the virgin lime. This happens with different intensities and lasts for a different number of cycles for the three samples: the upward trend of CO₂ uptake is in cycles 8-12 for CBW 1, 5-6 and 10-19 for CBW 2, and 4-6 for CBW 3. After this phase is finished, the CO₂ carrying capacity of the samples undergoes an eventual steady decay of performance comparable to that of virgin lime.

An insight on the characteristic behavior of the Ca-based residues can be obtained by comparing how the kinetics of CO₂ uptake changes upon cycling for sample CBW 1 and for the virgin lime (Fig. 3). For both sorbents, carbonation occurs according to two well-distinguished reaction stages: i) a fast regime controlled by

the chemical reaction rate in the first minute of reaction, followed by ii) a slow regime in which sorbent conversion is hindered by diffusional limitations. For the virgin lime (Fig. 3a), the CO₂ capture taking place in both the fast and slow stages of reaction progressively decreases with cycle number. Conversely, for CBW 1 (Fig. 3b), while the CO₂ uptake during the fast kinetically-controlled stage steadily declines upon cycling, the uptake during the following slow diffusion-controlled phase first increases (compare curves at cycle 5 and 10) and then decreases (compare curves at cycle 10 and 15) with cycle number. This produces the complex evolution of CaO conversion upon cycling presented in Figure 2. The increased performance during the diffusion-controlled stage of carbonation might be ascribed to the presence of the CaCl₂ phase, in agreement with experimental evidence pointing out the effect of doping with chloride salts in enhancing the reactivity of limestone during the slow reaction stage [8].

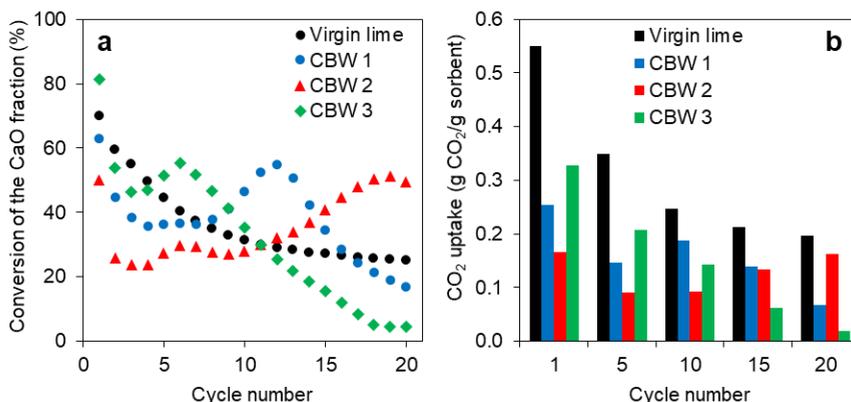


Figure 2. a) Conversion of available CaO over 20 cycles and b) CO₂ uptake at selected cycles for the three calcined CBW samples, compared to virgin lime.

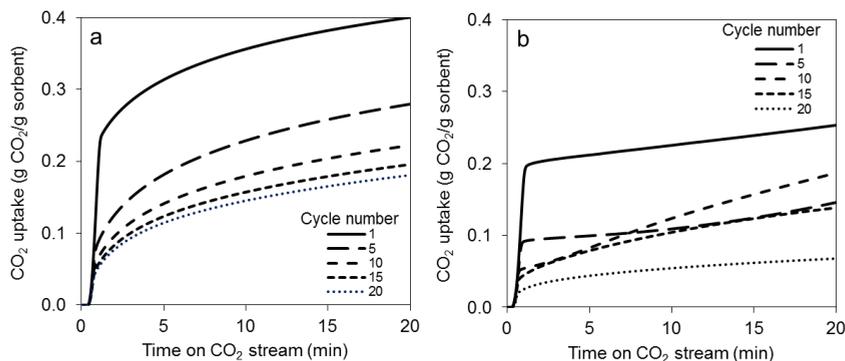


Figure 3. CO₂ uptake curve during different cycles for: a) virgin lime, b) CBW 1. Partially adapted from [9].

This preliminary analysis evidenced the potential of Ca-based APC residues as CO₂ sorbents for CaL applications. The relevant Ca content of the residues can be carbonated to a significant extent, achieving an appreciable CO₂ uptake, although expectedly lower than that of the virgin material. Nonetheless, an important share of CO₂ uptake (*e.g.* ranging from 21% in cycle 1 to 74% in cycle 10 for sample CBW 1, Fig. 3b) takes place during the diffusion-controlled stage and, as such, could not be completely exploited in the short residence times of typical CaL fluidized bed operation. Further tests, aimed at assessing the behavior of residues in harsher calcination conditions, closer to those of the industrial application, and at evaluating the resistance of residues to attrition, could contribute to give a complete picture of the suitability of CBWs for the CaL process.

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