



# Hydration-induced reactivation of spent sorbents for fluidized bed calcium looping (double looping)

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## ABSTRACT

The aim of this work was to study the hydration-induced reactivation of spent sorbents from a calcium looping process. The changes of the sorbent properties induced by hydration, the regeneration of the CO<sub>2</sub> capture capacity and the attrition tendency of the material once reused in the looping cycle were investigated. To this end, a reference limestone was subjected to multiple calcination/carbonation cycles in a lab-scale fluidized bed reactor and then reactivated by water hydration at room temperature for different times. Results suggested that the sorbent under investigation should be hydrated for times as short as possible compatible with complete chemical hydration. In fact, long hydration times bring about crumpling (chemical sintering) phenomena, lower enhancement in the active porosity, increased attrition tendency and reduced reactivation. Attrition/fragmentation data referring to as-received and reactivated sorbents were compared. Relationships among CO<sub>2</sub> capture capacity, surface properties and attrition tendency were presented and critically discussed, taking into account also the results obtained for a different sorbent.

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## 1. Introduction

Global warming due to anthropogenic CO<sub>2</sub> emissions is stimulating the development of novel combustion and gasification technologies ready for carbon capture and sequestration [1–6]. The calcium looping (CaL) cycle, illustrated in Fig. 1 (top), is based on the alternated temperature-swing uptake (in a Fluidized Bed –FB–carbonator) and release (in a FB calciner) of carbon dioxide from a calcium-based sorbent (e.g., limestone). This technology has reached the maturity of the demonstration stage. Reviews on this topic can be found in the literature [7–9]. In the carbonator, CO<sub>2</sub> entering with the flue gas is captured by CaO at around 650–700 °C following an exothermic reaction [10,11]. Thus, the carbonator emits a CO<sub>2</sub>-depleted flue gas and a stream of spent sorbent (a mixture of CaO and CaCO<sub>3</sub>, since carbonation is far from being complete) that is eventually fed to the calciner for the endothermic regeneration at around 900–950 °C. The calciner is typically operated as a combustor where an auxiliary fuel is oxyfired. Accordingly, the calciner yields a CO<sub>2</sub>-rich flue gas (ready for further processing and storage) and regenerates the CaO-based sorbent. Part of the CO<sub>2</sub>-rich stream is recycled.

It is well established that the sorbent CO<sub>2</sub> capture capacity and rate are progressively decreased by deactivation phenomena occurring over iterated looping. Deactivation is mainly due to sintering related to the particle thermal history [12–16]. Another issue is the competition

between sorbent reactions with CO<sub>2</sub> and SO<sub>2</sub> in the flue gas [17–22]. The latter may be present in the calciner if it is fired with a sulfur-bearing auxiliary fuel. It is well known that CaO-based sorbents quickly react with SO<sub>2</sub>, most often according to a core–shell conversion pattern [23–25]. Sulfation brings about a permanent loss of Ca otherwise available for CO<sub>2</sub> capture.

Limestone-based sorbents undergo attrition/fragmentation phenomena during FB processing. These phenomena result in the change of the particle size distribution of the sorbent which, in turn, affects the residence time distribution in the reactor thus leading to a net calcium loss from the circulating loop as elutriable fines. Sorbent attrition, which has been extensively characterized with reference to *in-situ* FB desulfurization [26–29], is relevant also in the context of CaL [10,20–22,30–35].

Optimal management of the CaL cycle [36] implies a continuous make-up of fresh limestone, to compensate for deactivation and attrition, and a purge of spent sorbent. Landfilling of spent limestone is problematic due to the CaO-rich composition of this residue [37–41]. The potential of spent sorbent from CaL as source of raw material in the cement manufacture is under scrutiny [42,43]. An attractive alternative (from both environmental and economic points of view) is the regeneration of the CO<sub>2</sub> uptake capacity by hydration-induced reactivation of the spent sorbent [44–57]. This process, extensively studied in the past with reference to spent sorbents derived from flue gas *in-situ* desulfurization [58–62], is based on the CaO conversion to Ca(OH)<sub>2</sub>, that gives rise to an increase in the molar volume from 16.9 cm<sup>3</sup> mol<sup>-1</sup> (CaO) to 33.7 cm<sup>3</sup> mol<sup>-1</sup> (Ca(OH)<sub>2</sub>) and to a density decrease from 3.32 g cm<sup>-3</sup> (CaO) to 2.20 g cm<sup>-3</sup> (Ca(OH)<sub>2</sub>). Swelling of CaO due to

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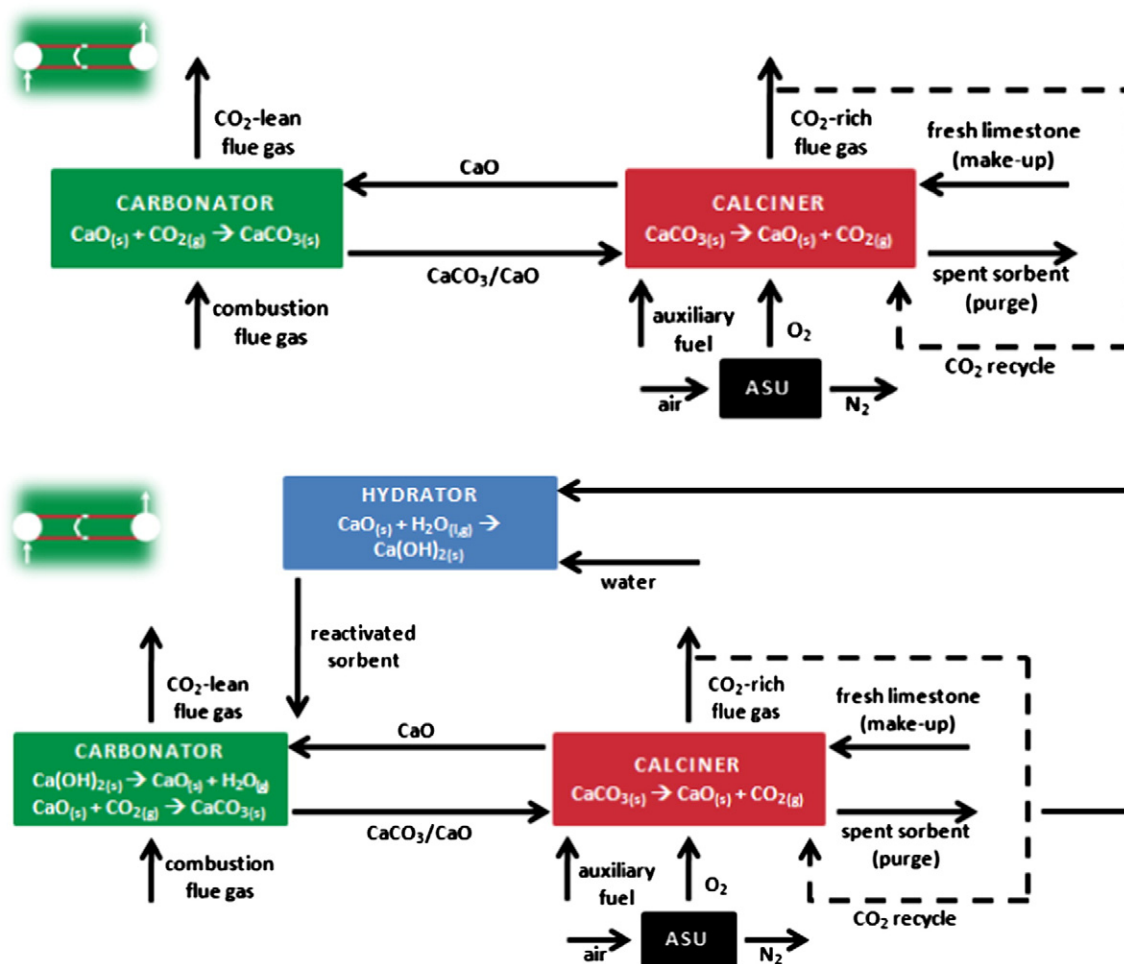


Fig. 1. The calcium looping process (top) and the double looping process for sorbent reactivation (bottom).

hydration is followed by dehydration of  $\text{Ca}(\text{OH})_2$  as the reactivated material is re-injected into the FB reactor. The resulting material is essentially again CaO, characterized by large specific surface area and porosity, hence more reactive toward acid gases ( $\text{CO}_2/\text{SO}_2$ ) than the parent CaO-based spent material. This *double looping* process is outlined in Fig. 1 (bottom). Typically, spent sorbent retrieved from the calciner, hence CaO-rich, is hydrated (without the limiting effect related to the significant presence of a hard  $\text{CaCO}_3$  shell). Eventually the hydrated sorbent is re-injected in the carbonator with a twofold benefit: *i*) the  $\text{Ca}(\text{OH})_2$  endothermic dehydration reaction occurs in parallel with the exothermic carbonation; and *ii*) feeding to the carbonator prevents excessive sorbent attrition upon fast dehydration, and early sintering (which would be promoted by the high temperature in the calciner). Furthermore, the steam released during dehydration could have positive effects on the concurrent, if any,  $\text{SO}_2$  capture from the flue gas in the carbonator. Hydration, however, might bring about enhanced attrition propensity of the reactivated material through the formation of cracks [63], even if only few results have been reported on this topic to date [8,64].

Hydration-induced reactivation of spent sorbents from CaL processes is a largely unexplored research topic that deserves investigation. In fact, though several papers have been recently published in the literature, results obtained by hydrating spent material generated in FB and by submitting the hydrated material to FB looping cycles are limited. Key issues are the changes in the sorbent physico-chemical properties induced by hydration, the reactivation of the  $\text{CO}_2$  capture capacity, and the influence of the sorbent hydration on the attrition tendency of the material once reused in the looping cycle. These issues have been

investigated in the present study with reference to an Italian limestone candidate for application in CaL.

## 2. Experimental methods and procedures

### 2.1. Looping cycles before hydration-induced reactivation

The raw sorbent used in the tests was an Italian high-calcium limestone (Massicci). The test rig was a bubbling FB lab-scale reactor made of stainless steel, 40 mm ID. The reactor, operated at atmospheric pressure, was electrically heated and equipped with purposely designed filters that enabled time-resolved collection of elutriated fines at the exhaust. Details on the sorbent properties and the reactor are reported elsewhere [20,21,35]. A cyclic sequence of five calcination/four carbonation stages was performed, starting with the raw sorbent (20 g sieved in the size range 0.4–0.6 mm). Each calcination step was carried out at 940 °C for 20 min fluidizing the reactor at  $0.7 \text{ m s}^{-1}$  with a gas containing 70%  $\text{CO}_2$  (balance air). The bed was fluidized with a gas mixture containing 70%  $\text{CO}_2$  to simulate calcination in an oxy-firing environment. Preliminary tests showed that at 70%  $\text{CO}_2$  a bed temperature of at least 940 °C was needed for calcination to proceed at a reasonable rate [21]. Each carbonation step was carried out at 650 °C for 15 min fluidizing the reactor at  $0.6 \text{ m s}^{-1}$  with a gas containing 15%  $\text{CO}_2$  (balance air). Both calcination and carbonation stages lasted until practical completion (calcination lasted 20 min and carbonation lasted 15 min). The  $\text{CO}_2$  concentrations in the fluidizing gases were set at values corresponding to realistic operating conditions. The reactor, loaded with a bed of sand (150 g, 0.85–1 mm), was pre-heated to 940 °C prior to

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