An assessment of water and steam reactivation of a fluidized bed spent sorbent for enhanced SO$_2$ capture

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Abstract

Hydration-induced reactivation of spent sorbents from fluidized bed combustion has long been proven as an attractive method to achieve better sorbent exploitation so as to positively affect waste disposal, consumption of natural resources and CO$_2$ emission issues. The present study addresses the reactivation of the sulphur capture ability of fluidized bed (FB) spent sorbent particles by either water or steam hydration. Sorbent particles are subjected to different treatments including calcination, sulphation, hydration by either water or steam, dehydration and resulphation. Processing of sorbents is accomplished by the combined use of a bench scale (40 mm ID) fluidized bed reactor (calcination, sulphation, steam hydration, dehydration and resulphation) and of a thermostated water hydrator (water hydration). Reactivation of the limestone-based sorbent is characterized in terms of hydration degree and extent/pattern of particle sulphation with a further focus on the analysis of the reactivation-induced modifications of particle microstructural/chemical properties and propensity to undergo attrition and elutriation. The effectiveness of the two processes is analyzed, with consideration on the influence of process parameters on the ultimate degree of sorbent utilization. The feasibility of sorbent reactivation is discussed in the light of the effectiveness of sorbent reactivation and of the likely operational issues associated with either process.
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1. Introduction

One of the main advantages of fluidized bed (FB) combustion resides in the possibility of accomplishing *in situ* removal of SO$_2$ by the injection of CaCO$_3$-based (e.g., limestone) sorbents, which display peak sulphur capture efficiencies just around the typical range of FB combustion temperatures (800–900 °C) [1,2].

Under oxidizing conditions and at atmospheric pressure limestone-based sorbents are first calcined to yield porous CaO, which is able to remove SO$_2$ upon sulphation giving compact CaSO$_4$. Sorbent sulphation often proceeds according to a "core-shell" pattern [3–6]: the reaction front in the sorbent particle divides the porous unreacted CaO inner core from the dense reacted CaSO$_4$-rich outer shell. Extensive sulphation of the core is prevented by the onset of a strong diffusional resistance to SO$_2$ migration across the CaSO$_4$-rich outer layer. Thus, the degrees of

Ca conversion seldom exceed 30–40%. Alternatively, and depending on the sorbent particle size and nature, sulphation may proceed according to "network" or "uniform" conversion patterns. The performance of Ca-based sorbents for *in situ* desulphurization is also largely influenced by the occurrence of particle comminution which can significantly affect the particle size distribution and enhance fines elutriation [7–9].

The present work addresses the reactivation of the sulphur capture ability of the spent sorbent particles by both water [10–13] and steam [14–18] hydration. Hydration by either water or steam is currently considered as a viable technique for sorbent reactivation, and implies the conversion of the unreacted CaO into Ca(OH)$_2$. This process leads to the swelling of the particle core that in turn induces the break-up of the CaSO$_4$-rich outer layer. When the hydrated sorbent is re-injected into the combustor, it loses its chemically bound water, which results into further shell breakage, and the newly formed CaO, characterized by a larger specific surface area and better accessibility to gaseous reactants, becomes available for further sulphation. The hydration-reactivation

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method is attractive since it enhances the SO_2 uptake of the sorbents, reduces the waste disposal costs and the consumption of natural resources, limits the CO_2 emissions associated with calcination of fresh sorbent.

The present paper reports results of a study on reactivation of an Italian limestone by either water or steam. The influence of the parameters of the hydration process on hydration degree, extent and pattern of particle sulphation, microstructural properties of the sorbent was investigated. The effectiveness of the regeneration processes was assessed by re-injecting the reactivated materials in an FB reactor under simulated desulphurization conditions and following the calcium conversion degree and the attrition rate during the sorbent processing. Differences and similarities between reactivation by water and steam are discussed.

2. Experimental procedures

The sorbent used in the experiments was a high-calcium (96.8% $CaCO_3$) Italian limestone (*Massicci*). It was sulphated (S) to exhaustion (at 850 °C and at a fluidization velocity of 0.8 m/s) in a laboratory-scale stainless steel atmospheric FB reactor (electrically heated) 40 mm ID and 1 m high [12]. The 0.4- to 0.6-mm particle size range was used in all the experiments. The bed material consisted of mixtures of limestone (20 g) and silica sand (150 g in the size range 0.85–1 mm), prepared from batches of the two materials independently sieved in given particle size ranges prior to mixing. The stream of SO_2 (1800 ppmv), O_2 (8.5% v) and N_2 used in FB desulphurization experiments was prepared by mixing air of technical grade with SO_2–N_2 mixtures supplied in cylinders. The reactor was equipped with on-line gas analysis, enabling the calculation of the degree of calcium conversion, and with a two-exit head connected to sintered brass filters, designed to allow the capture of the elutriated fines and the evaluation of the fines elutriation rate [7].

S samples were reactivated by either steam hydration (SH) or water hydration (WH). Steam hydration (SH) was carried out at 250 °C for hydration times (t_H) of 10 min, 30 min and 3 h in the FB reactor. During steam hydration experiments the bed (consisting of 40 g of spent sorbent particles) was fluidized at the gas superficial velocity of 0.2 m/s with an equimolar N_2-steam mixture. Steam was produced with the aid of a purposely designed steam generator [18]. Water hydration (WH) was carried out in a thermostatic bath at 25 °C for t_H=10 min, 30 min, 1 h, 2 h, 3 h, 6 h, 10 h and 24 h [12].

SH and WH samples were characterized by X-ray diffraction (XRD). Moreover multiparticle samples were embedded in epoxy resin and their polished cross-sections were observed under a scanning electron microscope (SEM) detector equipped with an energy dispersive X-ray (EDX) probe for the elemental mapping. SEM-EDX maps were analyzed by means of a purposely developed computer-controlled (CCSEM-EDX) technique to achieve semi-quantitative characterization of the sulphur distribution patterns across the particles. This was expressed in terms of relative percentages of the core-zone and shell-zone areas, as detailed in [11].

Table 1
XRD analysis results for steam-hydrated (SH) and water-hydrated (WH) samples (symbols indicate XRD peaks intensities: +=low; ++=medium; +++=high)

Sample	Anhydrite $CaSO_4$ ASTM #37-1496	Lime CaO ASTM #4-0777	Portlandite $Ca(OH)_2$ ASTM #4-0733
SH@10 min and 30 min	+++	+	+
SH@3 h	+++	None	++
WH (all t_H investigated)	+++	None	++

SH and WH samples were dehydrated (SH/D and WH/D) at 850 °C for 5 min in the FB reactor (fluidized by air at 0.8 m/s) and subjected to porosimetric characterization by mercury intrusion.

SH and WH samples were resulphated in the FB apparatus under operating conditions equal to those of the first sulphation (S) tests.

3. Results and discussion

3.1. Microstructural effects of reactivation by steam and water hydration on sulphated samples

Table 1 reports results of XRD analysis of the steam hydrated and the water-hydrated S samples. For each hydration time t_H and reactivation mode investigated it can be observed that hydration of $CaSO_4$ toward gypsum-like phases does not occur to any appreciable extent, whereas the chemical conversion of lime to $Ca(OH)_2$ reaches its completion in the range t_H= 30 min–3 h for steam hydrated (SH) samples or within the first 10 min for the water-hydrated (WH) samples. Altogether, hydration by water is faster than steam hydration, hydration times t_H on the order of some hours being sufficient to determine the complete conversion CaO ⇒ $Ca(OH)_2$.

Fig. 1 shows the results of SEM-EDX characterization of the cross-section of multiparticle samples of S sorbent and selected reactivated material. The relevance of the core-zone areas for all the samples investigated, obtained by means of the application of the CCSEM-EDX technique, is reported in Table 2. The S sample shows a well-defined core-shell particle structure. It is remarkable that both the SH and WH treatments induce a pronounced redistribution of sulphur across the particle, and in particular from the shell zone to the core zone. This feature is well revealed by the comparison of the core-zone areas of S samples with those of hydrated samples, the core-zone area decreasing as t_H increases beyond about 1 h. Steam hydration induces a faster sulphur redistribution when compared with water hydration. This sulphur redistribution phenomenon provides an important pathway to the hydration-induced enhancement of SO_2 uptake upon resulphation [11] inasmuch as it yields a greater fraction of unsulphated calcium available in the outer particle layer. The sulphur redistribution observed in the WH samples was explained in the light of a solubilization/precipitation mechanism involving calcium species via the aqueous phase [11]. It has been speculated [18] that similar redistribution processes might be at work during steam hydration, possibly promoted by the formation of an adsorbed