Reactivation of FBC Spent Sorbents by Water and Steam Hydration

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INTRODUCTION

Fluidized Bed Combustion (FBC) of sulphur-bearing fuels is accomplished with in situ capture of sulphur oxides by limestone-based sorbents. Sorbent sulphation patterns have been extensively investigated in the past [see e.g. 1,2]. Sulphation most typically conforms to the core-shell pattern: the reaction front in the sorbent particle divides the unreacted CaO inner core from a partly reacted less porous outer shell. The build up of the sulphated outer shell prevents complete sulphation of the unreacted CaO core, as SO$_2$ diffusion through the CaSO$_4$ layer becomes negligible over the typical process time-scales. Sorbents employed in FBC undergo comminution which can lead to changes in particle size distribution and to fines elutriation with consequences on the desulphurization process [3].

Among the techniques proposed to enhance calcium utilization, one of the most promising is the reactivation of the exhausted sorbent via water- or steam- hydration [4,5]. This process mainly implies the conversion of the unreacted CaO into Ca(OH)$_2$ which, having a larger molar volume, swells inside the particles leading to the formation of cracks and flaws. In this way enhanced access to SO$_2$ is provided upon further exposure of the reactivated sorbent to sulphur-containing atmospheres. Both techniques are attractive, as they enhance the sulphur uptake of sorbents, reduce waste disposal costs and consumption of natural resources, limit CO$_2$ emissions.

The aim of this experimental work was to characterize the influence of the water- and steam- hydration/reactivation processes of FB spent sorbent particles on sulphur capture ability and particles sulphation patterns, fragmentation and attrition phenomena upon resulphation in FB reactors.

EXPERIMENTAL

A laboratory scale stainless steel atmospheric FB reactor (electrically heated), 40mm ID and 1m high, was employed for sulphation, steam-reactivation and resulphation tests. Details of the reactor can be found elsewhere [3,6]. Sorbent particles (a high-calcium Italian limestone, Massicci) were sulphated to exhaustion at 850°C in the FB reactor, and then subjected to hydration-reactivation tests by means of water or steam (the 0.4-0.6mm particle size range was chosen for all the experiments). Water reactivation was conducted in a thermostatic bath at 25°C for a curing time of 3h (for other details, see [6]). Steam reactivation tests were carried out, at 250°C for a curing time of 3h, in the FB reactor by fluidizing the bed material, consisting of spent sorbent particles (40g), with an equimolar N$_2$-steam mixture. Polished cross sections of water- and steam- hydrated sorbent particles, embedded in epoxy resin, were observed under a SEM-EDX detector (for the sulphur elemental mapping) and analyzed with a Computer Controlled SEM-EDX (CCSEM-EDX) technique (for the quantitative characterization of the sulphur distribution patterns), described
in detail elsewhere [2,6]. In this context, it is only recalled that bimodal sulphur distribution functions are indicative of a core-shell sulphation pattern, while unimodal distribution functions reveal uniform sulphur distribution throughout the particles cross sections. Finally, the effect of the reactivation treatment on the particle size distribution was investigated by sieving the hydrated particles in 9 size ranges between 0-0.053mm and 0.4-0.6mm. The occurrence of further fragmentation of water- and steam- hydrated samples (re-sieved in the size range 0.4-0.6mm) upon calcination was investigated by injecting samples in the FB fluidized by air at 850°C for 5 min and then sieving the hydrated/calcined sorbent particles in the same size ranges as above.

Resulphation tests of water- and steam- hydrated samples were carried out under operating conditions resembling those of the 1st sulphation tests: batches of bed material consisted of mixtures of reactivated sorbent (25g in the size range 0.4-0.6mm) and silica sand (150g in the size range 0.85-1mm), fluidized at 0.8m/s for 180min by simulated flue gases consisting of a mixture SO\(_2\)+N\(_2\)+O\(_2\) with a SO\(_2\) inlet concentration of 1800ppmv. The FB reactor was equipped with a two-exit head connected to sintered brass filters (designed to allow capture of elutriated fines and characterization of the attrition rate) and with on line gas analysis (enabling calculation of the degree of calcium conversion, or sulphur uptake, as a function of time).

RESULTS AND DISCUSSION

**Reactivation of spent sorbent particles**

**FIGURE 1** reports SEM-EDX micrographs of Water-Hydrated (WH) and Steam-Hydrated (SH) samples (for comparison the Sulphated -S- sample is also included). Inspection of **FIGURE 1** reveals the establishment of a core-shell particle structure for the S sample, in line with previously reported findings [1,2]. Redistribution of sulphur between the shell and core zones for the WH sample is remarkable (similarly to [7]). Notably, sulphur redistribution was observed also for the SH sample. In order to quantitatively account for differences in the three samples, the extent of the sulphur redistribution was examined with the aid of the CCSEM-EDX technique (**FIGURE 1)**: WH and SH samples both show a bimodal sulphur distribution pattern similar to that of the S sample, but the relative significance of the core-zone and the shell-zone peaks strongly changes. This indicates a better sulphur distribution in the particles induced by sorbent water- and steam-hydration, and provides an important pathway to sulphur uptake enhancement by spent sorbent reactivation. A mechanism for the sulphur redistribution observed in the WH sample, based on dissolution/precipitation phenomena of calcium species via the aqueous phase, was reported in [7]; it can be speculated that a similar sulphate ions migration mechanism might be at work under steam hydration conditions.

**TABLE 1** reports the cumulative particle undersize distributions for WH and SH samples, whose original size (i.e., before the reactivation treatment) was 0.4-0.6mm. For the WH sample less than 5% of the particles mass was in the range 0-0.4mm after hydration, and no significant population of particles finer than 0.15mm was observed. On the contrary, more than 50% of the SH particles mass was in the range 0-0.4mm. **TABLE 1** also reports the same analysis conducted on calcined WH and SH samples. A non-negligible fragmentation of both water- and steam-reactivated/calcined samples is observed upon calcination: 22% (for the WH sample) and 44% (for the SH sample) of particles were in the range 0-0.4mm, and in both cases particles finer than 0.05mm were observed. It is recalled here that, after hydration, the sorbents were re-sieved in the original size range (0.4-0.6mm) prior to FB calcination.
Resulphation of the reactivated sorbents

Figure 2 reports the degree of calcium conversion ($X_{Ca}$) as a function of time during batch resulphation of WH and SH samples (the results achieved during the 1st sulphation test are also reported, for comparison purposes). Water- and steam- reactivation of the spent sorbents were both highly effective in promoting further sulphur uptake upon resulphation: ultimate calcium conversion degrees were 54% (for the SH sample) and 53% (for the WH sample), far larger than the value (28%) achieved during the S test. Sulphur uptake is faster for the SH sample, showing larger sulphur uptake in the first part of the resulphation test, and deactivates earlier with respect to the WH sample.

Figure 3 shows the fines elutriation rate $E(t)$ as a function of time during the resulphation of the WH and SH samples. Notably, data for the WH sample refer to 6h (and not 3h)-water-hydration, but in a previous investigation [6] it was found that the attrition rates of the 3h- and the 6h- water-reactivated samples were similar. For the WH sample, $E(t)$ decreases with time upon resulphation following a general trend similar to that observed during sulphation tests [3]: particle rounding off and removal of surface asperities prevail at first, then attrition is dominated by strengthening of the surface layer upon sulphation, making $E(t)$ vanishingly small in the long term as resulphation reaches completion. For the SH
sample, the trend of $E(t)$ is slightly different: attrition rate is much smaller than that of the WH sample at the beginning, but $E(t)$ decreases more slowly, overtaking the attrition rate of the WH sample. The total elutriated mass ($\int E(t)dt$) is almost the same (2.2g) in the two cases. One important key to this behaviour is represented by the consideration that steam reactivation was carried out in the FB, so that rounding off of SH particles was already effective during hydration. Once rounding off of the WH samples is over, the larger elutriation rate of the SH sample may be related to extensive particle fragmentation which increases the exposed surface per unit mass of the sorbent and enhances attrition.

**Fig. 2:** Degree of calcium conversion as a function of time during sulphation and resulphation tests.

**Fig. 3:** Fines elutriation rate during batch resulphation of reactivated sorbents.

**CONCLUSIONS**

Reactivation of FB spent sorbents by hydration with either water or steam is addressed. Both water- and steam- reactivations induce a strong sulphur redistribution throughout the particles cross sections, which, in addition to the swelling/fissuring mechanism related to hydration, enhances the sulphur capture ability of the reactivated particles to comparable extents. Steam-reactivated particles are much more prone to fragmentation upon FB calcination and to attrition upon resulphation than water-reactivated sorbent.

**REFERENCES**