Reactivation of FB Spent Sorbents for Enhanced SO₂ Capture: the Relationship between Microstructural Properties and Desulphurizing Ability

1Fabio Montagnaro, 2Marianna Nobili, 2Fabio Pallonetto, 2Piero Salatino, 3Fabrizio Scala

1Dipartimento di Chimica, Università degli Studi di Napoli Federico II, Complesso Universitario del Monte di Sant’Angelo, 80126 Napoli (Italy)
2Dipartimento di Ingegneria Chimica, Università degli Studi di Napoli Federico II, Piazzale Vincenzo Tecchio 80, 80125 Napoli (Italy)
3Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche, Piazzale Vincenzo Tecchio 80, 80125 Napoli (Italy)

OVERVIEW

One of the main advantages of fluidized bed (FB) combustion consists in the possibility of achieving in situ removal of SO₂ by the injection of CaCO₃-based (e.g., limestone) sorbents, which display peak sulphur capture efficiencies just around the typical range of FB combustion temperatures (800-900°C) [1]. Under oxidizing conditions and at atmospheric pressure the sorbent first calcines to yield porous CaO, which is able to remove SO₂ upon sulphation giving compact CaSO₄. The sorbent sulphation most typically conforms to the core-shell pattern [2]: the reaction front in the sorbent particle divides the porous unreacted CaO inner core from the dense reacted CaSO₄-rich outer shell. Extensive sulphation of the core is prevented by the onset of a strong diffusional resistance to SO₂ migration across the CaSO₄-rich outer layer. Thus, the degrees of Ca conversion seldom exceed 30-40%. Moreover, the sorbents employed in FB reactors undergo comminution which can lead to changes in the particle size distribution and to fines elutriation with consequences on the desulphurization process [3].

The present work addresses the reactivation of the sulphur capture ability of the spent sorbent particles by both water [4] and steam [5,6] hydration. The hydration method is currently considered as one 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 favours the break-up of the CaSO₄ layer. When the hydrated sorbent is fed again to the combustor, it loses its chemically-bound water yielding further shell breakage, and the new-formed CaO is characterized by a larger specific surface area. In this way new access to SO₂ is provided upon resulphation of the reactivated sorbent. The hydration-reactivation method is attractive since it enhances the SO₂ uptake of the sorbents, reduces the waste disposal costs and the consumption of natural resources, limits the CO₂ emissions related to the calcination of the fresh sorbent.

The aim of this paper is to investigate the reactivation of a limestone in terms of hydration degree, particle sulphation pattern and porosity. 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.
EXPERIMENTAL PROCEDURES

The sorbent used in the experiments was a high-calcium (96.8% CaCO₃) Italian limestone (*Massicci*). It was sulphated (S) to exhaustion (at 850°C and at a fluidization velocity of 0.8m/s) in a lab-scale stainless steel atmospheric FB reactor (electrically heated) 40mm ID and 1m high [7]. The 0.4-0.6mm particle size range was used in all the experiments. The bed material consisted of mixtures of limestone (20g) and silica sand (150g in the size range 0.85-1mm), prepared from batches of the two materials independently sieved in given particle size ranges prior to mixing. The stream of SO₂ (1800ppmv), O₂ (8.5%v) and N₂ used in FB desulphurization experiments was prepared by mixing air of technical grade with SO₂-N₂ mixtures supplied in cylinders.

S samples were reactivated by both steam hydration (SH) and water hydration (WH). SH was conducted at 250°C for hydration times (t_H) of 10’, 30’ and 3h in the FB reactor by fluidizing at 0.2m/s the bed material (consisting of 40g of spent sorbent particles) with an equimolar N₂-steam mixture. Steam was produced with the aid of a purposely designed water vaporizer [8]. WH was carried out in a thermostatic bath at 25°C for t_H=10’, 30’, 1h, 2h, 3h, 6h, 10h and 24h [7,9]. SH and WH particles were characterized by X-ray diffraction (XRD), 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 sulphur elemental mapping. A computer controlled (CCSEM-EDX) technique was employed for the semi-quantitative characterization of the sulphur distribution patterns in terms of relative percentages of the core-zone and shell-zone areas [10]. Moreover, SH and WH samples were dehydrated (SH/D and WH/D) at 850°C for 5’ in the FB reactor (fluidized by air at 0.8m/s) and analyzed by mercury porosimetry.

SH and WH samples were resulphated in the FB apparatus under operating conditions resembling those of the S tests. 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 [3].

RESULTS AND DISCUSSION

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

Table 1 reports XRD analysis results for the steam hydrated and the water hydrated S samples. For each t_H and reactivation mode investigated it can be observed that CaSO₄ does not hydrate toward gypsum-like phases, while the chemical conversion of lime to Ca(OH)₂ reaches its completion in the range t_H=30’-3h (SH samples) or within the first 10’ (WH samples). The results show that water treatment is able to improve the kinetics of the hydration reaction with respect to steam hydration, and in both cases t_H values on the order of some hours are sufficient to determine the complete conversion CaO⇒Ca(OH)₂.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anhydrite (CaSO₄, ASTM#37-1496)</th>
<th>Lime (CaO, ASTM#4-0777)</th>
<th>Portlandite (Ca(OH)₂, ASTM#4-0733)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SH@10’ and 30’</td>
<td>+ + +</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>SH@3h</td>
<td>+ + +</td>
<td>none</td>
<td>+</td>
</tr>
<tr>
<td>WH (all t_H investigated)</td>
<td>+ + +</td>
<td>none</td>
<td>+</td>
</tr>
</tbody>
</table>
Table 3: Porosimetric analysis results for steam hydrated/dehydrated (SH/D) and selected water hydrated/dehydrated (WH/D) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total porosity (%)</th>
<th>Specific finer pore volume (mm³/g)</th>
<th>Specific larger pore volume (mm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D (SH@10')</td>
<td>22.2</td>
<td>55.2</td>
<td>47.0</td>
</tr>
<tr>
<td>D (SH@30')</td>
<td>24.6</td>
<td>55.0</td>
<td>59.9</td>
</tr>
<tr>
<td>D (SH@3h)</td>
<td>31.8</td>
<td>72.0</td>
<td>101.5</td>
</tr>
<tr>
<td>D (WH@10')</td>
<td>46.6</td>
<td>89.3</td>
<td>201.6</td>
</tr>
<tr>
<td>D (WH@30')</td>
<td>47.2</td>
<td>92.5</td>
<td>197.2</td>
</tr>
<tr>
<td>D (WH@3h)</td>
<td>50.7</td>
<td>57.0</td>
<td>290.7</td>
</tr>
<tr>
<td>D (WH@24h)</td>
<td>35.4</td>
<td>74.5</td>
<td>127.5</td>
</tr>
</tbody>
</table>

Figure 1 shows the SEM-EDX characterization of 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. Both the SH and WH treatments induce a remarkable redistribution of sulphur between the shell and core zones, revealed by the values of the core-zone areas which
decrease as $t_H$ increases. Moreover SH treatment determines a fast sulphur redistribution with respect to WH. This redistribution phenomenon has been shown to provide an important pathway to SO$_2$ uptake enhancement upon resulphation [10] inasmuch as it yields a greater fraction of unsulphated calcium in the outer layer of the particles. 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 [10]; it has been speculated [8] that similar redistribution processes, potentially promoted by the presence of adsorbates, might be at work during steam hydration.

Table 3 shows the porosimetric analysis results on SH/D and selected WH/D samples (a detailed investigation is reported elsewhere [7-9]). In the range $t_H=10'\text{-3h}$, both treatments induce a development of total porosity (due to the combined effect of swelling/fissuring induced by hydration and by subsequent dehydration) which increases as hydration time increases. The WH treatment appears more favourable with respect to this effect. The influence of $t_H$ on total porosity is more noticeable for SH samples. The reason for this is that during steam hydration H$_2$O uptake is active during the whole hydration period investigated, determining a greater swelling/fissuring effect as $t_H$ increases. For the WH samples hydrated for $t_H>3h$ a reduction of the total porosity is observed. This could be related to the occurrence of low-temperature cramming phenomena associated with the presence of an aqueous phase and with ion mobility due to solubilization/precipitation dynamical processes. While both the specific finer pore (<100nm) and larger pore volumes for SH/D samples increase as $t_H$ increases, the phenomenology for the WH/D samples is more complicated. The coalescence of fine pores into larger ones (observed in the range $t_H=10'\text{-3h}$) could broadly resemble pore volume changes associated with high-temperature sintering upon prolonged calcination [11]; moreover, if sulphur redistribution is looked at as a recrystallization process, it should bring about an increasing relevance of the finer pores fraction according to the Ostwald ripening process [12] and this could be able to explain the trend observed after $t_H=3h$.

The relationship between microstructural properties and desulphurizing behaviour of the reactivated samples

Figure 2 reports the values of the degree of calcium conversion ($X_{Ca}$) as a function of the resulphation time for the SH samples and for selected WH samples (further details are given in [7,9]). The starting value of the $X_{Ca}$ curves represents the final degree of calcium conversion upon first sulphation. Both reactivation treatments were very effective in promoting further sulphur uptake upon resulphation in the FB reactor (the ultimate value of $X_{Ca}$ for the fresh limestone was only 28%). In particular, the renewal of SO$_2$ capture for SH and WH samples reactivated for $t_H\leq30'$ can be ascribed to the favourable swelling/fissuring phenomena related to the reaction CaO$\Rightarrow$Ca(OH)$_2$ which determine the development of accessible porosity. The high ultimate $X_{Ca}$ values obtained at $t_H=3h$ are due to the combined effect of the progression of the hydration reaction and of sulphur redistribution for the SH samples, while for the WH samples only the latter effect is active. The decrease of the total SO$_2$ capture as $t_H$ increases over 3h for the WH samples is related to the loss of overall porosity observed for these materials. When comparing the two reactivation techniques, the fast hydration reaction for the WH samples determines higher ultimate $X_{Ca}$ values for $t_H\leq30'$, while the strong redistribution of sulphur in both cases at $t_H=3h$ yields high (and comparable) values for both SH and WH materials.

Figure 3 shows the finest elutriation rate $E$ as a function of the resulphation time in the FB reactor for the SH samples and for selected WH samples. The $E$ curves decrease as time increases upon resulphation following similar trends observed during sulphation tests [3]. For SH samples the in-bed attrition is more pronounced as $t_H$ increases above 30', inasmuch as the
sulphur redistribution determines a higher concentration of softer unsulphated calcium in the outer of the particle and the progress of the hydration reaction makes the particles more fragile. The same trend is observed for WH samples hydrated for $t_H \leq 6h$, while for longer $t_H$ E decreases because the particles become more compact. The analysis of the results shows that SH leads to a lower attrition rate than WH. When comparing the two treatments, it has to be borne in mind that SH was carried out in the FB reactor, so that rounding-off of SH particles was already effective during reactivation determining the absence of the high initial E peak and the corresponding lower values of the elutriated mass.

Figure 2: Degree of calcium conversion as a function of time during resulphation of A) steam hydrated (SH) and B) selected water hydrated (WH) samples.

Figure 3: Fines elutriation rate as a function of time during resulphation of A) steam hydrated (SH) and B) selected water hydrated (WH) samples.
CONCLUDING REMARKS

Both steam and water hydration techniques were highly effective in the renewal of the SO₂ uptake ability of exhausted sorbent particles. Water treatment was able to improve the kinetics of the hydration reaction, which was however complete after some hours also upon steam hydration. Steam reactivation determined a fast sulphur redistribution throughout the particle cross-sections, and in both cases this phenomenon enhanced the sulphur capture ability of the reactivated particles. The type of treatment, the hydration kinetics and the sulphur redistribution strongly affected the development of porosity after dehydration of reactivated particles, and water hydrated/dehydrated particles appeared more porous than steam-treated ones. During resulphation in the FB reactor it was observed that for short hydration times the water reactivation was more effective, while the two treatments yielded comparable results when long hydration times are considered. Moreover, the microstructural properties of the hydrated particles markedly influenced their attrition behaviour upon resulphation.

ACKNOWLEDGMENTS

The authors wish to thank Mrs. Clelia Zucchini and Mr. Sabato Russo for the SEM-EDX particle characterization and Mr. Sabato Masi for the porosimetric characterization.

LITERATURE CITED