Steam Reactivation of the SO_2 Capture Ability of Fluidized Bed Combustion Wastes

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FBC processes enable *in situ* SO_2 removal, but generate large amounts of wastes difficult to reuse and landfill. The steam hydration/reactivation of the desulphurizing ability of these residues is considered a viable recycling pathway. A lab-scale investigation has been performed to correlate their chemical and physical properties with hydration operating conditions such as temperatures and times. It has been found that the reactivation process was able to give products with an improved overall accessible porosity, induced by both the extent of the reactions and the nature of the hydrated phases (calcium hydroxide and, secondarily, ettringite).

1. Overview

Sulphur oxides generated during the fluidized bed combustion (FBC) of sulphur-bearing solid fuels can be captured *in situ* by injection in the reactors of calcium-based sorbents, such as limestones (Anthony and Granatstein, 2001). Nonetheless, a drawback of this process is the only partial conversion of free CaO to the sulphation product ($CaSO_4$): this poses problems in landfilling of the spent sorbent, due to exothermal and expansive phenomena upon hydration (Bernardo et al., 2003). Moreover, FBC residues also contain fuel-derived ash characterized by a poor pozzolanic activity: hence, these wastes are generally unsuitable for recycling in traditional fields such as cement and concrete industries.

Reactivation (induced by hydration) of the desulphurizing ability of the unconverted CaO in FBC ash is considered a viable pathway to ash utilization. This process mainly relies on the ability of the waste to quantitatively yield $Ca(OH)_2$, whose larger molar volume determines the enhancement of the accessibility of the unconverted calcium by SO_2 when the reactivated material is re-injected into the FB reactor (Laursen et al., 2004; Montagnaro et al., 2006). Moreover, hydration of FBC waste can also generate products different from $Ca(OH)_2$, such as calcium silicate-, aluminate- and sulphoaluminate-hydrates (Bernardo et al., 2004). The formation of ettringite, a calcium trisulphoaluminate hydrate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), is particularly important as it yields reactive calcium oxide which can be effectively exploited as a sorbent (Anthony et al., 1997; Montagnaro et al., 2005).

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Only recently a particular attention has been paid to the characterization of the effects induced by the steam-reactivation treatment on industrial-scale FBC ashes (Góra et al., 2006). The aim of this work is to correlate hydration temperatures/times and characteristics of steam-reactivated fly ashes coming from an industrial-scale FBC reactor. The chemical/physical characterization of the reactivated wastes was carried out by means of X-ray diffraction analysis, mercury porosimetry and scanning electron microscopy.

2. Experimental

FBC fly ash came from a full-scale plant and its maximum particle size was 90 μm. From its chemical composition, determined by X-ray fluorescence (XRF) analysis and shown in Table 1, it is noted that: i) sulpho-calcic and silico-aluminous fractions were almost equivalent; ii) loss on ignition, mainly related to the presence of unburnt carbon, was relatively high; iii) the iron content was quite appreciable.

X-ray diffraction (XRD) data are collected in Figure 1. Figure 1a reports the XRD pattern for fly ash before hydration: the main detected phases were, in the order, anhydrite-quartz-lime-hematite-calcite. Altogether, these data revealed: i) the existence of unconverted CaO available for further sulphation in FBC, if suitably reactivated; ii) the potential for the formation, upon steam reactivation, of hydration products different from $Ca(OH)_2$.

Steam reactivation of fly ash was conducted in a tubular reactor electrically heated, equipped with a temperature controller and continuously fed with a distilled water stream of 1 mL/minute at room temperature. The reactor was heated up to the chosen temperature (either 200°C or 300°C) before introducing the sample (about 2 g). Three main treatment times were investigated, namely 10, 30 and 60 minutes (giving rise to the two group of samples SH200/10, SH200/30, SH200/60 and SH300/10, SH300/30, SH300/60 hydrated at 200°C and 300°C, respectively). After reactivation tests, each sample was submitted to XRD analysis, mercury porosimetry analysis and scanning electron microscopy (SEM) observation.

Finally, the steam-hydrated materials were fully dehydrated (giving rise to the samples SH200/10/D, SH200/30/D and so on) in an electric oven at 850°C, and then submitted again to the porosimetric analysis.

Table 1: Fly ash chemical composition in terms of major oxides, % by mass.

CaO	24.20
SO_3	12.80
SiO_2	23.23
Al_2O_3	13.71
Fe_2O_3	6.74
MgO	1.04
TiO_2	0.82
Mn_3O_4	0.07
loss on ignition	16.26
	98.87

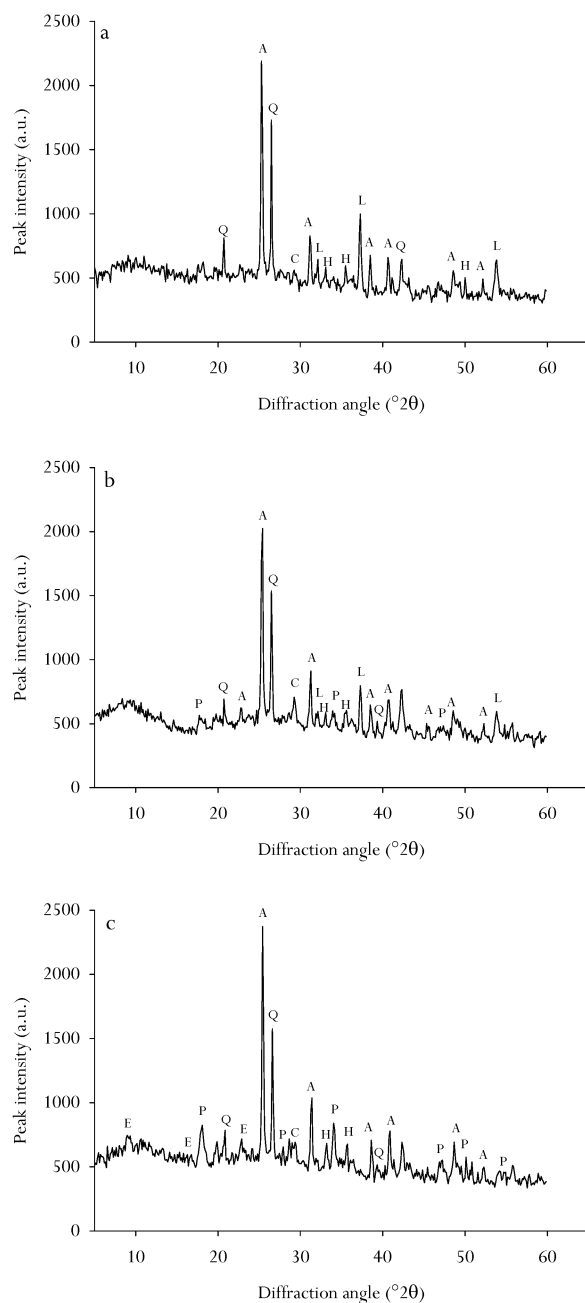*Figure 1: XRD patterns for (a) fly ash, (b) SH200/10, (c) SH200/60. (A=anhydrite, CaSO₄; C=calcite, CaCO₃; E=ettringite, 3CaO·Al₂O₃·3CaSO₄·32H₂O; H=hematite, Fe₂O₃; L=lime, CaO; P=portlandite, Ca(OH)₂; Q=quartz, SiO₂).*

3. Results and Discussion

3.1 Steam hydration/reactivation at 200°C

Figures 1b and 1c report the XRD patterns for SH200/10 and SH200/60, respectively: it can be observed that the chemical reaction $CaO \Rightarrow Ca(OH)_2$ already took place within 10 minutes and went to completion within 60 minutes, where the absence of lime as well as the pronounced formation of portlandite was observed. Furthermore, ettringite signals could also be recognized. Formation of ettringite was confirmed by SEM analysis (Figure 2) where plate-like and prismatic microcrystallites of calcium hydroxide and ettringite, respectively, were observed on the anhydrous surface of the grains. The preservation of the structure of ettringite, which is generally believed to decompose below 200°C, was observed by Tsuchiai et al. (1995) upon drying at 200°C.

Figure 3 shows the cumulative pore undersize distributions for fly ash, SH200/10, SH200/60, SH200/10/D and SH200/60/D. Fly ash was characterized by a quite narrow (*monodisperse*) pore size distribution and an overall porosity (in the pore size range investigated) of about 550 mm^3/g. The conversion of lime into calcium hydroxide after 10 minutes, although limited (*cf.* Figure 1b), resulted into an increased total pore volume (larger than 600 mm^3/g). The porosity enhancement was most likely due to the greater molar volume of $Ca(OH)_2$ compared with that of CaO.

For SH200/60 it can be observed: i) a dramatic increase in the overall porosity (about 1250 mm^3/g); ii) a broader pore size distribution. This peculiar result could be also related to the presence of ettringite. As a matter of fact, beside the completion of the hydration reaction $CaO \Rightarrow Ca(OH)_2$, the influence of a low-density (1775 kg/m^3) compound such as ettringite on both the shape of the distribution curve and the value of the overall porosity may be taken into account.
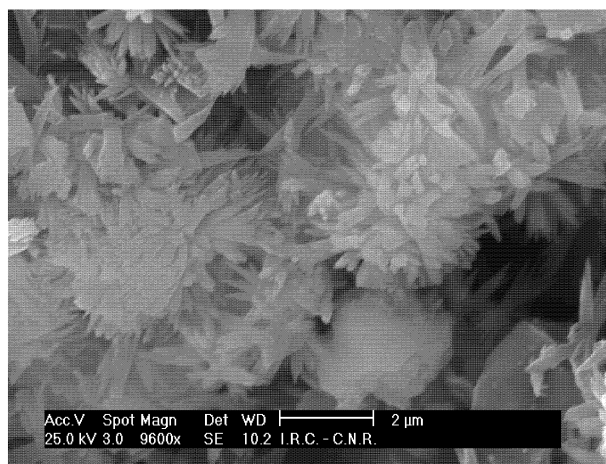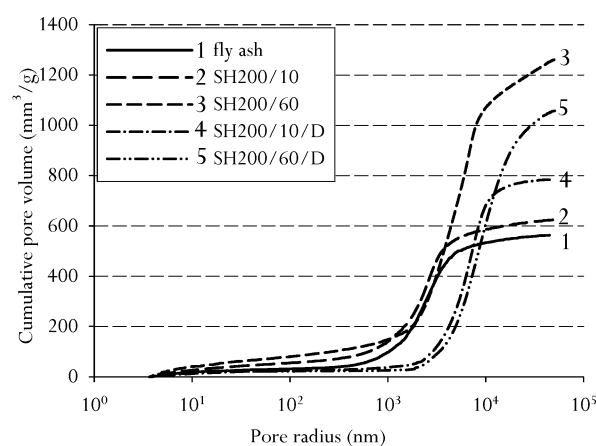

Figure 2: SEM micrograph of SH200/60.

Figure 3: Cumulative pore undersize distributions for fly ash before hydration and some steam-hydrated and dehydrated sample.

The investigation of the dehydration behaviour is somewhat interesting since, upon FBC resulphation at 850°C, loss of water occurs over a much shorter time-scale than sulphur uptake. Accordingly, sorbent particles in the dehydrated form are those encountered by SO_2 during the gas-solid desulphurization reaction. As far as the role played by the pore size of dehydrated particles in controlling the desulphurizing ability is concerned, both finer/intermediate pores (resulting in a higher sulphation rate) and larger pores (promoting an increased SO_2 uptake capacity) must be considered. Moreover, the pore geometry and the contribution to porosity given by chemically inactive phases have to be taken into account.

When the fly ash porosimetric characteristics before hydration and after dehydration are compared, an increase in overall porosity and a shift of the distribution curve toward larger pore sizes are observed. The SH200/10/D total pore volume was further increased (about 800 mm^3/g) with respect to that of the sample hydrated for 10 minutes whereas the SH200/60/D total pore volume (nearly 1050 mm^3/g) was somewhat reduced if compared with that of the sample hydrated for 60 minutes. Most likely, for the shortest curing time, the $Ca(OH)_2$ calcination effect played a leading role while, for the 60 minutes-curing time, it was overcome by the effect of the complex microstructural modifications associated with the ettringite thermal decomposition toward its constituents (CaO, $CaSO_4$ and an alumina-bearing phase). As regarding the shift of the average pore size, the role played by the coalescence of pores of intermediate size range occurring at 850°C was dominant for both the dehydrated samples. Accordingly, an increased relevance of the bigger pores was inferred.

3.2 Steam hydration/reactivation at 300°C

XRD and porosimetric results for samples reactivated at 300°C were the following. The hydration at 300°C was, at the beginning, as fast as hydration at 200°C but, differently from the latter, neither consumed all the available CaO nor generated ettringite within

60 minutes of reaction. The extent of the $Ca(OH)_2$ formation was hampered by the temperature increase, probably due to the fact that, under these operating conditions, the chemical reaction ceases to be the rate-limiting step giving rise to a diffusion-controlled regime. The two porosimetric features underlined for the samples reactivated at 200°C and then dehydrated (*i.e.*, the increase in the overall porosity and, to certain extent, the pores coalescence) were still active, though the overall porosities of these hydrated/dehydrated ashes were smaller than those achieved by reactivation at 200°C. These porosimetric characteristics are related to the incomplete CaO conversion and the absence of ettringite among the hydration products.

4. Concluding Remarks

From the results of this investigation the following conclusions can be drawn: i) the steam-reactivation treatment of FBC ashes generates materials with an improved overall accessible porosity. The SO_2-CaO contact during FBC resulphation is significantly improved accordingly; ii) steam temperatures should not be increased beyond certain values, since the competition between intraparticle gas diffusion and chemical reactions could slow down particle hydration; iii) reactivation times should be at least long enough to obtain a quantitative CaO conversion to $Ca(OH)_2$; iv) the favourable development of porosity is mainly associated with $Ca(OH)_2$ formation. The generation of hydrated phases different from calcium hydroxide, such as ettringite, may also have a role.

5. Acknowledgements

6. References

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