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Reactivation of fluidised bed combustor ash for sulphur capture

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Abstract

The efficiency of limestone utilisation for sulphur capture in fluidised bed combustors (FBC) is low due to incomplete sulphation of CaO. The disposal of the spent sorbent is problematic and costly. Reutilisation of the spent sorbent is highly desirable both in terms of improving overall plant economics and process efficiency. In this work, wet grinding of the bottom ash from a CFBC unit was used to reactivate the spent ash. The ash was then reinjected into a CFBC pilot plant and the performance of sulphur capture was compared with that of limestone. The activated ash showed higher sulphur capture efficiency, which is attributed to the more porous structure or larger specific surface area of the particles of the ash brought about by hydration of CaO and the subsequent dehydration of $Ca(OH)_2$. The kinetics related to sulphur capture and the wet grinding process are also discussed.

Keywords: Sulphur capture; Limestone sorbent; Reactivation; Fluidised bed combustion; Flue gas

1. Introduction

Fluidised bed combustion (FBC) uses limestone for sulphur capture. The limestone first calcines and then reacts with SO_2 via the global reaction scheme:

$$CaCO_3 = CaO + CO_2 \quad (1)$$

$$CaO + SO_2 + \tfrac{1}{2}O_2 = CaSO_4 \quad (2)$$

Unfortunately, the level of limestone utilisation is rather low and 30–40% utilisation is considered to be good [1–3]. As a result, a considerable amount of unreacted lime remains in the ash, typically from 15 to 30%, and ends up in the landfill [1]. This excess free lime content confers various undesirable properties on the ash, including: very strong exothermic reactions when in contact with water; high pH leachate; and the potential for expansion thus damaging the integrity of the landfill site [4–6]. In consequence, ash disposal is often one of the greatest costs associated with FBC technology. A reduction in the production of ash would significantly improve the overall economics of FBC technology for high-sulphur fuels.

2. Reactivation of the sorbent

The low level of limestone utilisation can be attributed to pore plugging of limestone sorbent particles by $CaSO_4$, whose molar volume is larger than that of both $CaCO_3$ and CaO [1,7,8]. Because of the plugging near the surface of the particles, the core region of the particles is not sulphated. Reactivation of the spent sorbent can be achieved by hydration, but this is normally quite slow, taking hours to complete at ambient conditions [1]. The hydration process can be accelerated by simultaneously grinding and wetting the ash particles. CaO reacts with water and forms $Ca(OH)_2$, which has a larger molar volume. The grinding/hydration process breaks the sulphate shell which blocks off unreacted lime, permitting a much more rapid hydration process (Fig. 1), and the subsequent dehydration of $Ca(OH)_2$ in the combustor yields CaO with larger specific surface area, which is favourable for sulphur capture.

In this work, activated ash was reinjected into a pilot-scale FBC, and the efficiency of the sulphur capture process was examined. The activated ash showed excellent potential for sulphur capture. With a view to applying the process to large FBC units, factors related to optimisation of the reactivation and sulphur capture processes are discussed.

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Fig. 1. SEM of hydrated spent sorbent particles. Cracks can be seen.

3. Experiments

3.1. Sorbent reactivation

Bottom ash from the Point Aconi 165 MWe CFBC unit of Nova Scotia Power Inc. (NSPI) was used to produce reactivated sorbent. The ash was first analysed for free lime and sulphur content. The free lime content was determined by the sucrose method, which is described in ASTM C-25. The sulphur content was analysed by X-ray fluorescence. Ca speciation and porosity measurement results have been reported earlier [4]. For reactivation the ash was ground by a mill with addition of water. The mill was a Szego Mill™ (trademark of General Comminution Inc., Canada, for its planetary ring-roller mills) SM-320/400, with internal diameter of 320 mm and grinding cylinder length of 400 mm, and was equipped with four helically-grooved rollers (10 mm grooves spaced 10 mm apart, 5 mm deep, groove bottom rounded).

3.2. Combustion test

To evaluate the performance of the reactivated sorbent, combustion tests with and without limestone sorbent were carried out. Combustion with reactivated ash was then carried out and SO_2 concentration in the flue gas was monitored. The combustor used for the tests was a 100 mm diameter 5.5 m high circulating FBC pilot plant operating at typical FBC temperature of 850 °C (Fig. 2). Devco Prince coal and Calpo limestone, both from Nova Scotia, Canada, were used. The coal had a sulphur content of 2–4.5%. The variation was due to changes in the mine seams. The proximate analysis data are (wt.%): moisture 4.2; ash 10.1; volatiles 33.1; fixed carbon 52.6. The limestone had a CaO content of about 53 wt.% (about 94.7% $CaCO_3$). The composition is shown in Table 1.

Table 1
Analytical data for composition of the limestone (Calpo limestone from Nova Scotia, Canada)

	wt.%
SiO_2	4.5
Al_2O_3	0.28
TiO_2	0.03
CaO	53.02
MgO	0.43
SO_3	0.79
Na_2O	0.33
K_2O	0.32
NiO	0.01
LOF (loss on fusion)	40.87

4. Results and discussion

4.1. Sulphur capture performance

Results for SO_2 concentration in the flue gas are shown in Table 2. The concentration level decreases with increasing Ca to S molar ratio (Ca/S) in the feed. SO_2 concentration in the flue gas of a second batch of coal appears to be higher if the results are extended to the same Ca/S levels as the first batch, and may be attributed to varied sulphur content in the coal. However, regardless of the SO_2 level, the data suggest that the activated ash gives higher efficiency for sulphur capture compared to the parent limestone.

A quantitative comparison can be given as follows: assuming plug flow for the flue gas, perfect mixing of solid and rapid mass transfer in the combustor, we can expect the

Table 2
Comparison of sulphur capture efficiency for limestone and activated ash in the CFBC pilot plant

	Ca/S	SO_2 (ppm)
Without sorbent	0	2090
Limestone	2.35	120
	3.77	39
Activated ash	1.21	413
	2.31	142
Results with a second batch of coal		
Limestone	2.5	598
Activated ash	2	437
	2.5	138

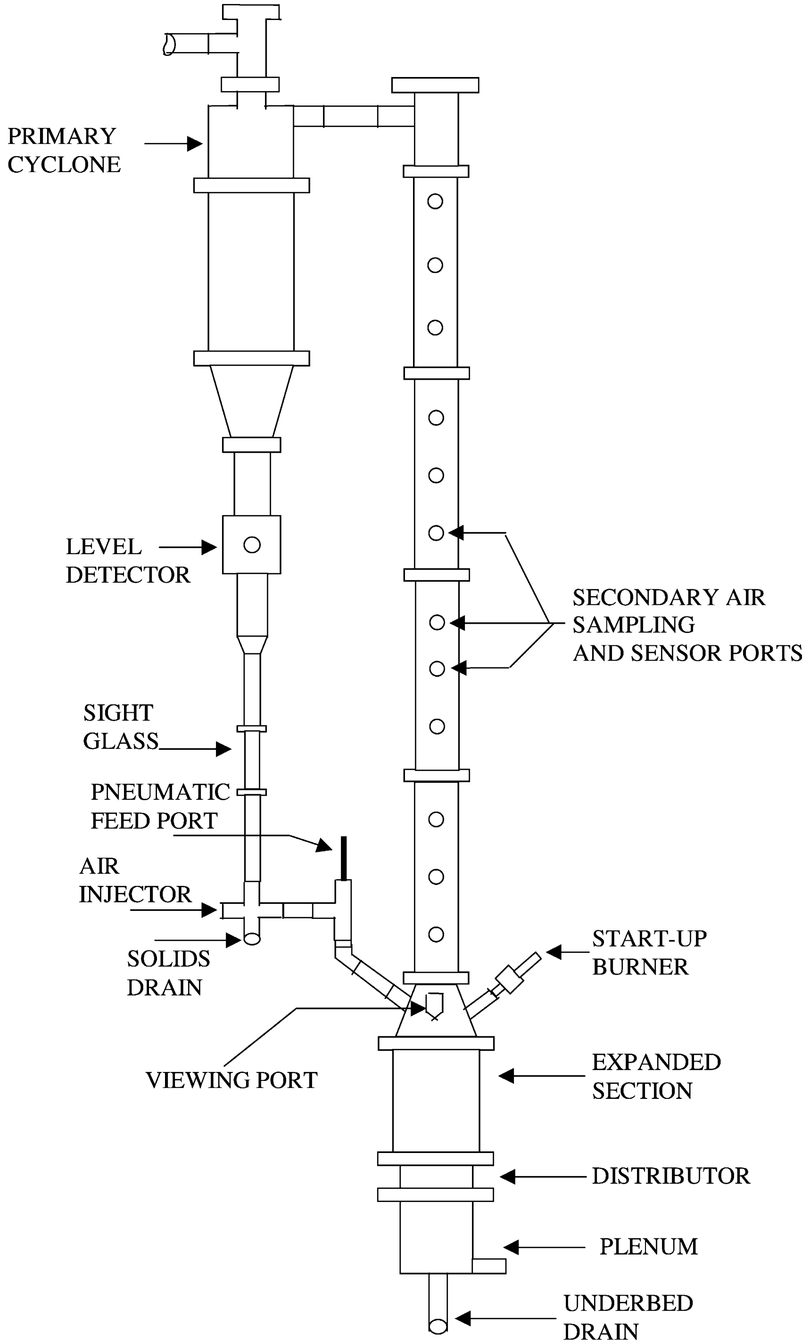

Fig. 2. Schematic of the pilot CFBC facility.

concentration of SO_2 to be a function of the height from the bottom of the combustor. The relation may be given as

$$\frac{dy}{dz} = -\frac{V_0 \rho}{Q C_0} R \tag{3}$$

where y is the mole fraction of SO_2 in the gas; $z = h/h_0$ the dimensionless height, with h and h_0 representing the height from the bottom and the height of the fluidised bed, respectively; V_0 the volume of the combustor; ρ the bulk density of sorbent in the bed; Q the gas flow rate; C_0 the equivalent initial concentration of SO_2; and R is the rate of sulphur removal by the sorbent, which may be given as

$$R = \sigma k C \tag{4}$$

where σ is the effective surface area per unit weight of sorbent and k is the mean rate coefficient for the sulphur removal. Here σ is affected by other factors such as particle size and pore structure, and may not be identical to the mean specific surface area of the particles. C is the SO_2 concentration in the gas phase. Substituting Eq. (4) into Eq. (3), one obtains

$$\frac{\mathrm{d}y}{y} = -\frac{V_0}{Q}\sigma k \rho(z)\,\mathrm{d}z \tag{5}$$

Integration of Eq. (5) from $z = 0$ to $z = 1$ yields the SO_2 concentration in the flue gas

$$y = y_0 \exp\left(-\frac{V_0 \sigma k \bar{\rho}}{Q}\right) \tag{6}$$

where $\bar{\rho} = \int_0^1 \rho(z)\,\mathrm{d}z$ is the averaged sorbent density in the combustor. By taking $\bar{\rho}/C_0 \cong \mathrm{Ca/S}$, the capture efficiency can be expressed as

$$\eta = 1 - \frac{y}{y_0} = 1 - \exp\left[-\left(\frac{V_0 C_0 \sigma k}{Q}\right)\left(\frac{\mathrm{Ca}}{\mathrm{S}}\right)\right] \tag{7}$$

In Fig. 3, the first set of data from Table 2 has been replotted to show the efficiency of sulphur capture in terms of reduction of SO_2 concentration in the flue gas, in comparison with the no-sorbent case, as a function of Ca/S. The curves are the result of fitting Eq. (7) to the experimental data and they describe the data reasonably well. The numerical values in the exponential terms correspond to the value of the product $V_0 C_0 \sigma k/Q$ in Eq. (7). In comparison with the limestone, it can be seen that the reactivated ash exhibits the same or better sulphur capture performance. In reality, the sulphation process is much more complex, and many more elaborate models have been proposed [9–12]. However, detailed models often result in mathematical expressions that are too complicated for practical applications or require process data that are difficult to obtain [12]. To compare the sulphur capture efficiency of the limestone and activated ash in the present work, the above simplified treatment appears to be sufficient. As can be seen from Eq. (7), if all other conditions or parameters are kept constant, the sulphur capture efficiency will increase with increasing σ, the effective surface area of the sorbent. It was observed in a previous study that after the hydration the specific area may increase from about 1 to 10 m^2/g [4], and the surface area is known to strongly influence sulphur capture [13–15]. Although the sulphur capture shown by the ash in Fig. 3 does not seem to be greatly enhanced, qualitatively the results agree with the observation of increased surface area. The surface area increase is likely to depend on the reactivation conditions. With optimised process conditions, greater surface area and hence higher sulphur capture efficiency would be achievable.

The wet grinding may have affected the fluidisation characteristics of the particles such as size distribution, which will be shown later, density and shape, and thus affect entrainment, cyclone loss and mass transfer. However, as can be seen from the data, as far as the sulphur capture efficiency is concerned, the results look promising.

In a recent paper on sorbent reactivation, it has been suggested that hydration promotes a pronounced redistribution of sulphur inside the spent sorbent particle structure, which enables further access to unconverted calcium oxide [16]. In the present study, we have not attempted to relate this process to the observed sorbent reactivation. The reason is that the sulphur redistribution requires a comparatively long time, whereas in our wet grinding process, the residence time of the particles in the mill was within 1 min or less.

4.2. Grinding process for ash activation

It was observed that, for Point Aconi bed ash and a CANMET CFBC pilot plant ash, wet grinding could achieve high conversions of CaO to $Ca(OH)_2$ (80%+), although grinding itself is not an effective technique for sorbent reactivation [1]. However, it requires very careful control of water levels, otherwise a hard concrete-like material results. Such

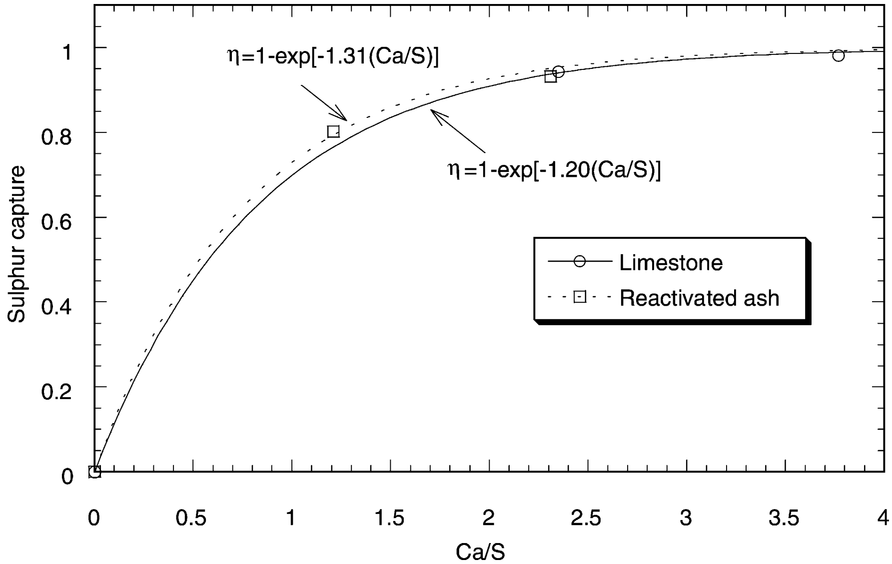

Fig. 3. Efficiency of SO_2 capture as a function of Ca to S ratio in the coal-sorbent stream. The curves represent calculated results in terms of Eq. (7).

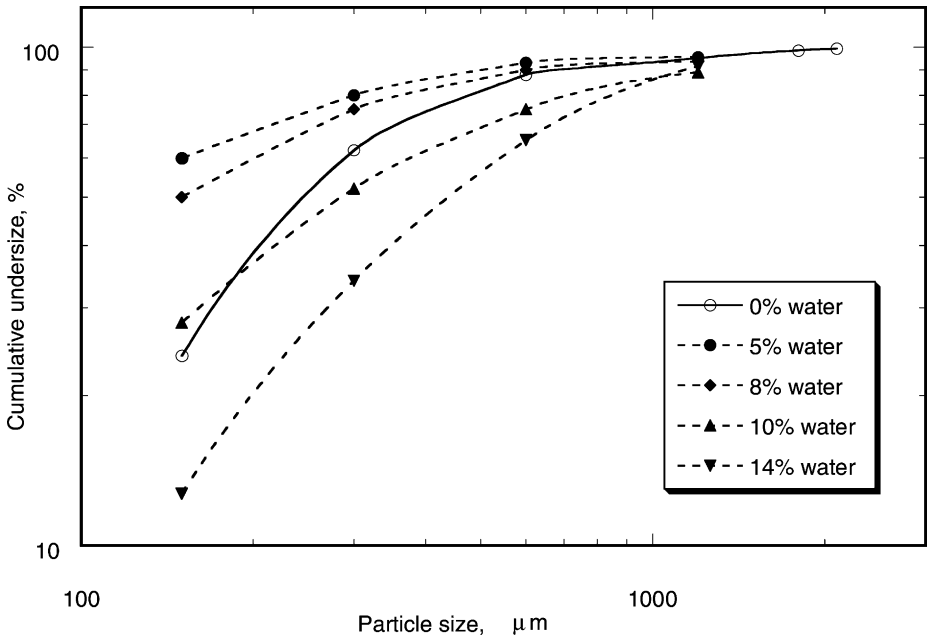

Fig. 4. Particle size of grinding product as a function of the water content.

material increases the power consumption of the grinding process and is extremely difficult to handle.

Fig. 4 shows the particle size of the grinding product. The size increased with increasing water content. The products with 10 and 14% water became coarser than the feed material. Visually, agglomeration was also observed for products with 5 and 8% water (about 6–8% water is required for stoichiometric conversion of the CaO component of the ash). Moreover, for runs where 10 and 14% water was added, the roller grooves soon became obstructed. A trial with 17% water failed right at the beginning because of rapid obstruction of the grooves and high power consumption. To achieve higher hydration levels, more water is desirable. However, within limits, the cementing reaction appears to increase with increasing amount of water.

The cementing process seems to be inherent in wet grinding of the ashes. For best results for reactivation, the kinetics related to the wet grinding process should be considered.

The cementing process and the hydration of CaO may be taken as two parallel reactions involving water:

$$H_2O + CaO = Ca(OH)_2 \tag{8}$$

$$H_2O + Cem = HC \tag{9}$$

where Cem denotes the cementing components in the ash (i.e. such as monosulphate and ettringite, etc. [17]), and HC denotes the hardened concrete-like product. The mill for the wet grinding may be modelled as a backmixing reactor, where the composition of the exit stream is the same as that of the material being ground in the mill. The relation between the material flow and reaction rate can be given as

$$F_0 - F = R_m V_m \tag{10}$$

where F_0 and F denotes the flow rate at the inlet and the outlet, respectively; R_m the rate of the reaction in the mill; and V_m is the volume in the mill. The rates of the two reactions may be given as

$$R_{mA} = k_A \rho [CaO][H_2O]^l \tag{11}$$

$$R_{mB} = k_B \rho [Cem][H_2O]^n \tag{12}$$

where R_{mA} and R_{mB} are the rates of reactions (8) and (9), respectively; l and n the reaction orders; k_A and k_B the rate coefficients; [CaO] and [Cem] the weight fractions of CaO and cementing components in the ash, respectively; $[H_2O]$ the amount of water added to unit mass of the ash; and ρ is the density of the ash. From Eqs. (10)–(12), one obtains

$$\frac{F_{A0} - F_A}{F_{B0} - F_B} = \frac{k_A [CaO]}{k_B [Cem]} [H_2O]^{l-n} \tag{13}$$

where F_{A0}, F_{B0}, F_A and F_B denote the equivalent flow rates of CaO and the cementing components at the inlet and outlet of the mill, respectively. By noting the following relations:

$$F_A = F_{A0}(1 - X_A) \tag{14}$$

$$F_B = F_{B0}(1 - X_B) \tag{15}$$

$$\frac{[CaO]}{[Cem]} = \frac{F_A}{F_B} \tag{16}$$

where X_A and X_B denote the conversion of CaO and the cementing materials, Eq. (13) can be simplified to

$$\frac{X_A/(1 - X_A)}{X_B/(1 - X_B)} = \frac{k_A}{k_B} [H_2O]^{l-n} \tag{17}$$

It can thus be seen that the ratio of the conversions depends on the ratio of the rate coefficients and amount of water. Clearly, if $l = n$, the ratio of the conversions would be independent of the amount of water. If $l < n$, the amount of water needs to be controlled to avoid excessive formation of the concrete-like product. Another controllable variable is temperature. k_A and k_B may not have the same temperature dependence. The temperature can be controlled to make the ratio k_A/k_B as large as possible. However, the values k_A, k_A, l and n depend largely on the properties of the ash, and probably need to be determined case by case. When the temperature is fixed, the conversion levels should be controlled. Suppose there is a maximum allowable conversion level for the cementing material, $X_{B,\max}$, above which the grinding becomes difficult, and for simplicity we consider the case where the conversion ratio is independent of water content ($l = n$). Eq. (17) can then be rearranged into

$$X_B = \frac{1}{1 - \gamma(1 - (1/X_A))} \tag{18}$$

where $\gamma = k_A/k_B$. Fig. 5 shows the relation of X_B with X_A as a function of γ. Clearly, the conversion of CaO to $Ca(OH)_2$ should be controlled so that conversion of the cementing components does not exceed $X_{B,\max}$. For ashes with large values of γ, higher conversion rates of CaO can be achieved. The figure also suggests that as the conversion of CaO approaches completion, the conversion of the cementing materials also approaches completion. Therefore, complete hydration of CaO by wet grinding is probably not feasible, due to handling problems, without the application of some other strategy. This discussion can be extended to the case that the cementing reaction rate depends more on the water content, i.e. $l < n$. In Eq. (18) γ should then be multiplied by $[H_2O]^{l-n}$, and with water increasing, the curves in Fig. 5 will cross the $X_{B,\max}$ line at lower X_A level. That is to say, the achievable CaO conversion will be lower.

4.3. Further utilisation of spent sorbent by repeated reactivation

The reactivation process may be repeated to fully utilise the available calcium. However, as has been discussed earlier, owing to the inherent limitations, for each reinjection process of the reactivated sorbent only a part of the CaO is utilised. Marquis et al. carried out repeated hydration of ashes followed by sulphation in a thermogravimetric analyser (TGA) using simulated flue gas [18,19]. They concluded that after four cycles the sorbents were essentially inert [18]. Here we use a simple treatment to estimate the extent of CaO utilisation as a function of reactivation time. As has been mentioned earlier, currently an acceptable level of limestone utilisation in CFBC is 30–40%. Assuming that the amount of sulphated CaO is approximately proportional to the total amount of CaO so that after each reactivation process, the degree of CaO utilisation remains unchanged, we have

$$Y = (1 - X)^N \tag{19}$$

where Y is the unconverted fraction of CaO; X the degree of conversion of CaO in the combustor in one cycle; and N is the number of cycles. Fig. 6 shows predicted values for Y as a function of N according to Eq. (19), in comparison with the conversion of CaO observed by Marquis et al. [18]. The value of X is taken to be 0.32, which is the conversion of CaO in the limestone prior to the first reactivation cycle. It

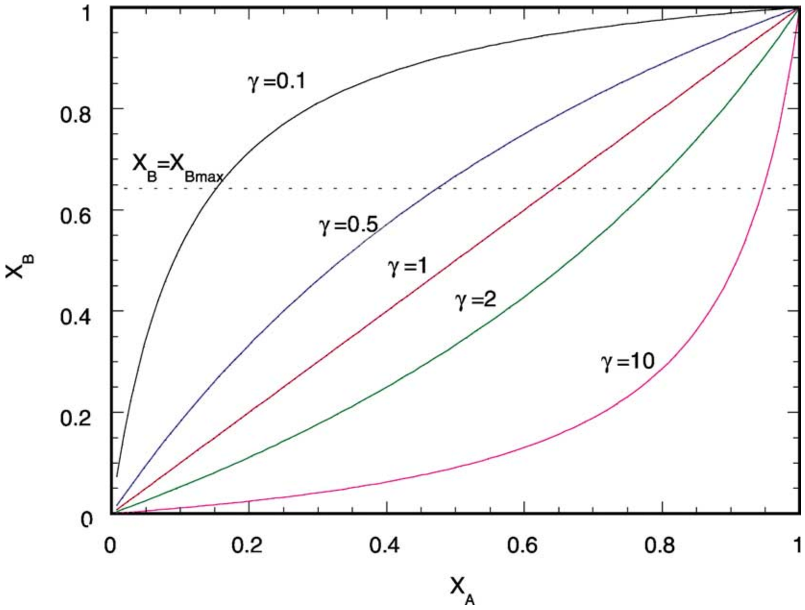

Fig. 5. Predicted conversion of cementing materials as a function of conversion of CaO to $Ca(OH)_2$ in wet grinding of FBC ash: X_A and X_B are the conversion rates of CaO and the cementing materials, respectively; γ the ratio of hydration rate coefficients k_A/k_B; $X_{B,\max}$ the acceptable conversion level of the cementing materials, which would depend on properties of ash.

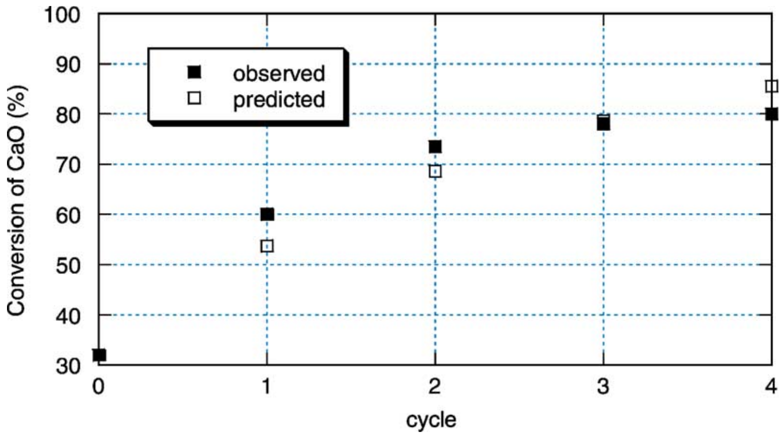

Fig. 6. CaO sulphation with repeated hydration of spent sorbent. The solid symbols represent measured values [17]. The open symbols represent predicted values based on Eq. (19).

can be seen that for the first two cycles, the sulphation rate of the reactivated ash was higher than the predicted values, structural changes in the ash which gave better sulphation performance than the original sorbent. With further reactivation, the difference diminished and overall the prediction based on Eq. (19) gives reasonable agreement with the observed result. It should be noted that the reactivation process used by Marquis et al. did not include grinding. With incorporation of grinding, the conversion level of CaO may be higher. However, as can be understood from Eq. (19), the conversion decreases with increasing cycles. For FBC applications, an optimum for the extent of CaO utilization should be determined.

5. Conclusions

Pilot plant experiments have shown that reactivation of spent sorbent by wet grinding appears to be quite effective. With a given Ca/S stoichiometry, sulphur capture efficiency of the reactivated sorbent was higher than that of the parent limestone. The wet grinding process and subsequent dehydration of $Ca(OH)_2$ increased the porosity or specific surface area of the particles, and enhanced the SO_2 capture. However, the wet grinding process itself requires good control, which may be difficult to achieve in an industrial process, to avoid excessive formation of concrete-like material due to cementation of ash components. To find a solution to the problem, further studies on the wet grinding process are required.

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