

The Effect of Hydration on the Reactivation of CFBC Ash

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ABSTRACT

A detailed study has been carried out on how hydration methods and conditions influence the sulphur capture potential of ash from a 165 MWe circulating fluidized bed combustion (CFBC) boiler. CFBC ashes hydrated with water and high-pressure steam were sulphated for 90 min in simulated flue gas (SO₂ 5000 ppmv, CO₂ 15%, O₂ 2.5%, N₂ balance) in a thermogravimetric analyzer (TGA) at 850°C to investigate how reactivation conditions affect the final sulphur capture behaviour of the ash. Fly ash and two size fractions of bottom ash were tested. The unhydrated bottom ash showed additional Ca utilization of 15-25% and the SO₂ removal ability was increased significantly after hydration with either water or steam. By contrast, the fly ash showed no such improvement. Untreated fly ash demonstrated maximum SO₂ absorption capacity of 500 mg SO₂/g for the three ash samples tested, and hydration with high-pressure steam or liquid water was ineffective in enhancing this value. In fact, more severe steam hydration treatment actually worsened the sulphur capture potential of fly ash. This work suggests that hydration is an effective measure for reactivating the bottom ash but not fly ash, which should either be re-used directly or reactivated in some other manner to improve its sulphur capture potential.

INTRODUCTION

Fluidized bed combustion (FBC), both circulating and bubbling, is an attractive technology that can achieve *in situ* SO₂ removal by injecting calcium-based sorbent in the combustor (Anthony and Granatstein, 2001). Limestone and dolomite can be used for this purpose, although calcitic limestone is the most commonly employed sorbent. In the atmospheric FBC limestone first calcines and then sulphates in a manner which can be described by the overall reactions:



The molar volumes of CaCO₃, CaO and CaSO₄ are 37, 17 and 46 cm³/mol, respectively (Lide, 2001). When limestone calcines it produces a porous CaO matrix which then sulphates. As the sulphate layer forms, the original pores are filled and blocked, preventing SO₂ reaction with the unreacted CaO core. Consequently, Ca utilization in FBC systems is rather low, typically less than 45% and Ca/S molar ratios of 2 to 2.5 are commonly used to achieve 90% SO₂ removal efficiency.

Ash produced in the FBC process usually contains 20-30% unreacted CaO because of the excess Ca sorbent use. The reactivation of spent sorbent by hydration with either water or steam can improve the sorbent utilization. During hydration of the partially-sulphated residue, water or steam permeates the outer CaSO₄ layer and reacts with CaO in the core. Since the reaction

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product, $\text{Ca}(\text{OH})_2$, has a larger molar volume ($33 \text{ cm}^3/\text{mol}$) than the CaO , the core swells, leading to cracking of the sulphated shell. When the reactivated sorbent particles are re-injected into the fluidized bed, the $\text{Ca}(\text{OH})_2$ in these particles decomposes and previously inaccessible CaO becomes available for further sulphation (Couturier *et al.*, 1994; 1999; Laursen *et al.*, 2000).

EXPERIMENTAL

The partially-sulphated material (including fly ash (FA) and bottom ash (BA)) used in this study was obtained from the NSPI 165 MWe CFBC boiler at Point Aconi, Nova Scotia, Canada, which currently fires petroleum coke and coal blends at a mass ratio of about 60:40. Proximate and ultimate analyses for the fuels, which were fired in a 50:50 blend during the production of the ash examined here, are listed in Table 1. The sorbent used in the boiler for capturing SO_2 was a local calcitic limestone called Kelly Rock and the CaCO_3 content in the limestone is typically 90-92%.

The bottom ashes were first sieved into several size fractions: <75, 75-150, 150-300, 300-600, 600-1400, and >1400 μm . The size distributions are given in Table 2. The medium size ranges of 150-300 and 300-600 μm accounted for most of the bed ash sample mass, 62% and 23% respectively, and it was decided to use these two size fractions in this study. These separated bottom ash fractions and the “as-received” fly ashes were then hydrated both with liquid water and saturated steam. The water hydration temperatures employed in this study were 5°C , ambient condition (*i.e.*, room temperature at about 20°C), 40, 60 and 80°C , and the hydration periods were 0.5 h, 1 h, 2 h, 3 h and 4 h at each temperature. The mass ratio of ash to water was 1:20 (Wu *et al.*, 2002, 2003a). Hydration with saturated steam was carried out in a pressure bomb (Parr 4522M Pressure Reactor) using tap water. A small amount of sample ($\sim 2 \text{ g}$) was put in a basket, which was suspended in the middle of the bomb and immersed in the steam during hydration. The hydration temperatures were 150, 200 and 250°C , with the corresponding saturated pressures of 4.8, 15.6 and 39.9 bar, respectively, for periods of 0.5 h, 1 h and 2 h at each temperature and pressure (Wu *et al.*, 2003b).

Once hydrated, the solids were rinsed with deionized water, filtered under suction for 1.5-2 min and transferred to a vacuum oven, maintained at 45°C , to dry for 3-4 h. This low temperature minimizes any effect of heating on gypsum or ettringite, if formed, and also helps to minimize any subsequent reaction of the sample with surface moisture. In practice, earlier studies have demonstrated that no gypsum or ettringite is formed under our conditions, and that reaction with any surface water is also minimal (Anthony *et al.*, 1999, Wu *et al.*, 2002, 2003a).

A selected series of hydrated fly ash and the two sizes of bottom ash specified above (BA150-300 and BA300-600), which represent 85 wt.% of the whole bottom ash, were chosen for sulphation tests. A limited number of tests were also carried out with bed ash fraction less than 75 μm . The sulphation was conducted for 90 min at atmospheric pressure in a simulated flue gas (SO_2 5000 ppmv, CO_2 15%, O_2 2.5%, N_2 balance) using TGA maintained at 850°C . A schematic of the equipment is shown in Fig. 1. Details of the TGA system are described elsewhere (Wu *et al.*, 2002a). The SO_2 stream was controlled by means of a mass flow controller at 100 mL/min in sulphation. About 30 mg of sample was placed in a holder suspended in the middle of the reactor tube for each run, and was quickly heated in N_2 from room temperature to 850°C in 40 min prior to the experiment. Upon attaining 850°C , the N_2 flow was switched to the SO_2 gas mixture, and the sample held under these conditions for the designated 90 min sulphation. Weight loss and gain during both heating and sulphation were continuously recorded. The sample weight used for the sulphation calculation was based on the weight recorded at 850°C just prior to switching to

the SO₂ gas mix. At this temperature all Ca(OH)₂ and CaCO₃ in the sample can be expected to have decomposed completely prior to the sulphation process.

RESULTS AND DISCUSSION

Chemical analyses of the original fly ash and the two bottom ash fractions were obtained by X-ray fluorescence (XRF) and are given in Table 3. Carbonate analysis is provided in Table 4, and the extent of carbonation is negligible for the bed ash, but not for the fly ash. Ca utilization in the received samples was 30% in the FA, 32% in the BA300-600 and 44% in the BA150-300, which is typical of normal sorbent conversions in CFBC systems. Table 5 shows the free lime and Ca(OH)₂ content in the original samples. Free lime is defined as the sum of [CaO + Ca(OH)₂], expressed as CaO percent (Iribarne *et al.*, 1994). Back calculation of free lime from the chemical analysis is significantly higher than that determined by the modified sucrose method, which provides a direct chemical measurement of free lime (Wu *et al.*, 2002). In the case of the bottom ash fraction this difference is much larger than would be possible as a result of experimental error and indicates that some of the CaO has combined with fuel ash components, the so-called other calcium compounds (OCCs), *e.g.*, Ca aluminate, silicate, ferrite, and in the case of any ash produced from petcoke firing, also vanadates, *etc.* (Anthony 1997a, b).

Sulphation without Hydration

The effective conversion of the free lime in the bottom ash after 90 min of sulphation is shown in Fig. 2a. It increased by 15 and 25% for BA300-600 and BA150-300, respectively. However, untreated fly ash had a very strong ability to absorb additional SO₂, resulting in an apparent final Ca conversion far greater than 100%, calculated based on the utilization of free lime or available CaO in the sample. An alternate measure of SO₂ absorption, based on mg SO₂ absorbed/g sample was, therefore, used hereafter to compare sample performance. Fig. 2b shows the remaining absorption of the two bottom ash fractions was similar, 55 and 48 mg SO₂/g sample for BA300-600 and BA150-300, respectively, while the untreated fly ash showed the highest value of ~510 mg SO₂/g.

A simple explanation of these results is provided by the observation that when fly ash was heated to 850°C in N₂, a significant weight loss was observed starting around 820°C demonstrating that some of the original CaSO₄ decomposed because the char carbon in the fly ash acted as a reducing agent. The quantitative X-ray diffraction (QXRD) analyses for the original fly ash and the residue after heated in N₂ at 850°C for 1 h are shown in Table 6. It should be noted that CaSO₄ in the original sample decomposed to a major extent and a significant amount of CaS was detected. A detailed Fourier Transform Infrared/Thermogravimetric (FTIR/TG) test was also conducted on the original ash holding at 1000°C in helium for 15 min and it showed that 25% of the CaSO₄ decomposed over this time based on the SO₂ emitted. In the following sulphation tests on the fly ash, the temperature was, therefore, maintained at 850°C in N₂ for 1 hour until completion of this decomposition occurred, before switching to SO₂ for 90 min sulphation. The initial weight for the sulphation calculation on fly ash was thus at a lower level, allowing the high SO₂ absorption observed to occur. It should be noted that the calculation presented here reflects the total capacity of SO₂ absorption, and prior CaSO₄ decomposition should still give comparative results; it should also be noted that calcinations of reactivated ashes under N₂ have been used by other workers (Volmerange, 1994; Couturier *et al.*, 1999; Agnihotri, *et al.*, 1999). However, to deal with this issue, some fly ash was first treated in an open crucible at 800°C, to remove any char carbon and this material was then investigated to determine its potential to be reactivated by hydration, and these results are presented later.

Sulphation with Hydration

The sulphation performance of hydrated bottom ash and fly ash are shown in Figs. 3-5, along with the data for the untreated ashes, for comparison. The behaviour of the two bottom ashes appears very similar when expressed in terms of the total SO₂ absorption. The sample hydrated at 5°C and ambient conditions showed a clear increase of SO₂ absorption with increasing hydration time (Figs. 3a, 3b, and 4a, 4b). The results for 4-h hydration in ambient condition show increases of more than 3 fold up to 150 and 190 mg SO₂/g for BA150-300 and BA300-600, respectively, when compared with the nonhydrated ashes.

It is worth commenting here that direct hydration studies (Wu *et al.*, 2003a) on this ash have failed to indicate the sulphate ion migration effect noted by Scala *et al.*, 2001, and this has also been confirmed by the originators of this observation in a joint study (Montagnaro *et al.*, 2003) with this bed ash and hence this phenomenon should not be used to explain the improvement in performance over longer hydration times.

a) Hydration with Liquid Water

Equally interestingly, longer hydration times at 60°C, shown in Figs. 3c and 4c, were less effective than for hydration at ambient conditions, as shown in Figs. 3b and 4b. Thus, the BA300-600 ash fixed about 220-250 mg SO₂/g from 30 min to 4 h hydration, while the SO₂ absorption for BA150-300 showed only a small increase at 60°C over the 30-min-hydration result of 145 to ~190 mg SO₂/g for the longer time. Higher hydration temperatures also increased the amount of SO₂ absorption significantly. One way of explaining these results is to note that hydration for this ash consists of a two-step process, a rapid hydration period which typically finishes in 5 to 10 minutes, followed by a much slower process that lasts for several hours [Wu *et al.*, 2003a] and that, for the rapid hydration period, the absolute amount of Ca(OH)₂ produced increases at higher temperatures. For instance, in BA150-300 the Ca(OH)₂ content increased from 6.2 wt.% at ambient hydration for 30 min, to 8.8 wt.% for 4 h (Wu *et al.*, 2003a), thus providing more available CaO for sulphation after a longer period of hydration. Also, vigorous hydration has been shown to be associated with the development of a much greater degree of fragmentation in the bed ash particles [Wu *et al.*, 2003a, b]. Therefore, one could envisage that, for short-term hydration at low temperatures, not only is the absolute amount of Ca(OH)₂ lower, but the mechanical damage to the particle sulphate shell (Fig. 6) due to expansion and dehydration is also reduced with a corresponding decrease in reactivation. Hence, longer hydration which can produce more Ca(OH)₂, makes more calcium available and thus enhances ash reactivation.

For ashes hydrated at higher temperatures, not only is the absolute amount of Ca(OH)₂ increased at shorter times, but the morphology of the particle also changes more rapidly, making the reactivated ash a more effective sorbent. Namely, there is more pronounced cracking of the sulphate shell earlier on. At higher temperatures, since more of the original CaO is converted to Ca(OH)₂ in the first 30 minutes, longer residence times are subject to the law of diminishing returns and produce only marginal gains. Furthermore, since the solubilities of both Ca(OH)₂ and CaSO₄ fall with increasing temperature [Bott, 1995], any mechanism that involves solubilization of these salts ought to be less effective when hydrating bed ash with water at higher temperatures and so a cracking explanation which produces a more active sorbent seems the most likely explanation for these results.

b) Hydration with Steam

For the steam hydrated sample (Figs. 3d and 4d) SO₂ absorption was enhanced over treatment by water. Thus, 30 min in 150°C steam greatly improved the SO₂ absorption for the sample to levels of 250 mg SO₂/g sample of BA150-300, and to levels of 290 mg/g after 2 h in the steam. For the BA300-600 sample, sulphation levels reached 320 mg/g at 150°C and 2 h in contact with steam,

and up to 370 mg SO₂/g in 200°C steam for 2 h. However, at a higher temperature of 250°C, the conversions decreased to about 330 mg/g. This result implies that the use of very high temperature steam may not only fail to improve SO₂ absorption of a bed ash but may actually reduce its SO₂ carrying capacity. These results are not in agreement with the work of Couturier *et al.*, 1994, and Laursen *et al.*, 2001, which found that water was normally more effective than steam in reactivating ashes. However, perhaps the difference is due to the use of pressurized steam in this work, which achieves complete hydration within one half hour in our experiments, and it should be noted that the CERCHAR process which involves pressurized steam up to about 6-10 bars, is also able to achieve complete hydration of bed material in a matter of minutes [Blondin, 2003]. However, it does agree with previous work in terms of suggesting that a severe hydration process (*i.e.*, either due to hydration at longer times or higher temperatures) reduces the activity of the reactivated sorbent.

The surface measurement of steam-hydrated BA300-600 (based on N₂ adsorption-desorption analysis on a Micromeritics ASAP 2100 Analyzer), shown in Table 7, also supports the hypothesis that increasing the severity of the steam hydration conditions actually impairs the sulphur capture capability of the sorbent. Here, the Brunauer-Emmett-Teller (BET) surface area of the BA300-600 material increased from 1.03 m²/g (untreated) to 6.6 m²/g (2 h in 150°C steam). However, using a steam temperature of 250°C for 2 h, the BET surface area fell to 2.4 m²/g. The pore volume and pore average diameter in the samples showed a similar trend. These results are consistent with Davini's (2002) work in that they suggest that there is an optimum surface area, and that more severe conditions actually cause structural impairment of the sorbent which reduces its ability to react with SO₂. In Davini's work he investigated the BET area of three calcium-based spent sorbents hydrated by atmospheric pressure steam at different temperatures and found an optimal BET and hydration temperature at 300°C in his tests.

c) Fly Ash Hydration/Sulphation

Fly ash shows very different sulphation behaviour. Hydration with either water or pressurized steam caused no enhancement of the sulphur capture capability of this ash, and if anything actually produced a deleterious impact on SO₂ absorption, although this ash had the highest remaining SO₂ removal ability when untreated. Fig. 5a shows the residual SO₂ absorption at about 510 mg SO₂/g sample for hydration at ambient conditions. In Figs. 5b and 5c, the final conversion levels were found to fall to ~460 mg SO₂/g for hydration at 60°C and down to 410 mg SO₂/g after 2 h in steam at 200°C. The surface analysis of steam-hydrated fly ash, shown in Table 7, did not reveal any significant increase in surface area of the sample and actually showed a decrease for longer steam treatment, leading to a negative influence on SO₂ absorption, which agrees with the sulphation results.

Scanning electron microscopic (SEM) analysis was undertaken on BA300-600 ash using a Hitachi S-750 with a Link AN 10/85S energy dispersive X-ray (EDX) system. SEM photographs in Fig. 6 show the effect of hydration on the surface structure of this bed ash. It is clear that there is a whole or integrated shell of sulphation product surrounding most of the untreated particles. After hydration, the shell was cracked and broken or completely lost, thus exposing the unreacted Ca core, making it available for re-sulphation. EDX mappings in this study show no evidence of the sulphate ion migration phenomenon observed on another type of ash by Scala *et al.*, 2001. An obvious explanation for the discrepancy might be that these workers have hitherto worked with synthetic ashes whereas in the Point Aconi CFBC boiler, residence time scales experienced by bed particles are much longer, and probably more importantly, the temperatures and temperature fluctuations are higher, *e.g.*, 900°C or more in the upper part of the Point Aconi boiler is not unknown (Richards, 2003). However, a more detailed investigation of this difference is beyond the scope of this paper, and is currently being investigated as part of a joint study (Montagnaro *et*

al., 2003). Another important fact is that the failure of fly ash (which here has a mean size of $\sim 30 \mu\text{m}$) to respond to reactivation agrees very well with the observation for bed ash by Laursen *et al.*, 2000, 2001, that the existence of a well-defined core/annulus structure in the sulphated particle is critical. The failure of fly ash to be reactivated by water also agrees with the earlier work of Couturier *et al.*, 1994, who studied the reactivation of fly ash with both water and atmospheric pressure steam, and with the work of Schmal, 1985, who showed that filter ash could not be reactivated by hydration. Similarly, Argonne National Laboratories also found that for baghouse ash from the 6'x6' FBC unit owned and operated by Babcock and Wilcox, performance actually deteriorated following hydration treatment (Johnson *et al.*, 1981). The fly ash particles are too small to have the core/annulus structure and instead show continuous sulphation (Fig. 7). Certainly, physical effects were found to be very limited for fly ash after hydration. In light of these facts their failure to be reactivated might be expected. However, it should be noted that reactivation of fly ash has been reported several times (Julien *et al.*, 1995; Khan *et al.*, 1995; Tsuo *et al.*, 1999). In the first two cases the ashes examined came from small pilot-scale rigs, and so this may explain this result (*i.e.*, particles are coarser than fly ash from a full-scale industrial boiler); in the last case there is no obvious explanation other than that the tests were done in a small industrial boiler, and if the fly ash suffered some agglomeration from the hydration process, then its residence time and utilization may have increased even if this ash was not actually reactivated by hydration.

An important difference between fly ash and bed material is a potentially quite significant amount of char carbon (3%+) in the former. In order to determine what effect this might have fly ash was also heated in a crucible to 800°C for 2 hours to remove char carbon. Fig. 8 gives the results, which show that the sulphur uptake is dramatically reduced from 500 to 250 mg SO_2/g of sample, and that again reactivation with water fails to reactivate such ashes.

Fly ash often represents the majority of the solid ash product produced by a CFBC. Further, it will tend to have relatively low sulphation levels given its extremely short residence times in a boiler (typically seconds to minutes). This raises the question as to what strategies are there for using it in a reactivation step. It has been long known that, since fly ash is extremely reactive [Lyngfelt and Leckner, 1991], it can be reinjected directly. However, that does not deal with the issue of short residence times. This work clearly shows that hydration is an ineffective strategy, albeit that it has yet to be shown that the current findings are general. However, since we have a basic explanation from the work of Laursen *et al.*, 2000, 2001, it is reasonable to assume that this is a general finding. This leaves pelletization of such material as one solution, and CETC work showed that this was an effective, although expensive reactivation method [Anthony and Granatstein, 2001]. The benefits of pelletization of fly ash have also been demonstrated at the industrial level (Moe *et al.*, 1995). However, there is a new way of carrying out this step, in a cost-effective manner, and this idea has been jointly patented by General Communion and CETC, and demonstrated with a small industrial CFBC boiler at Purdue University [Anthony *et al.*, 2003]. Here, the bed ash is wet ground to accelerate the hydration process to occur in a few minutes. The fly ash (or any other suitable material such as stoker ash) is backmixed into the resulting slurry to produce a "dry pelletized material, which is then lightly ground and reintroduced into the boiler. In this way fly ash can be reinjected into the bed in a manner that is likely to increase its residence time without wasting energy by hydrating it, something that this study has shown to be ineffective.

As a check on whether fly ash is distinctly different from bed materials, a number of tests were also done on fine materials: the fine limestone used by NSPI, following 120 minutes sulphation in a gas-fired FBC [Montagnaro *et al.*, 2003], and the fine bed fraction from the Point Aconi boiler ($<75 \mu\text{m}$). In the case of the synthetic fine bed ash, it is clear that some agglomeration or simple

removal of very fine material is occurring (Table 8) and the mean size increased from 80 to 200 μm , although the bed material still remains extremely fine. However, as Fig. 9 shows, this material is clearly reactivated by hydration. Similarly, fine bed material ($<75 \mu\text{m}$) also showed that it could be reactivated by means of hydration (Fig. 10), albeit that fine sorbent particles are already very reactive and hence, any improvement by hydration is more marginal, as has been noted earlier by Schmal, 1985.

CONCLUSIONS

Fly ash and two sizes of bottom ash (BA150-300 and BA300-600) from a 165 MWe CFBC boiler was hydrated with liquid water and high-pressure steam and then resulphated in a TGA at 850°C for 90 min. The unhydrated bottom ashes showed an additional Ca utilization of 15-25% and the SO_2 removal ability was significantly increased following hydration by either water or steam. For ashes hydrated at ambient or lower temperatures, longer hydration times corresponded to better sulphation performance, while for ashes hydrated at higher temperatures, longer hydration times produced much smaller effects, even though the ashes were not completely hydrated in either case. The fly ash, however, has shown quite different behaviour. Fly ash first heated in N_2 and then sulphated, gave a maximum SO_2 absorption of 500 mg SO_2/g for the three samples examined. Moreover, there was no evidence of reactivation due to any hydration treatment attempted. Also, drastic steam hydration treatment actually reduced SO_2 carrying capacity of the fly ash. This work suggests that, while hydration is an effective measure for reactivating bottom ash, it is ineffective for fly ash. If this ash stream is to be used it might as well be used directly rather than being hydrated. This observation agrees with the hypothesis on steam hydration which suggests that particles with a well-defined core/annulus structure are most readily reactivated by hydration treatments and that particles which show continuous sulphation cannot be reactivated by hydration treatments. What is less clear is why very fine bed materials are reactivated by hydration. A complete explanation of this difference is currently lacking.

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Table 1. Proximate and Ultimate Analyses of the Fuels

Delayed Petroleum Coke			
Proximate Analysis (as received, wt.%)		Ultimate Analysis (dry basis, wt.%)	
Moisture	5.89	Carbon	86.18
Ash	0.31	Sulphur	6.65
Volatile Matter	9.37	Hydrogen	3.56
Fixed Carbon	84.43	Nitrogen	1.45
		Oxygen (by difference)	1.83
		Ash	0.33
		Gross Calorific Value (MJ/kg)	35.3
Colombian Steam Coal			
Proximate Analysis (as received, wt.%)		Ultimate Analysis (as received, wt.%)	
Moisture	7.9	Carbon	68.44
Ash	6.94	Sulphur	0.73
Volatile Matter	35.88	Hydrogen	5.14
Fixed Carbon	49.28	Nitrogen	1.35
		Oxygen (by difference)	9.47
		Ash	6.94
		Chlorine	0.03
		Moisture	7.9
		Gross Calorific Value (MJ/kg)	28.6

Table 2. Particle Size Distributions of the Bottom Ash

Size Fractions, μm	Distribution, wt.%
>1400	4.16
600-1400	2.03
300-600	22.49
150-300	61.99
75-150	8.21
<75	1.13

Table 3. Chemical Analyses in Oxide Form, wt.%

	Fly Ash	Bottom Ash <75 μm	Bottom Ash 75-150 μm	Bottom Ash 150-300 μm	Bottom Ash 300-600 μm
SiO₂	15.92	15.34	7.98	6.77	7.27
Al₂O₃	4.72	3.57	2.24	2.23	2.30
Fe₂O₃	1.57	1.39	0.71	0.67	0.63
TiO₂	0.20	0.15	0.11	0.11	0.10
P₂O₅	0.052	0.029	0.024	0.032	0.032
CaO	46.44	43.55	51.08	52.59	59.11
MgO	0.78	0.68	0.59	0.61	0.67
SO₃	19.25	25.35	32.83	32.60	26.79
Na₂O	0.20	< 0.20	< 0.20	< 0.20	< 0.20
K₂O	0.86	0.46	0.21	0.18	0.27
BaO	0.213	0.875	0.093	0.043	< 0.030
SrO	0.039	0.061	0.037	0.037	0.040
V₂O₅	0.368	0.602	0.639	0.784	0.356
NiO	0.071	0.093	0.097	0.115	0.051
MnO	0.177	0.135	0.163	0.156	0.185
Cr₂O₃	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008
LOF	9.14	7.58	3.09	3.07	2.12
Sum	99.998	99.88	99.89	100.00	99.92

Table 4. Carbonate Analyses (wt.%)

	Fly Ash	Bottom Ash <75 μm	Bottom Ash 75-150 μm	Bottom Ash 150-300 μm	Bottom Ash 300-600 μm
Total Carbon	4.27	2.45	0.23	0.10	0.36
Carbon Dioxide	2.69	0.72	0.50	0.34	0.56

Table 5. Free Lime and Ca(OH)₂ Content Before Hydration (expressed as CaO, wt.%)

Bottom Ash	Free Lime^a	Ca(OH)₂^b
Unsieved sample (as-received)	19.1	-
Size Fractions, μm		
600-1400	27.1	2.23
300-600	31.1 (39.63 ^c)	1.31
150-300	15.4 (29.32 ^c)	0.89
75-150	18.2 (27.44 ^c)	1.32
<75	19.1 (24.87 ^c)	5.44
Fly Ash (as-received)	26.7 (29.53^c)	4.55

a: by sucrose method; b: by TGA pyrolysis; c: by back-calculation from chemical analysis

Table 6. QXRD Analysis of Fly Ash (wt.%)

	Original Fly Ash	Heated in N₂ at 850°C for 1 h
CaSO ₄	43.09	4.77
SiO ₂	9.37	9.88
CaCO ₃	4.05	-
Fe ₂ O ₃	0.75	-
Ca(OH) ₂	5.32	1.31
CaO	12.05	44.18
CaSO ₃	-	2.39
CaS	-	7.82
Ca ₃ Fe ₄ O ₄ S ₃	-	1.99
Crystallinity	74.64	72.32
Amorphous	25.36	27.68

Table 7. Surface Analysis of Steam-hydrated Fly Ash and Bottom Ash (300-600 µm)

	BET, m²/g	BJH adsorption pore volume, cm³/g	BJH adsorption pore average diameter, Å
BA, untreated	1.03 ± 0.0066	0.00337	156.6
BA, 150°C, 2 h	6.57 ± 0.05	0.0457	297.4
BA, 200°C, 2 h	3.37 ± 0.031	0.0138	194.7
BA, 250°C, 2 h	2.44 ± 0.012	0.0116	189.6
FA, untreated	5.08 ± 0.018	0.0256	223.9
FA, 200°C, 0.5 h	7.02 ± 0.032	0.0405	241.8
FA, 200°C, 1 h	5.77 ± 0.042	0.0381	288.3
FA, 200°C, 2 h	4.77 ± 0.016	0.0236	215.4

Table 8. Size Change of Original and Sulphated NSPI Limestone (wt.%)

Size (µm)	Limestone	Ash after Sulphation
<38	33.57	0
38-45	2.8	0
45-75	11.19	0
75-106	7.69	3.47
106-150	10.49	16.12
150-250	13.99	39.9
>250	20.28	40.51

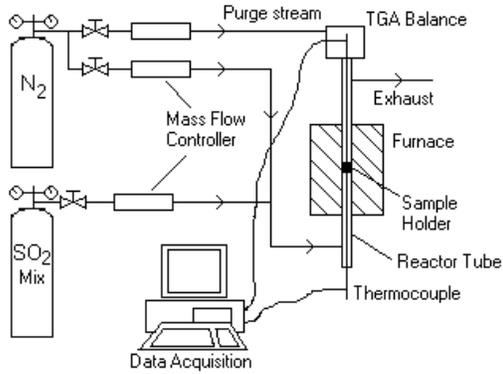


Figure 1. Schematic Diagram of Sulphation Apparatus

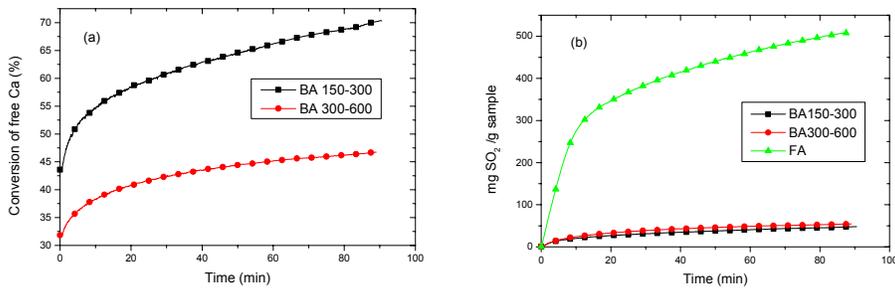


Figure 2. Remaining SO₂ Absorption of Untreated Ash

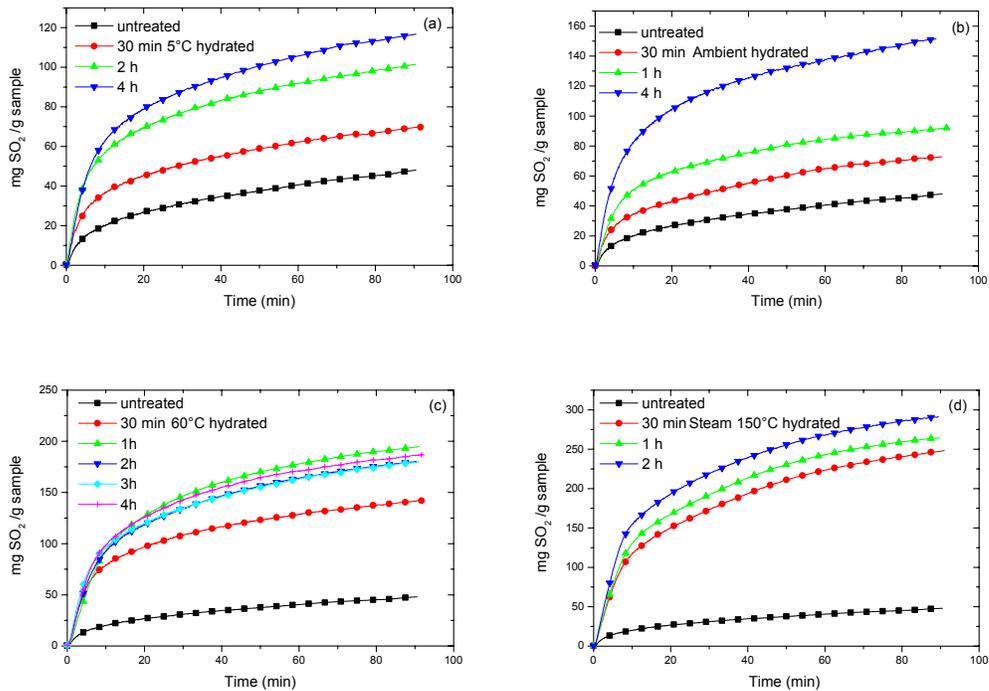


Figure 3. Sulphation of Hydrated Bottom Ash (150-300 μm)

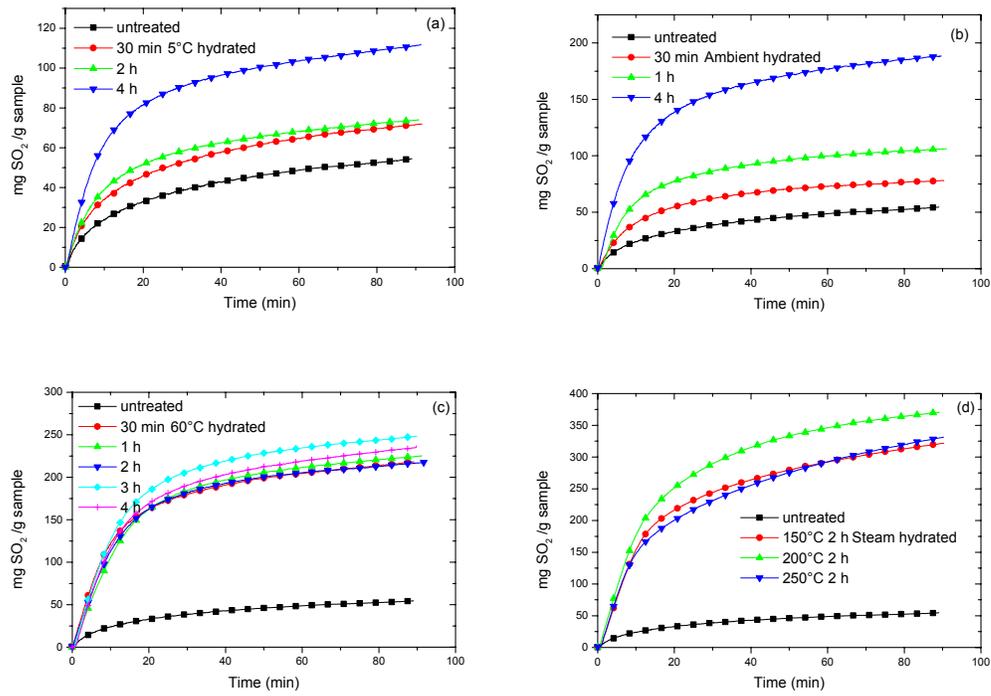


Figure 4. Sulphation of Hydrated Bottom Ash (300-600 μm)

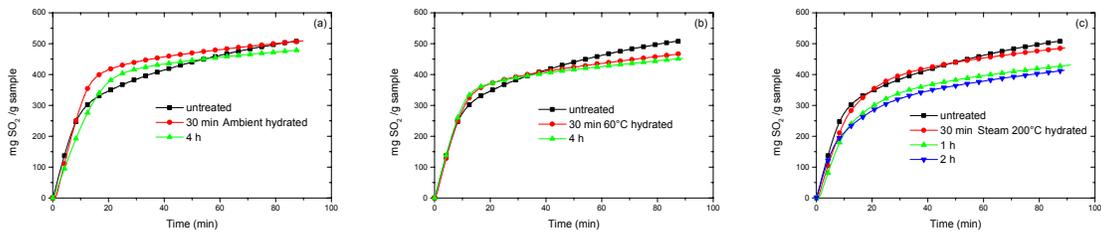
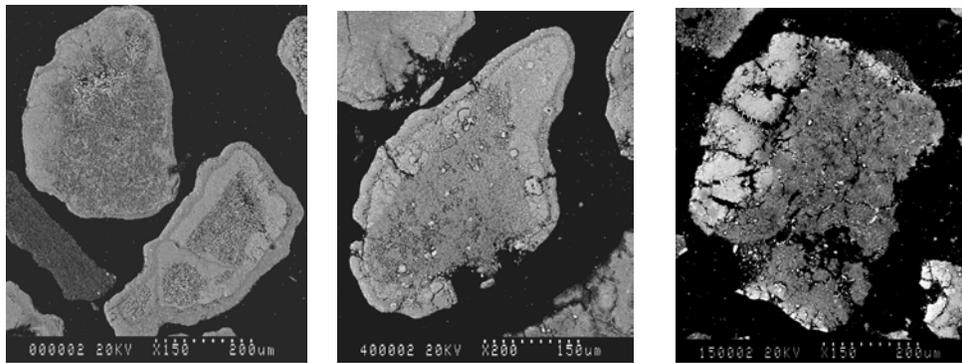


Figure 5. Sulphation of Hydrated Fly Ash



(a) untreated (b) water, 40°C, 0.5 h (c) steam, 150°C, 0.5 h
Figure 6. Hydration Effect on Bottom Ash (300-600 μm)

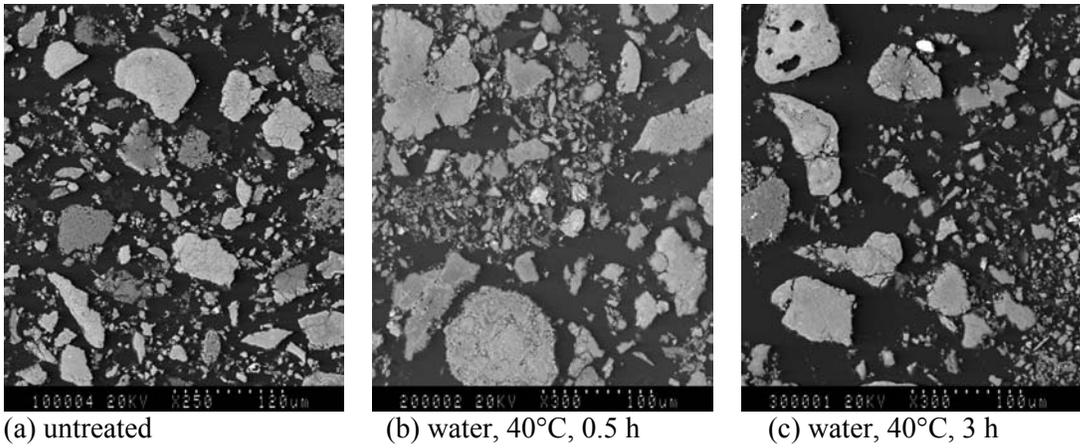


Figure 7. Hydration Effect on Fly Ash

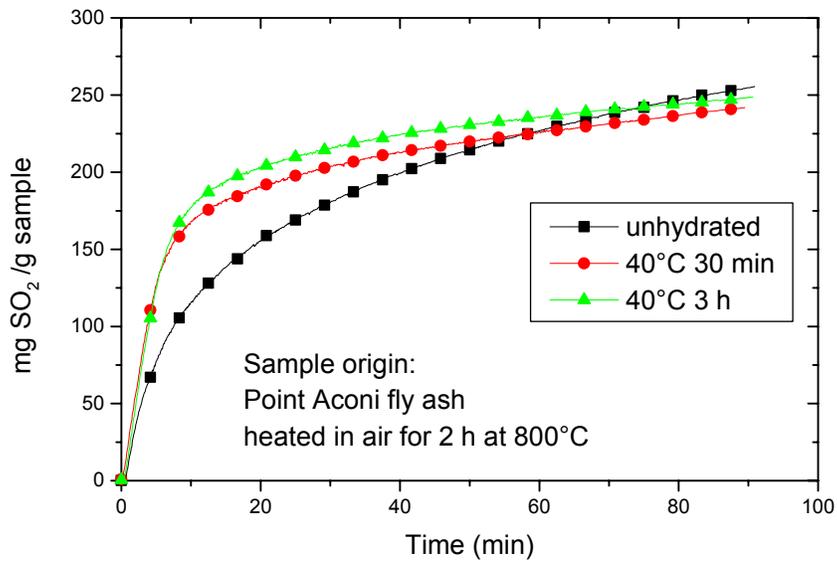


Figure 8. Reactivation Characteristics of Preashed Fly Ash

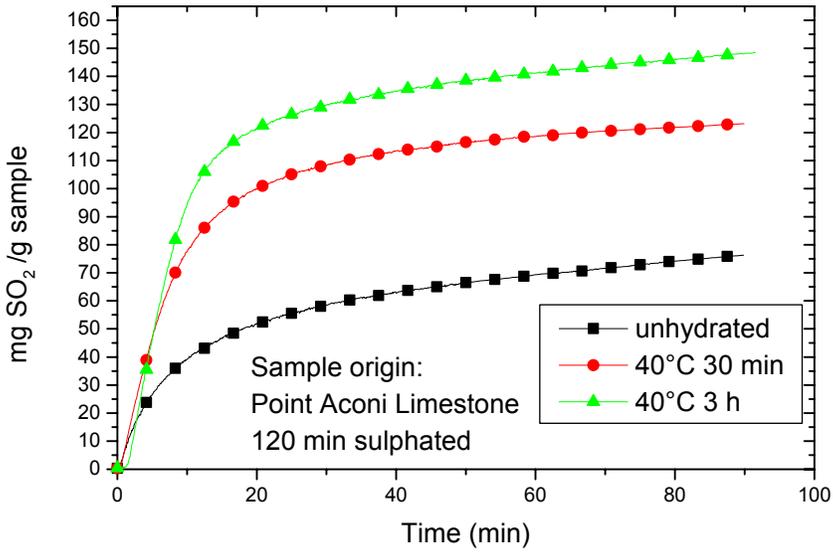


Figure 9. Reactivation Characteristics of Fine Synthetic Bed Ash

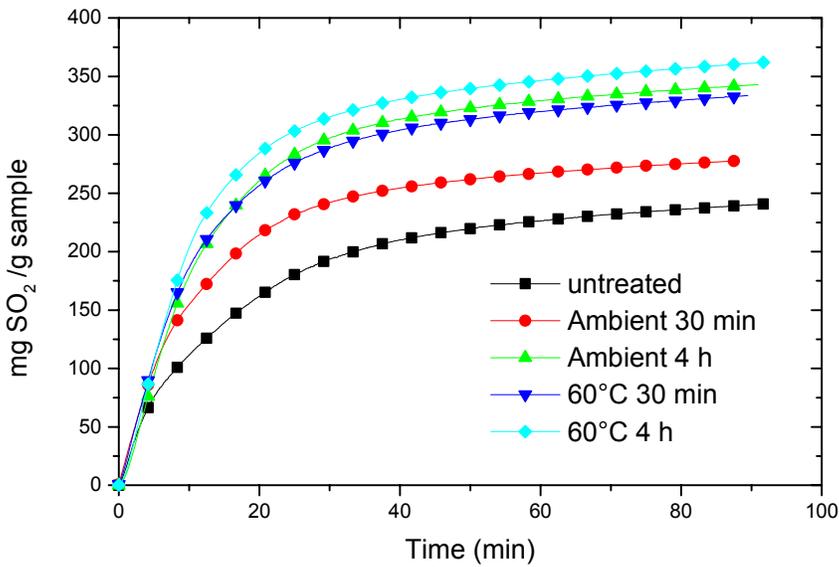


Figure 10. Reactivation Characteristics of Fine Bed Ash (< 75 µm)