Strength Development Due to Long Term Sulfation and Carbonation/Sulfation Phenomena

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CFBC boilers firing high sulfur, low ash fuels can produce deposits consisting of almost pure $CaSO_4$. Test work has shown that if sorbents or bed materials are sulfated for long times (several days or more), they develop compositions similar to those deposits. Sulfation increases with temperature from 650°C to 900°C, and strength increases continuously in the temperature range of 650°C to 950°C. When sulfation occurs under conditions where $CaCO_3$ is stable, the overall strength of the deposit increases but the degree of sulfation diminishes. Finally, this work suggests that pellet tests using crushed and calcined sorbents can give misleading information and should be used with caution to study the phenomena described here.

Les chaudières CFBC brûlant des combustibles à faible teneur en cendres et forte teneur en soufre produisent des dépôts formés de CaSO4 presque pur. Les essais montrent que si les sorbants ou les matériaux de lit sont sulfatés pendant une longue période (quelques jours ou même davantage), ils développent des compositions semblables à ces dépôts. La sulfatation augmente avec la température de 650°C à 900°C, et la teneur augmente en continu dans la gamme de températures de 650°C à 950°C. Lorsque la sulfatation a lieu dans des conditions où le CaCO3 est stable, la teneur globale du dépôt augmente mais le degré de sulfatation diminue. Enfin, ce travail suggère que les essais basés sur des pastilles constituées de sorbants concassés et calcinés peuvent fournir des informations trompeuses et devraient être utilisés avec précaution dans l'étude des phénomènes décrits ici.

Keywords: CFBC, agglomeration, sulfation, carbonation.

Circulating fluidized bed combustion (CFBC) boilers burn high-sulfur fuels such as petroleum coke and high-sulfur coal, while meeting stringent SO_2 emission standards by feeding limestone to the boiler. At atmospheric conditions, the limestone first calcines and then sulfates in a process that can be described in terms of a two-step global reaction scheme:

$$CaCO_3 = CaO + CO_2 \tag{1}$$

$$CaO + SO_2 + 1/2O_2 = CaSO_4 \tag{2}$$

For pressurized fluidized bed combustion (PFBC), where the pressure is typically 1 to 2 MPa (Alaverez-Cuenca and Anthony, 1995) the sulfation process for calcitic limestones can be described by means of the following global reaction:

$$CaCO_3 + SO_2 + 1/2O_2 = CaSO_4 + CO_2 \tag{3}$$

Sulfation (or conversion levels) of the spent sorbent leaving the CFBC is typically limited to 30% to 50%. This incomplete conversion is due to the greater molar volume of $CaSO_4$ compared to that of both $CaCO_3$ and CaO (46 mL/mol, compared with 37 and 17 mL/mol, respectively (Weast, 1980). The sulfate product forms a dense sulfate shell, which blocks off the centre of the particle, leaving a significant amount of Ca in the sorbent-derived particle unconverted (Anthony and Granatstein, 2001). This type of reaction is commonly referred to as the core-shell or unreacted core model. Although, limestones are in fact capable of sulfating in at least three different modes (see Figure 1): via the core-shell pattern as noted above; via a network of cracks and macropores in the sorbent; and homogeneously (Laursen et al., 2000). Most limestones show some combination of these patterns, although the core-shell arrangement seems more common for larger sized particles (probably > 0.1 mm). Nonetheless, the universal experience from FBC boilers is that sorbent conversions are well below quantitative values.

Two major operational problems are often attributed to the addition of limestone to FBC: bed agglomeration and fouling. Traditionally,

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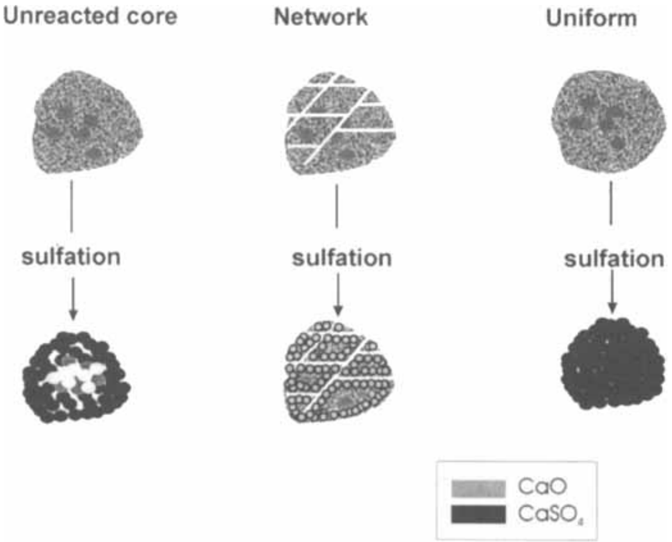


Figure 1. Sulfation patterns according to Laursen et al. (2000).

calcium rich agglomerates and low temperature fouling in the convective pass, have been reported to be strongly associated with the presence of Na or K (for FBC and pulverized coal (PC) systems) and also V (for petroleum coke fired system) (Walsh et al., 1992; Benson et al., 1995; Vuthaluru et al., 1999; Bott, 1995). However, Anthony and co-workers (1997, 2000, 2001) have identified high levels of sulfation as a cause of strength development in deposits seen in boilers firing high-sulfur fuels (normally petroleum coke). Specifically, they found monolithic deposits often with characteristic lengths of metres in the upper part of the furnace, the cyclone, and on superheaters. These deposits consisted of almost pure $CaSO_4$ (i.e., 80% to 95%), or mixtures of $CaCO_3$ and $CaSO_4$ in cooler regions of CFBC boilers (<780°C). These workers have further shown that the V content of the fuel is not responsible for the fouling in petroleum coke fired boilers by demonstrating that the V is bound-up in high melting point Ca or Mg vanadates.

Experiments conducted in a temperature-controlled oven have shown that the original bed ash or parent limestone will show strength development by sulfating them for sufficiently long periods (28 to 100 days). Since these materials typically have very low levels of Na, K or V (normally less than a few hundred ppm) (Anthony et al., 1998, 2000, and Anthony and Jia, 2000), this provides strong evidence that the sulfation and carbonation processes cause strength developments in deposits by themselves. However, this does not rule out that Na, K or V may be implicated in creating "stickiness" on surfaces, initiating such deposits.

There are at least four possible mechanisms, which either separately or, more likely in combination, might create solid deposits from the sulfated limestone-derived particles: 1) chemical reaction sintering, whereby reaction between the CaO or the $CaCO_3$ and SO_2 causes formation of $CaSO_4$ bridges, which bind the particles together; 2) molecular cramming, where particle expansion associated with product formation causes the sorbent particles to bond together; 3) bulk diffusion, arising because $CaSO_4$ is at or above its Tamman temperature (860°C) under normal FBC conditions (the Tamman temperature is half the absolute melting point of a solid compound, and is the temperature at which bulk diffusion and solid-solid reactions are known to become appreciably rapid (Garner, 1955)); or 4) appearance of a liquid eutectic between CaS and $CaSO_4$ created during the sulfation process.

The authors believe that strength development is most likely caused by a combination of mechanisms one and two. While chemical reaction sintering certainly occurs with FBC ash and limestones (Skrifvars et al., 1998), it is not by itself viewed as a sufficient explanation. This is because many of the limestone particles that sulfate by the core-shell pattern are 80% to 95% converted throughout the shell (Laursen et al., 2000). In consequence, they ought not to lend themselves readily to chemical reaction sintering. Molecular cramming is a process in which particle expansion (which must occur in the range of 60% to 70% conversion of CaO to $CaSO_4$ (Mattisson, 1998)) drives the initial bonding process, and, as the sulfate layer peels off, fresh unreacted CaO is exposed which can undergo chemical reaction sintering or pressure assisted sintering.

In the case of mechanism three, i.e., bulk diffusion, there is very little work specifically on the properties of $CaSO_4$ in FBC ash. However, $CaSO_4$ should show increasing signs of sintering by bulk diffusion as a function of boiler temperature and residence time. Iribarne et al. (1997) used the rate of dissolution of $CaSO_4$ as a measure of the reactivity of $CaSO_4$ from various boiler ashes. They showed that sulfated ashes from PC systems dissolved much more slowly than did similar ashes from FBC systems, and hence, in terms of this study, were much less "reactive", as would be expected given the much higher temperatures in PC boilers. Interestingly, the sulfate from an agglomerated CFBC deposit showed similar characteristics to those from PC boilers, but "unagglomerated" CFBC ash that had been exposed to sulfating conditions in a temperature-controlled oven at 850°C for 100 d behaved very similarly to other FBC ashes. Further, attempts to cause agglomeration of $CaSO_4$ by leaving it exposed to sulfating conditions for up to 100 d were unsuccessful. Only when the $CaSO_4$ was compressed with a pressure of 150 kPa (equivalent to a column of 9 m of loose material) did it form weak agglomerates (Anthony et al., 1998; Anthony and Jia, 2000). Thus, the current evidence suggests that while the characteristics of the $CaSO_4$ are likely to be modified in the process of agglomeration, any enhancement of bulk diffusion because the Tamman temperature is exceeded under CFBC conditions only contributes to strength development, but does not cause it.

Where strength development occurs, it is usual to look for evidence of ash softening or melting. In the case of sulfation processes, it has been known for many decades that above 900°C CaS will react directly with $CaSO_4$ in an apparent solid–solid reaction (Equation 4) (Partington, 1951). Hence, the idea that a melt might appear in this system has long been considered a possibility.

$$CaS + 3CaSO_4 = 4CaO + 4SO_2 \tag{4}$$

As one of reactions involved in sulfation at or above 850°C is probably:

$$4CaSO_3 \rightarrow CaS + 3CaSO_4 \tag{5}$$

this makes it appear likely that a melt could be involved in any agglomeration process involving sulfation and quite recently it has been suggested that the existence of a melt might explain the well-known temperature maximum for optimum sulfur capture that occurs in FBC systems (Davies and Hayhurst, 1996). The existence of a melt at FBC temperatures is now regarded as

Table 1. Properties of limestones and bed materials used in this work.

Comp.	Limestones						Bed Materials		
	Yucatan	Barnhart	Kaskaskia	Kukdong	KellyRock	Fort James	NISCO	NSPI	Kukdong
CaO	54.36	51.92	54.38	52.4	51.74	45.8	54.39	47.7	54.9
Al_2O_3	<0.23	0.55	0.26	0.54	1.54	0.49	<0.38	5.24	a0.43
SiO_2	<1.07	3.07	<1.07	4.04	5.31	8.58	2.88	11.31	8.81
Fe_2O_3	<0.30	0.41	<0.30	0.31	0.36	0.24	<0.55	4.99	0.38
TiO_2	<0.37	<0.37	<0.37	<0.001	0.08	0.02	0.16	0.29	<0.01
MgO	0.53	0.66	0.33	0.62	0.58	4.15	2.00	0.85	0.46
Na_2O	*<0.20*	*<0.20*	*<0.20*	*0.16*	*0.07*	*0.09*	*<0.17*	*0.25*	*0.1*
K_2O	<0.063	0.09	<0.063	0.12	0.36	0.25	<0.08	0.55	0.08
P_2O_5	<0.024	0.21	<0.024	0.05	0.00	<0.01	0.03	0.02	0.04
SO_3	-	-	-	-	0.98	-	34.86	23.26	31.5
MnO	<0.007	0.095	<0.007	0.04	0.16	<0.01	<0.02	0.01	0.03
BaO	<0.03	<0.03	<0.03	-	0.18		0.08	0.10	-
SrO	0.087	0.017	0.021	-	0.04	-	0.05	0.03	-
V_2O_5	<0.02	<0.02	<0.02	-		-	0.73	0.02	0.17
NiO	<0.007	<0.007	<0.007	-		-	0.11	0.01	0.04
LOF	44.35	42.58	43.76	41.5	43.14	-	4.48	5.21	2.91
SUM	99.34	99.62	98.75	99.8	104.55	100.1	99.61	100.0	99.7
CO_2	43.4	41.38	44.48	-	-	40.46	-	-	-

"proven" by some workers discussing reaction (4), e.g., "It is lately agreed that this reaction takes place via a liquid eutectic" (Marbán et al., 1999). However, some workers favour a higher temperature of 1000°C or more for the formation of a melt in this system (Anthony and Granatstein, 2001). The current work cannot disprove the existence of a liquid eutectic, but it does demonstrate strength development via the extended or quantitative sulfation occurs down to 650°C, which is well below that at which the existence of liquid eutectics or melts has been postulated.

Many methods have been used to study sintering of FBC ashes; for instance, by using a dilatometer to determine the initial sintering temperature (Kunii and Levenspiel, 1991). However, one method that has been frequently used is the pellet test. This method was initially developed by Barnhart and Williams (1956) to evaluate coal ash sintering, and then developed by Skrifvars (1994) into a sophisticated test for chemical reaction sintering.

Pellet tests are cheap, versatile, quick and involve only small amounts of material, permitting test replication with a limited sample size. However, while they can be carried out at the temperatures and gas concentrations appropriate to a FBC, they do so with a transformed sorbent comprised of finely ground material (typically <75 μm) with void sizes between the particles equivalent to the mean particle size of the ground limestone. This material has little relationship to the actual particles sulphated in a commercial CFBC, the bulk of which lie between perhaps 100 to 1000 μm. In consequence, any influence of particle size, the sulfate layer, surface morphology or even reaction time is likely to be eliminated by the grinding and pelletization process. Another problem with pellet tests is that the degree of compaction can have a strong influence on the strength development results as noted by Skrifvars (1994) and they must be carefully prepared at constant compaction conditions.

The aim of this study is: 1) to determine the relationship, if any, between short-term sulfation and extended sulfation, 2) to extend previous work to a wider temperature range (650°C to 950°C); 3) to study in more detail carbonation/sulfation such as might occur at lower temperatures in a CFBC (<780°C at typical CO_2 partial pressures) or under PFBC conditions; and 4) to compare and contrast classical pellet tests with the test developed by the authors.

Experimental

To evaluate the strength development of limestones and ashes due to sulfation, experiments were conducted in three types of reactors: 1) a fixed bed reactor (for-short and medium-term sulfation of limestone particles); 2) a box furnace (for medium- and long-term sulfation of particles and pellets of limestone as well as bed ash); and 3) a tube furnace (for selected long-term sulfation of bed ashes). In addition to the sulfation experiments the combined effect on agglomeration of sulfation–carbonation was evaluated through box furnace experiments.

Characteristics of the six limestones and the three bed ashes included in the experiments are listed in Table 1. All limestones, except Fort James, are fairly pure calcitic limestones. In addition to some MgO (probably associated with dolomite), Fort James also contains a rather high level of SiO_2.

Sulfation Experiments

A packed bed quartz reactor placed in two electrically heated ovens was used for both calcination and sulfation of fresh limestones. The reactor consists of three main parts: the main body, a removable upper section and a removable lower section. In total the reactor is 1800 mm long and has a diameter of 30 mm. The sample holder is located at the centre of the reactor and consists of a tube with a sintered quartz filter acting as the bed support. Figure 2 shows a schematic flow diagram for the experimental setup. The two furnaces were located on top of each other on a scissors lifting table.

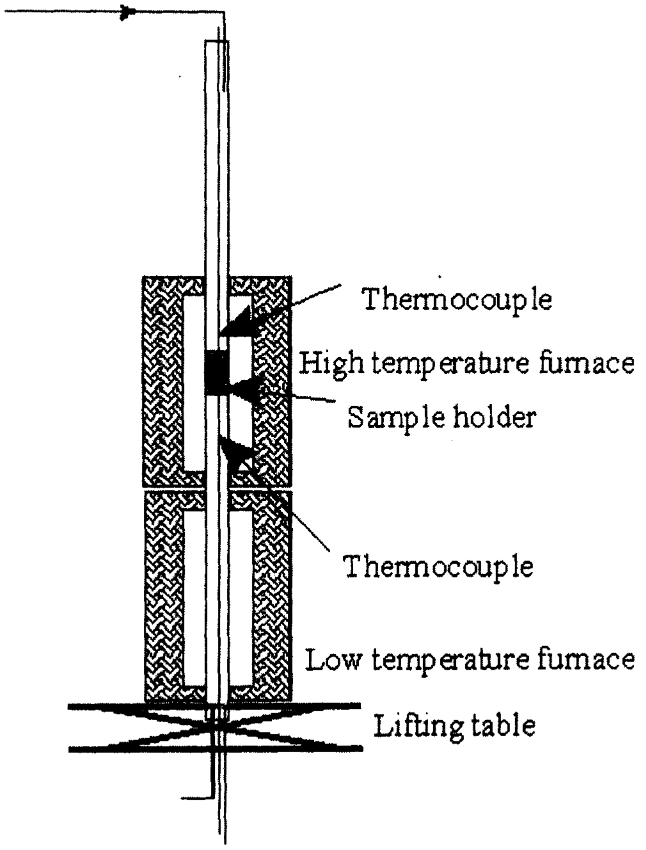


Figure 2. Test apparatus for short and medium term sulfation experiments.

The experiments included: 1) calcination of fresh limestone; 2) initial sulfation of the calcined limestone; and 3) long-term sulfation of the fully sulfated limestones. The as-received pure limestones were dried overnight in an oven at 125°C and sieved. The 212 to 355 μm size-fraction was calcined at 850°C for 90 min in the reactor with air passing through at a flow rate of 300 mL/min. After calcination the limestones were subjected to initial sulfation for 6 h followed by longer-term sulfation for 24 h. During the sulfation tests the gas was fed to the bottom of the reactor, and heated as it passed upward along the outer part of the reactor and downward through the central parts towards the sample holder. The gas stream passed through the quartz filter, while a gas analyzer continuously monitored the SO_2 concentration in the outlet stream. For both initial sulfation and longer-term sulfation the sample size was 3 g and the flow rate was set at 1600 mL/min with an SO_2 inlet concentration of 2250 ppm. After both initial and longer-term sulfation, the samples were carefully removed from the sample holder, and the agglomeration tendency of each sample was assessed. Before long-term sulfation, any agglomerated parts of each of the initially sulfated samples were carefully removed and not included in the long-term tests.

In the bulk of the box furnace sulfation experiments, the samples were first placed in crucibles (4 mm high flat V4-Vitersol crucibles) and arranged on two racks, in rows of 3 or 4, in a temperature-controlled oven. The 4 mm height was chosen because previous work has shown that this is an effective penetration depth for sulfation under these conditions (Anthony et al., 1998). A standard practice adopted was to sieve all the crushed limestones or bed materials to exclude particles larger than 1.4 mm. This constraint was originally adopted to exclude shale in bed ashes from the Point Aconi 165 MWe CFBC unit (owned and operated by Nova Scotia Power Inc (NSPI)); it has been used here to ensure consistency with previous results for other bed ashes (Anthony et al., 1998, Anthony and Jia, 2000).

The particle size of the limestones supplied to CETC was about 25 to 40 mm (1 to 1.5 inches). These samples were crushed twice using a laboratory jaw crusher, first to −10 mm and then to −1.4 mm. The −1.4 mm size limestones were used in crucible tests. The pellets were prepared using 1.9 g samples of ground limestone (<75 μm), which had previously been calcined in an oven. The die diameter was 13 mm and pelletization force was 890 N. Typically, five or six pellets were made for each limestone for each experiment in order to ensure reproducible data were generated. The pellets were then sulfated in the box furnace with a gas mixture of 1% SO_2, 3% O_2, balance N_2, at the desired temperature in a manner analogous to the crucible tests. The strength of the pellet was then determined in a standard crush test, which is related to the degree of sintering. The test duration was 4 to 16 h for the bulk of the tests, but one set of pellets was sulfated for 4 weeks, at 750°C. In addition, a number of pellet tests were extended to 4 weeks, to see if this made a significant difference in strength development, since it has been shown in crucible tests that strength develops with time (presumably until complete conversion has been achieved).

Sulfation tests in the box furnace were conducted at 650°C, 750°C, 850°C, or 950°C (±2°C). A synthetic flue gas containing 1% SO_2, 3% O_2 and balance N_2 was employed for most tests at a flow rate of about 200 mL/min. For those experiments to study carbonation-sulfation, a 1% SO_2, 3% O_2, balance CO_2 flue gas was used at the same flow rate. The 1% SO_2 concentration was deemed necessary to reduce the amount of cylinder gas used during the course of a four week experiment. The SO_2 concentration was not expected to greatly influence the results. For high levels of CaO to $CaSO_4$ conversion, it has been claimed (De Hemptinne, 1990), diffusion through product layer controls the sulfation process for larger particles while bulk diffusion controls the process for smaller particles, with overall reaction orders of 0.25 and 0.2, respectively. This also appears to have been demonstrated for FBC bed ash and other limestones (Anthony and Jia, 2000; Abanades et al., 2001).

For a few tests, a Lindberg tube furnace was used to test the effect of bed temperature and ensure very precise control of SO_2 gas concentrations. Two ash samples were placed in the centre of the tube for each test. All samples produced were subjected to X-ray fluorescence (XRF) analysis. The total sulfur content was determined by the LECO method, and the CaO content was determined by inductively coupled plasma (ICP) analysis.

Results and Discussions

Sulfation Experiments

Four limestones were included in the fixed bed experiments: Barnhart, Kukdong Oil, Kaskaskia, and Fort James (Table 2). The SO_2 emission curves were very similar for three of the limestones: Barnhart, Kaskaskia and Fort James (Figure 5). At the start of the experiments these three limestones absorbed all the SO_2 resulting in zero emission for an extended time (110 min, 65 min, and 100 min, respectively) after which the emission increased significantly. In the case of the Kukdong Oil limestone the initial breakthrough of SO_2 occurred much earlier than for the other

Table 2. CaO-utilization and sulfation patterns of four tested limestones. (The calculated Ca utilizations assume pure limestones and that all CaO is available for sulfation.)

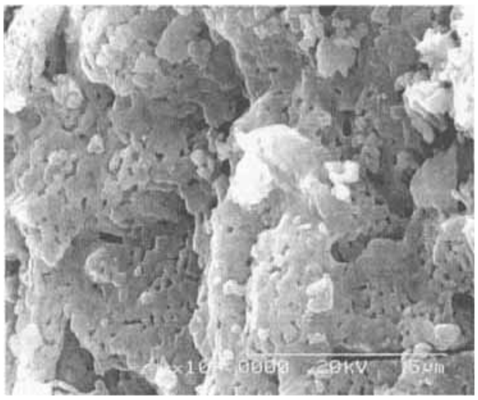
Limestone	Sulfation time	Ca-utilization		Sulfation pattern		
		Integration (%)	Mass gain (%)	Unreacted core (%)	Uniformly sulfated (%)	Network (%)
Barnhart	6 h	51.3	39.7	5	85	10
	30 h	64.6	44.8	10	90	0
Fort James	6 h	42.9	38.3	50	50	0
	30 h	49.6	41.5	45	50	5
Kaskaskia	6 h	35.7		85	15	9
	30 h	41.7	32.4	90	0	10
Kukdong Oil	6 h	30.4	24.9	90	0	10
	27 h	39.2	31.0	85	10	5

three limestones. However, the emission curve was less steep than those registered for Barnhart, Kaskaskia and Fort James. Thus, Kukdong Oil limestone did not reach its apparent maximum capacity (illustrated by the curve becoming effectively horizontal) as early as the other limestones, and the resulting CaO-utilization of Kukdong Oil limestone is only slightly lower than that measured for the other limestones (Table 2). In this context it is interesting to note that this limestone was associated with very severe agglomeration problems in the CFBC boiler where it has been used (Anthony et al., 1997, 2000).

The CaO-utilization based on integration of the SO_2 emission curves is consistently larger than utilization based on the weight gain associated with the formation of $CaSO_4$. Similar differences (4% to 6%) have been observed in earlier work at the University of British Columbia (UBC). The difference has been attributed primarily to conversion of SO_2 to SO_3, which leads to an overestimation of the integration method. As seen in these experiments, we have also observed that the differences become more severe with longer periods of sulfation. The major differences in the two calculated utilizations for Barnhart are much greater than previously observed.

Recent SEM analyses of nine different limestones showed that sulfated limestone particles could be divided into three groups: a) unreacted-core; b) network; and c) uniformly sulfated particles (Laursen et al., 2000). The unreacted-core particles are characterized by a highly sulfated shell (70% to 95%) and a slightly or unsulfated core (0 to 5%). The uniformly sulfated particles exhibit a relatively homogeneous degree of sulfation (40% to 65%). The network particles are characterized by sulfation around the periphery and in the proximity of fractures and slightly or unsulfated in the central part of each of the "sub-grains" separated by the fractures. The distribution of sulfation patterns observed in the individual particles in the four limestones are listed in Table 2. The changes in the sulfation patterns observed after 6 and 30 h of sulfation are minor. In general, there is a slight increase in the percentage of uniformly sulfated particles and a small decrease in unreacted core or network sulfated particles.

SEM image of calcined Kukdong



SEM image of Kukdong Oil limestone sulfated for 6 h

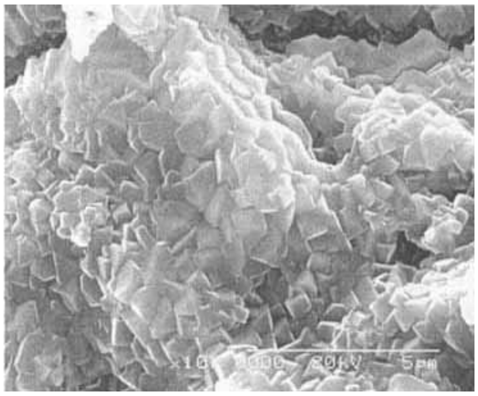


Figure 3. SEM image of calcinced (a) and sulfated (b) Kukdong limestone.

The majority of the voids in all four limestones are present as pores between the individual grains in the particles (intergrain pores). The size of these pores is generally in the range of 0.05 to 0.5 µm. Larger voids in between clusters or groups of grains are less common, but seen in all four limestones. These macropores have diameters ranging from 0.5 to 3 µm, but they do not appear to be very long or interconnected. In addition to the pores, Kaskaskia and especially Barnhart contain micro-fractures (50 to 100 µm long). The initial sulfation process led to

Table 3. Agglomeration tendencies observed during calcination, initial sulfation and long term sulfation of four limestones.

Limestone	Test conditions	Agglomeration tendencies
Barnhart	Calcined	None
	6 h sulfation	Top one piece, lower part non agglomerated
	30 h sulfation	One piece, broke apart by light touch
Fort James	Calcined	None
	6 h sulfated	One piece except for some particles in the bottom, breaks easily
	30 h sulfated	One piece at the top, breaks easily
Kaskaskia	Calcined	None
	6 h sulfated	Upper part one piece, broke apart by light touch
	30 h sulfated	Upper part one piece, broke apart by light touch
Kukdong Oil	Calcined	None
	6 h sulfated	One piece, appears less agglomeated than observed for others limestones
	27 sulfated	One piece, appears less agglomerated than observed for other limestones

plugging of all inter-grain pores and the majority of the macropores due to a significant increase in the grain size (see Figure 3 for a typical result). The grain sizes in the calcined limestone particles vary from 0.05 to 1.0 µm, from 0.5 to 2.5 µm in the initially sulfated samples, and 0.5 to 4.0 µm in the limestone sulfated over 30 h. In all limestones, long term sulfation led to formation of more distinct crystal facets on all the grains. In addition to the larger grains formed during longer term sulfation, the surface of the particles also became smoother, probably due to "filling" of the grooves, which were remnants of macropores. There also appears to be a distinct reduction of small grains or clusters of grains sticking to the surfaces of re-sulfated particles compared to the initially sulfated particles. However, there was no evidence of melting or the development of liquid eutectics.

One noteworthy point is that in this apparatus the degree of sulfation does continuously increase as a function of time. The same observation has been noted in the few published studies available on TGA experiments carried out over many hours. Namely, the conversions determined in standard limestone reactivity tests, which typically last several hours, do not represent a limit for sulfur capture even though it is clear that the rate of sulfation falls dramatically after the first few hours of sulfation (Matttisson, 1998, Abanades et al., 2000). The fact that significant strength development does not arise in these tests suggests that it is not simply surface reaction that determines whether agglomeration occurs.

Agglomeration of the limestone particles was rather limited both during initial sulfation and long-term sulfation (Table 3). During both sulfation stages, the upper part or in some cases the whole sample fell out of the sample holder as one piece when the sample holder was turned upside down. However, the weakly agglomerated samples fell apart as they hit another surface or upon a light touch with a probe. In the long term sulfated samples, it was only possible to pick up agglomerated pieces of Fort James and Kukdong Oil limestones for examination by SEM. The SEM images show that the bonding between individual particles in the agglomerates consists of small bridges of fine particles shared between two adjacent particles and no major bridging or actual bonding is seen (Figure 4).

Based on the sulfation experiments in the fixed bed, which led to only minor agglomeration, it is hard to rank the four limestones with respect to tendency to agglomerate. It is thus not possible to determine if the sulfation pattern has any effect on the differences observed in agglomeration behaviour in different limestones. It is also clear that this type of differential reactor cannot be used to characterize limestones in terms of their agglomerating characteristics via short- or medium-term runs.

Initially, three sulfation tests were carried out at 850°C, 900°C and 950°C in the temperature-controlled box furnace, over a 4-week period. The limestones tested were Yucatan (which is the current limestone being used in the two 100 MWe CFBC boilers owned and operated by Nelson Industrial Steam Company (NISCO)), and two other limestones from the same geographical area (Kaskaskia and Barnhart). All three limestones formed hard agglomerates, and the sulfation results are presented in Table 4. The sulfation capacity of the limestones

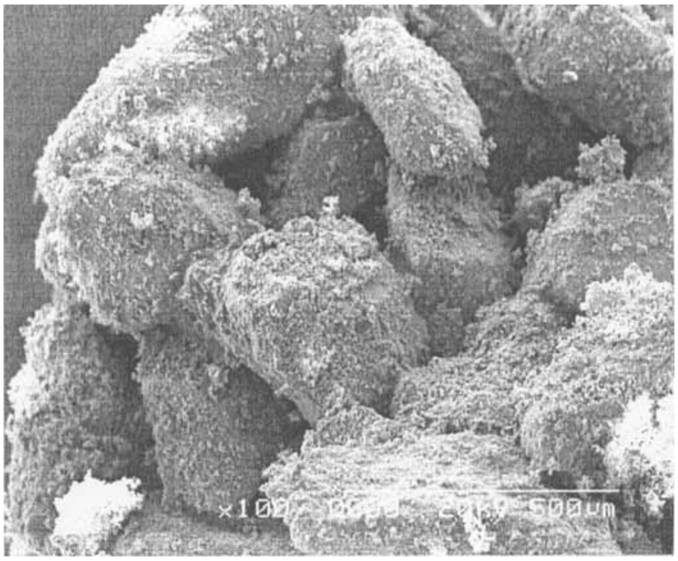


Figure 4. SEM image of agglomerated particles for Fort James limestone.

Table 4. % Conversion to $CaSO_4$ at 850°C, 900°C and 950°C, after four weeks of sulfation.

CaO Conversion %	Limestones		
	Yucatan	Kaskaskia	Barnhart
At 850°C	59.5±16.5	63.2±3.5	74.9±5.6
At 900°C	65.2±4.4	65.6±8.3	80.9±9.8
At 950°C	60.8±18.8	58.0±6.1	68.8±8.2
TGA Conversion, at 850°C	61.2	40.4	27.4

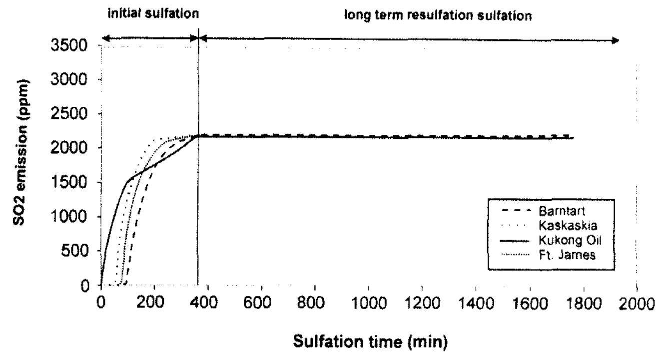


Figure 5. SO_2 emissions curves for initial and resulfation of the four limestones.

was also measured in a TGA and these data are also given in Table 4, This was determined at 850°C in a Cahn 1100 TGA using a sieved sample (of size between 0.15 to 0.25 mm) using gas containing 5000 ppm SO_2, 2.5% O_2 and 15% CO_2, balance N_2.

Several things are apparent from the sulfation data. First, long-term sulfation data bear no relation to those obtained in short-term TGA sulfation tests in that the limestone which shows the lowest conversion in a TGA test shows the highest conversion to $CaSO_4$ in an oven test. This suggests that differential reactors and TGA cannot give useful information on long-term sulfation behaviour and agglomeration tendencies if they operate over short periods of time (e.g., hours) as is the case for standard determinations of limestone sulfation capacity. These results also seem to suggest that there is indeed a temperature related sulfation maximum for extended sulfation. However, it occurs at a higher temperature than typical for short-term sulfation (825°C to 850°C) (Anthony and Granatstein, 2001), namely around 900°C, and that in the absence of carbonation, sulfation falls off continuously at lower temperatures.

To confirm the effect of temperature on sulfation at lower temperatures (down to 650°C), tests in a tube furnace were also carried out with NSPI bed ash for two periods of time, one week and three weeks. Three temperatures were employed (650°C, 750°C and 850°C) and gas with a composition of 1% SO_2, 3% O_2 and balance N_2 was used (Table 5). These results clearly show that long-term sulfation increases with temperature for $SO_2/O_2/N_2$ environments, just as it does for higher temperatures (up to 900°C) and that it increases as a function of time over the whole range of 650°C to 950°C.

A series of strength tests were carried out on the samples of Yucatan, Kaskaskia and Barnhart limestone sulfated in the box furnace under an SO_2-O_2-N_2 atmosphere at 750°C, 850°C, 900°C and 950°C (Table 6). These strength tests clearly show an increase in strength over the whole temperature range, but as noted above sulfation begins to fall at 950°C. These data are interesting also in terms of their implications for a liquid eutectic or melt being involved in the agglomeration. Long-term or extended sulfation has been shown to increase as a function of temperature and time over the range 650°C to 900°C. As it has

Table 5. % CaO conversion to $CaSO_4$ in sulfated NSPI bed ash.

Temperature (°C)	650	750	850
One week (CO_2-SO_2-O_2)	54.3 (Not agglom.)	66 (agglom.)	67.8 (agglom.)
One week (N_2-SO_2-O_2)	63.6 (Not agglom.)	69.3 (agglom.)	76.9 (agglom.)
Three weeks (N_2-SO_2-O_2)	67.9 (Weakly agglom.)	73.8 (agglom.)	82.3 (agglom.)

Table 6. Results of strength tests on samples sulfated at 850°C, 900°C and 950°C for four weeks. All values are given in MPa.

Sulphation temperature	Limestones			Bed material
	Yucatan	Kaskaskia	Barnhart	NSPI[1]
At 750°C	0.58±0.49	0.28±0.31	0.72±1.21	-
At 850°C	0.61±1.1	0.52±0.36	1.14±1.2	8.77±2.90
At 900°C	0.465±0.31	0.883±0.64	3.33±2.4	-
At 950°C	2.46±2.06	4.26±1.86	4.01±1.64	6.0±1.6

[1] Anthony and Jia (2000).

Table 6. Results of strength tests on samples sulfated at 850°, 900° and 950°C for four weeks. All values are given in MPa.

Sulphation temperature	Limestones			Bed material
	Yucatan	Kaskaskia	Barnhart	NSPI[1]
At 750°	0.58±0.49	0.28±0.31	0.72±1.21	-
At 850°C	0.61±1.1	0.52±0.36	1.14±1.2	8.77±2.90
At 900°C	0.465±0.31	0.883±0.64	3.33±2.4	-
At 950°C	2.46±2.06	4.26±1.86	4.01±1.64	6.0±1.6

[1] Anthony and Jia (2000)

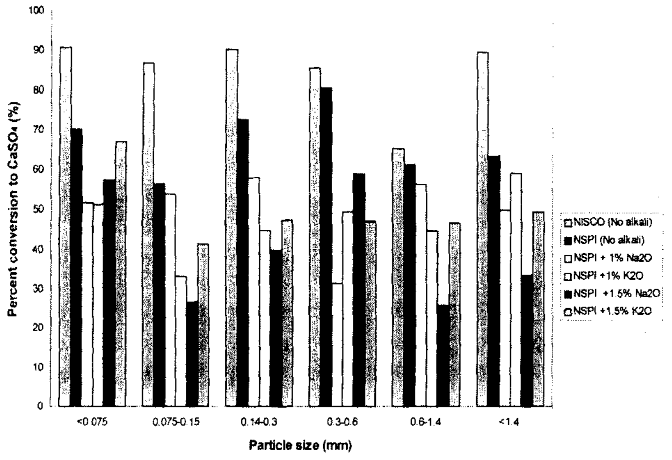


Figure 6. Percent conversion to $CaSO_4$ as a function of particle size for 950°C and a 100 d sulfation.

never been suggested that a melt or liquid eutectic is involved in the sulfation process below 830°C to 850°C, it is clear that the formation of such a melt is not a necessary hypothesis for either long-term sulfation or agglomeration and strength development up to 900°C. Also given that the strength increases but the sulfation levels decreases at 950°C, such an explanation could be invoked for these temperatures. Thus, as the idea of a melt has been suggested to explain the temperature maximum (because melts should result in reduced porosity, and decreased conversion) (Davies and Hayhurst, 1996), it could be also be invoked here to explain reduced conversion with increased strength development.

In this context, the existence of a melt could be in agreement with results from some earlier experiments. These data showed that samples of NSPI bed ash doped with 1% to 1.5% Na_2O or K_2O (introduced as sulfates) failed to convert to the same $CaSO_4$ levels as seen at lower temperatures (sometimes dramatically so, see Figure 6), after 100 d under sulfating conditions at 950°C. In the case of alkali metal addition at these levels the existence of a liquid eutectic is certain and could be seen by the fact that many of the samples were fused to the crucible bottoms. The implication of these data is that, if a melt can form at 950°C, it is sufficient to eliminate or diminish the residual porosity to such low levels that conversion to $CaSO_4$ is reduced.

The strength development at four different temperatures for four limestones (Yucatan, Kaskaskia, Barnhart and Fort James) based on pellet tests is given in Table 7. These results show that the pellet tests give much more uniform strength with, for the most part, smaller or significantly smaller variation than the crucible tests. Unfortunately, it appears that there are no consistent trends for temperature or for time. It is also clear that the pellet behaviour at four weeks is very similar to that seen at short periods of time. As sulfation increases as a function of time in the crucible tests (Anthony et al., 1998; Anthony and Jia, 2000) it appears that pelletization completely suppresses strength development as a result of the extended sulfation process over long periods of time.

Table 7. Mean pellet strength development (MPa).

Temperature (°C)	Yucatan	Kaskaskia	Barnhart	Fort James	Test duration
In SO_2-O_2-N_2 environment					
800	0.69±0.38	0.51±0.16	0.92±0.14	0.42±0.05	16 h
850	0.84±0.17	1.38±0.11	0.79±0.10	0.53±0.04	16 h
900	0.51±0.12	1.42±0.07	0.38±0.07	0.07±0.03	16 h
750	0.61±0.31	0.53±0.27	0.66±0.35	0.44±0.35	4 weeks
In SO_2-O_2-CO_2 environment					
750	1.10±0.16	1.1±0.06	0.89±0.21	0.72±0.06	4 weeks
850	0.31±0.14	0.88±0.21	0.53±0.09	0.58±0.11	4 weeks

Table 8. Phase analysis of Fort James pellets (four weeks sulfation) and outer sulfated shell (16 h).

Phase	Crushed Pellet	Sulphate Shell
CaO (lime)	49.2	2.0
$CaSO_4$ (anhydrite)	27.4	91
$Ca(OH)_2$ portlandite	17.4	4.0
MgO (periclase)	6.2	-
SiO_2 (Quartz)	0.6	-
$MgSO_4{\cdot}5H_2O$ (pentahydrite)	-	3.0
Crystallinity (wt%)	100.9	

To check the composition of the pellets, the crushed Fort James limestone pellets produced at 850°C were subjected to quantitative X-ray diffraction. The mean composition is given in Table 8 (the composition shows samples have been hydrated by the atmosphere during preparation, but this is not significant for this study). These results demonstrate that for a similar period of time the pellet achieves only a low level of overall sulfation compared with crucible tests where samples contain $CaSO_4$ levels in the range of 60% to 80%. Interestingly, data from a 16 hour test carried out at 800°C (see Table 8) show that the outer layer of the pellet is much more highly converted.

These results show that while pellet tests give extremely reproducible results, they are unlikely to be able to simulate the actual behaviour of ashes in a CFBC boiler. Therefore, they should be used with considerable caution, if they are used for anything else beyond determining whether a sorbent will undergo chemical reaction sintering or not under given conditions.

Sulfation–Carbonation Experiments

The effect on the conversion during sulfation in a $SO_2/O_2/CO_2$ atmosphere was tested on the NSPI bed ash (Table 5) (Anthony and Jia, 2000). The ashes were sulfated at 650°C, 750°C and 850°C in mixed gas containing 1% SO_2, 3% O_2 and balance CO_2. It should be noted that an actual FBC boiler could be expected to have a partial pressure of CO_2 of the order of 15 kPa. Thus, $CaCO_3$ would be thermodynamically stable below about 780°C, and sulfation ought to proceed via global reaction (3) as the carbonation process is much faster than sulfation (Tullin and Ljungström, 1989). The results listed in Table 4 indicate that in the presence of CO_2, there is no strong increase in the sulfation rate with temperature over the range of 750°C to 850°C and the sulfation process appears to be retarded by the presence of CO_2. In this respect, extended or long-term sulfation appears to be different from short-term sulfation since it is known that in PFBC environments for instance, where $CaCO_3$ is stable, short-term sulfation is enhanced (Hajaligol et al., 1988; Snow et al., 1998; Liu et al., 2000; Zhong, 1995; Iisa et al., 1991). Iisa et al. (1991) has also found a difference between direct sulfation of $CaCO_3$ and simultaneous sulfation and recarbonation with sulfation being slower in the latter case. Similarly, in a study of sulfation of material over a hot gas filter Duo et al. (1999) found that conversion decreased under conditions where $CaCO_3$ was thermodynamically stable. By contrast Fuertes et al. (1994a) found that recarbonated calcined particles exhibited higher sulfation rates than uncalcined $CaCO_3$ particles.

The most likely explanation for the reduction in the rate of sulfation is that $CaCO_3$ formed by reaction with CO_2 reduces the residual porosity of the bed material, thus retarding the sulfation process. It should also be noted that in most of these studies the particle size was much less than a 100 µm, except for the Iisa et al. (1991) study that used particles in the size range of 110 to 230 µm. Fuertes et al. (1994b) suggested that at a high degree of conversion, sulfation through $CaCO_3$ is controlled by solid state diffusion rather than molecular or Knudsen diffusion. If this is the case and the direct sulfation of $CaCO_3$ is initially dominated by molecular and Knudsen diffusion (Abanades et al., 2000), then the decreased sulfation levels associated with carbonation/sulfation would be easily explicable. Another interesting observation from the work of Fuertes and his co-workers (1993) was that "for bigger particles sizes the conversion hardly changed with temperature." In this context bigger means particle in the size range of 710 to 850 µm, and this conclusion agrees with the present results. Finally, it is important in this context to note that a reduced sulfation level is not synonymous with decreased agglomeration, since it is quite likely that agglomeration first occurs by carbonation and then the carbonated deposits are sulphated (Skrifvars et al., 1998).

As noted above, the fact that sulfation is retarded in the presence of sufficient CO_2 to form $CaCO_3$ does not in and of itself imply that agglomeration will be less at intermediate temperatures (650°C to 780°C). First, since carbonation is a faster process than sulfation, agglomerates may form more rapidly, due initially to the formation of $CaCO_3$, prior to substantial conversion to $CaSO_4$. Second, the overall strength may still be greater because of differences in ionic mobility, enhanced chemical reaction sintering, and/or differences in the nature of the strength development process for carbonation, carbonation–sulfation, sulfation, etc. Such differences in strength have been suggested before by Skrifvars et al. (1998), who based their work on using pellets which were exposed to reacting gases for 4 h nominal test times. Those results, which were obtained using Yucatan limestone, suggested that carbonation should be associated with much greater strength development than sulfation.

Ultimately, the only way of making such a determination is via a strength development test, either using samples produced via the crucible method (Anthony and Jia, 2000) or pellet tests. While this work suggests that pellet tests may have limits in ranking limestones for this type of agglomeration (see below), they should give an indication of the relative behaviour of a given limestone. The pellets here were also sulfated for the full 4 weeks, and then subjected to a strength test. It is assumed that for a pellet a longer period of reaction will either have no effect or increase the strength of the pellet, as compared to tests done over a few hours.

Table 9 gives the data for the crucible tests and pellet tests for a number of limestones at 750°C, a temperature at which $CaCO_3$ should be stable in an atmospheric FBC. For each test five samples were sulfated and the results presented below represent the average results.

While there is scatter in the tests, particularly the crucible tests, there seems no doubt that under identical conditions if $CaCO_3$ can form, the strength development is greater. Note this does not mean that strength development is necessarily greater at lower temperatures because higher temperatures are usually associated with increased strength development (see below), but that for the same conditions, carbonation–sulfation

Table 9. Strength development of limestones at 750°C (MPa).

Crucible Tests Limestone	Yucatan	Kaskaskia	Barnhart	Kelly Rock	Kukdong
SO_2-O_2-N_2	0.58±0.49	0.28±0.31	0.72±1.21	0.26±0.14	1.44±0.94
SO_2-O_2-CO_2	1.19±0.84	1.38±0.87	5.97±2.85	0.68±0.54	3.31±1.75
Pellet Tests Limestone	Yucatan	Kaskaskia	Barnhart	Fort James	
SO_2-O_2-N_2	0.61±0.31	0.52±0.27	0.66±0.35	0.43±0.25	-
SO_2-O_2-CO_2	1.10±0.16	1.10±0.06	0.89±0.22	0.72±0.06	-

Table 10. Strength Tests (MPa) at 750°C and 850°C after 4 weeks sulfation in SO_2-O_2-CO_2 atm.

	Limestones					Bed material
	Yucatan	Kaskaskia	Barnhart	Kelly Rock	Kukdong	Kukdong
Mean Strength at 750°C	1.19±0.84	1.38±0.87	5.97±2.85	0.68±0.54	3.31±1.75	5.29±2.74
Mean Strength at 850°C	1.87±0.43	2.44±1.56	4.3±4.09	2.35±1.78	4.79±2.56	7.03±2.58

produces stronger deposits than sulfation of CaO, even though the degree of sulfation itself is reduced. One can speculate that a faster agglomeration process allows particles less opportunity for movement and readjustments in the unconfined powder matrix, which may allow strain to be reduced. While this explanation would not explain earlier results with pellet tests it seems clear that the carbonation-sulfation process is worse than sulfation of CaO, sometimes significantly so in terms of strength development, in line with previous results (Skrifvars et al., 1998).

Finally, results are given in Table 10, which shows strength increase over the range of 750°C to 850°C in SO_2-O_2-CO_2 atmospheres for crucible tests. As with the case for SO_2-O_2-N_2 atmospheres, the strength increases with temperature, the single exception for this being Barnhart, for which the data has too much scatter for a judgement to be possible.

Conclusions

Long-term sulfation and carbonation sulfation tests have been carried out on a number of limestones and bed materials. These have shown that sulfation and agglomeration increase both as a function of temperature and time over the temperature range 650°C to 900°C. Above this temperature the degree of sulfation falls, but strength continues to develop, and it is suggested that a liquid eutectic caused by CaS-$CaSO_4$ would explain such an effect, although it is not necessary to explain results for lower temperatures.

Sulfation decreases under conditions in which carbonation can occur and it is suggested that this may be caused by a shift in sulfation mechanism from gas-phase to solid state diffusion. Interestingly enough, strength of deposits formed under carbonation-sulfation conditions are often significantly greater than those formed under purely sulfating conditions and these results confirm earlier findings carried out using a chemical reaction sintering test.

Finally, pellet tests are shown not to agree in terms of strength development or sulfation behaviour with the crucible tests, and it is suggested that they should be used with caution in any circumstance whereby particle size or morphology is expected to be important.

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