ASH SPLITS AND GAS EMISSIONS FROM THE COMBUSTION OF COAL REJECTS IN A CFBC

by

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The CANMET Energy Technology Centre (CETC), sponsored by Luscar Ltd. and the Alberta provincial government, carried out a series of combustion trials on a number of washery rejects to determine whether they could be burned in an environmentally acceptable manner using both conventional and fluidized bed combustion (FBC). The paper presents details of tests using CETC 0.8 MW_{th} circulating fluidized bed combustor (CFBC). The starting bed material (silica sand) and fuel ash have very distinctive SiO_2 and Al_2O_3 contents, therefore, the SiO_2/Al_2O_3 ratio of the bed material may be used as an indicator of the chemical steady state. The three fuels burned in the reactor were: raw coal (Obed #4), Obed Jig Rejects (Obed #7) and Obed Jig Middlings (Obed #10). These fuels required an additive, Cadomin limestone, to achieve the allowable SO_2 emission levels recommended under the Canadian National Guidelines for Stationary Sources. However, NO_x levels were always below the allowable emission levels for all three fuels. Other emissions such as CO and N_2O appeared to be low and unlikely to pose problems. The combustion efficiency associated with these fuels was high, as might have been expected with a very reactive fuel, and at 850 °C was typically about 99%. Therefore, the CFBC technology appeared to be an entirely satisfactory technology for burning these fuels.

INTRODUCTION

The CANMET Energy Technology Centre (CETC), sponsored by Luscar Ltd. and the Alberta provincial government, carried out a series of combustion trials on a number of washery rejects from Obed Mountain coal mine owned by Luscar Ltd., to determine whether they could be burned in an environmentally acceptable manner using both conventional and advanced combustion technologies - namely fluidized bed combustion (FBC). Obed Mountain mine is located 30 km east of the town of Hinton, Alberta, in the outer foothills of the Rocky Mountains and produces a high volatile bituminous coal. The mine began operations in 1984. Current production capacity is 1.8 million tonnes per year. In 1998, the Obed Mountain mine produced 1.6 million tonnes of coal. The majority of the coal is exported abroad for electricity generation. The run-of-mine

(ROM) coal is cleaned and dried at the preparation plant which features a Batac jig operation. This paper focuses exclusively on the pilot-plant scale trials performed on CETC's 0.8 MW_{th} circulating fluidized bed combustor. Luscar Ltd. also conducted a similar study to develop a preliminary plan to burn heavy media cyclone rejects in a CFBC at its Coal Valley mine site to produce hot flue gas for the coal drying facilities and raise enough steam to generate 30 MWe [1].

With the advent of new higher energy prices there is also renewed interest in using such fuels for power generation. Typically, pilot-scale tests are carried out assess the suitability of such a fuel, and an interesting question is ash behaviour for these high ash fuels, and how this affects steady state behaviour, especially in situations where fuel sulphur is low, and the fuel derived ash, or if necessary sand makeup will contribute significantly to bed composition.

EXPERIMENTAL

The pilot-scale CFBC

The pilot-scale CFBC unit has been described extensively elsewhere [2]. Major features of this versatile unit include a refractory-lined combustor 405 mm in diameter and 7 m high, a refractory-lined hot cyclone and an inclined L-valve loop seal system for recirculation of solids (Fig. 1). Four individually retractable bayonet type vertical cooling

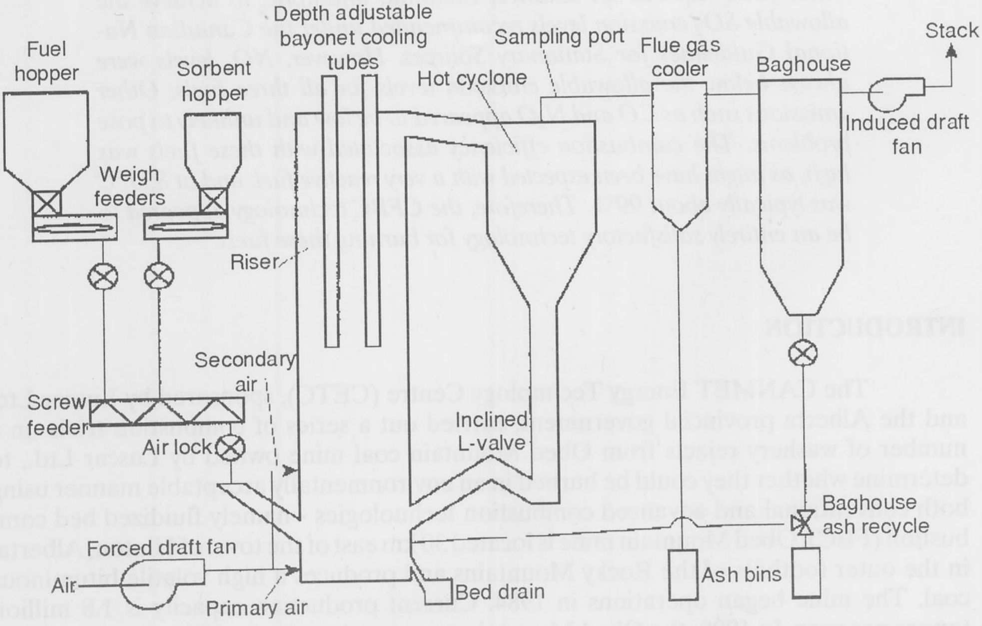

Figure 1. Schematic of CANMET 0.8 MWth CFBC pilot plant

tubes permit control of the combustor temperature during operation at various test conditions. It is complemented by a comprehensive instrumentation and control system. The combustor can operate at temperatures up to 1100 °C and at a superficial gas velocity of up to 8 m/s. The research facility generates a database useful for the design and process optimization of full-scale units, study of emissions of pollutants, and prediction of the combustion performance of feedstocks. The unit has been successfully used with high-sulphur petroleum coke, pitch, coal, wood waste and paper sludges. The unit has also been used to generate ash from the CFBC combustion of high-sulphur coals in order to study various ash management applications.

CFBCs typically operate at temperatures between 800 °C and 950 °C. Lower temperatures normally reduce combustion efficiency, decrease sulphur capture and increase production of incomplete combustion byproducts. Higher temperatures by contrast, run the risk of producing bed agglomeration, increasing NO_x emission levels, and also reducing sulphur capture.

Test conditions

Three fuels were burned in the CFBC: Obed raw coal (Obed #4), Obed Jig Rejects (Obed #7) and Obed Jig Middlings (Obed #10). Experimental conditions are given in Table 1. Fuel feed rate was 140 kg/h for all test trials. For further details concerning the various properties of the fuels themselves, see Tables 2–4. Cadomin limestone (Table 2), from Genstar Cement Ltd., was used to achieve the allowable SO_2 emission levels recommended under the Canadian National Guidelines for Stationary Sources. This particular limestone had been previously tested by CETC using thermogravimetric analysis (TGA) and was shown to be only a moderately reactive sorbent. As some difficulties were experienced in achieving adequate sulphur capture under the test conditions employed, a trial was also carried out using Havelock limestone (Table 2), a relatively reactive eastern Canadian limestone.

Table 1. Experimental conditions

Trial	Fuel	Bed temperature [°C]	Oxygen concentration [%]	Primary to secondary air [kg/h]	Duration [h]
1	Obed #4, Raw coal	850 & 800	3	558/150	27
2	Obed #7, Jig coarse rejects	850	3	830/179	24
3	Obed #10, Fine jig middlings	850	3	780/150	22
4	Obed #4, Raw coal	800	3	780/150	10
5	Obed #7, Jig coarse rejects	800 & 900	3	660/150	7

Table 2. Ash analysis of limestones and fuels, wt %

	Cadomin limestone	Havelock limestone	Raw coal (Obed #4, Trial #1)	Raw coal (Obed #4, Trial #4)	Jig rejects (Obed #7)	Jig middlings (Obed #10)
SiO_2	1.50	1.23	22.04	69.53	71.16	62.65
Al_2O_3	0	0.38	5.04	16.83	15.35	15.88
Fe_2O_3	0	0.55	0.92	2.73	2.58	3.60
TiO_2	0	<0.04	0.14	0.45	0.52	0.60
P_2O_5	0	<0.02	0	0	0	0.22
CaO	55.12	53.99	1.47	4.24	3.61	7.48
MgO	2.25	0.59	0.59	1.88	1.63	1.39
SO_3	0.32	0.20	0.12	1.79	1.44	4.69
Na_2O	0	<0.17	0.34	0.93	1.27	0.75
K_2O	0.21	<0.08	0.28	0.73	0.85	0.88
BaO	0	0.02	0.09	0.26	0.25	0.30
SrO	0	0.02	0.03	0.05	0.05	0.07
V_2O_5	0	<0.02	0	0	0	0.01
NiO	0	0.01	0	0	0	0.05
LOF	42.77	43.34	69.70	0.25	0.35	1.14
SUM	102.19	99.48	100.76	99.73	99.06	99.71

Table 3. Proximate, ultimate and calorific analysis of fuels

	Raw coal (Obed #4, Trial #1)	Raw coal (Obed #4, Trial #4)	Jig rejects (Obed #7)	Jig middlings (Obed #10)
Proximate analysis*				
Moisture	10.77	10.15	8.98	10.71
Ash	31.43	37.04	42.38	21.50
Volatile		24.04	23.37	29.16
Fixed carbon		28.77	25.27	38.63

Table 3. Continuation

	Raw coal (Obed #4, Trial #1)	Raw coal (Obed #4, Trial #4)	Jig rejects (Obed #7)	Jig middlings (Obed #10)
Ultimate analysis*				
Carbon	44.60	40.88	37.44	52.84
Hydrogen	3.12	3.12	2.03	3.51
Nitrogen	0.89	0.69	0.64	0.71
Sulphur (total)	0.34	0.34	0.31	0.53
Sulphate	–	0.01	0	0.02
Pyritic	–	0.25	0.16	0.22
Organic	–	0.08	0.15	0.29
Oxygen	8.85	7.78	8.22	10.20
Calorific analysis				
Cal/g	4120	3777	3459	4955
MJ/kg	17.25	15.81	14.48	20.75
Btu/lb	7416	6799	6226	8920

* Analysis in weight %

Table 4. Ca/S and Alkali/S molar ratio for fuels

Alkali to sulphur molar ratio	Ca/S	[Ca + Mg + 0.5K + 0.5Na]/S
Obed #4, Raw coal	2.63	5.04
Obed #7, Jig rejects	2.86	5.97
Obed #10, Jig middlings	1.74	2.47

Test durations

One of many considerations that must be taken into account during any experimental campaign is the duration of the test runs. For the CETC CFBC thermal steady state is normally achieved after 8 to 10 hours of continuous operation. However, achieving a constant bed composition, otherwise described as chemical steady-state, can take significantly longer. Chemical steady state is important for fuels which require in-situ sulphur capture by limestone addition or any situation where the bed might be expected to influence gas phase emissions. Thus, chemical steady-state is required to ensure that sulphur capture is correctly determined and that data such as NO_x and N_2O emissions (which can depend on the bed composition) are also reliable. This may also be true of a high-ash fuel if the ash component is retained in the bed and has significant propensity to capture SO_2. Ideally, a bed must be operated for between three to five bed turnovers to achieve 90–95% replacement of the bed material and ensure representative conditions [3].

An estimate of the residence time of particles, τ_p , in the bed can be obtained from the following:

$$\tau_p = \frac{m_b}{m'_p} \tag{1}$$

$$m'_p = m'_b + m'_f \tag{2}$$

where:

m_b – total bed holdup,
m'_p – total mass efflux of solid products,
m'_b – total mass efflux of bed solids withdrawn from the bed,
m'_f – total fly ash product flux.

The bed holdup in the CETC CFBC unit is approximately 160 kg. If the fuel feed rate is 140 kg/h with an ash content of about 30%, then the ash fed to the unit is of the order of 40 kg/h. Given that there is no net accumulation of bed material, *i. e.*, a constant solid inventory is maintained in the bed, then one bed turnover requires about 4 hours. However, this time will increase dramatically if the start-up bed material (in this case silica sand) is preferentially maintained in the bed.

If the fuel fed has a sulphur content of approximately 0.3% and limestone provides the sulphur capture, the limestone feed rate for a typical Ca/S molar ratio (2 to 3) would be about 3 or 4 kg/h (assuming the limestone contains 95% $CaCO_3$ and the fuel feed rate is 140 kg/h) . This implies that residence or bed turnover time is about 38 hours if only limestone derived ash is to replace the initial bed material, which would require operation for about 114 hours before chemical steady-state is achieved.

The time necessary to achieve X% replacement of the bed material may be estimated by:

$$X = 100\left[1 - \exp\left(-\frac{\tau}{\tau_p}\right)\right] \tag{3}$$

Assuming 95% replacement of the initial bed material by the fuel ash is equivalent to "chemical steady-state" then the time necessary is approximately 12 hours (assuming that bed ash is important in sulphur capture and the starting bed material (sand) is not preferentially maintained in the bed). Thus, allowing for a start-up of 5 to 6 hours to bring the bed to temperature, followed by about 12 hours with test fuel to reach chemical steady state, and a steady-state test run period of 5 hours to accumulate sufficient data to ensure reliable results, a test run should be approximately 23 hours. By contrast, assuming the ash completely elutriate and the sulphated limestone makes up the bed material, then the time to achieve chemical steady-state is 114 hours for the same assumptions as in the analysis above.

Any attempt to run the CFBC for such long periods would be excessively expensive especially as sulphur capture is unlikely to be a major goal for the combustion of such a low-sulphur fuel. It was, therefore, decided to run the unit for periods of about 24 hours to determine whether there was any significant change in sulphur capture due to a "build-up" of bed ash in the primary reaction loop, *i. e.*, combustor and hot cyclone.

These arguments are further complicated by the fact that it is not certain that the start-up material (silica sand) will be attrited and elutriated at the same rate as fuel ash or limestones, so that the attempt to determine holdup based on input of ash solids or limestone may not be correct. In fact, subsequent experiments showed that the various fuels burned in these series of trials behaved very differently in terms of the rate at which their ashes were removed from the primary reaction loop and that the sand was indeed preferentially maintained in the bed. These differences and their implications for the combustion trials are discussed in this paper.

RESULTS AND DISCUSSION

In total, five trials were carried out. Each of the test runs is described first below.

Test Trial #1 (Obed #4, raw coal)

There was initially a concern that test duration might be an important parameter in the event that the fuel-derived ash was able to act as a sulphur sorbent. Given the high ash content of the coal and the relatively high level of natural calcium and alkali metals versus sulphur content (Table 4) it was hoped that the coal ash would be able to display significant inherent sulphur capture eliminating the need for limestone addition.

To allow for the possibility that inherent capture might be significant, the first test was run for 22 hours. This long test was meant to simulate a situation in which bed ash could build up in the combustor. Unfortunately, only a relatively low inherent sulphur capture was seen in the test.

After 3 hours of heating with natural gas, wood pellets were introduced to bring the bed to final temperature and after another 2 hours coal feed was started. Thermal and operational steady state were judged to have been achieved after 4 hours of coal feed. Obed #4 raw coal was fed at 140 kg/h and the fluidizing velocity was 5.5 m/s, which is typical of CFBC operating conditions. This fuel was by far the most reactive of the materials burned, although all the fuels could be classified as very reactive and burned extremely well.

The ash production based on the coal feed rate was approximately 47 kg/h. This would mean that, providing the ash was not selectively attrited, steady-state based on bed composition should have been achieved in 10 h (since the bed was initially charged with 160 kg of silica sand). The total ash expected on the basis of fuel analysis is 1028 kg, the actual ash removed was 1097 kg, which gives a mass closure for ash of 106.7% which is acceptable for this type of work. The actual bed ash production was 224 kg and baghouse ash was 873 kg, *i. e.*, 80% of the ash was removed from the baghouse.

These data are still open to question in that they do not provide clear information about the fate of the sand used for bed inventory at the start of the run. If sand is preferentially elutriated from the bed, this would lead to a very rapid change in bed composition to one composed primarily of fuel derived ash. Alternatively, sand may be maintained in the bed, so that all of the baghouse material is fuel ash derived. In the latter case, chemical steady-state would be determined by the rate at which solids were drawn directly from the bed to maintain a constant bed solid inventory or pressure drop. This would mean that the holdup time in the bed was about 15.6 hours (average bed drain rate was 10.3 kg/h in this test) and that to achieve 95% replacement of bed material, which we would consider effective chemical steady-state, the duration of the run should have been 47 hours.

To clarify this situation, an analysis was made of the SiO_2 and Al_2O_3 ratio of the various ash streams (Table 5). The use of this ratio has the advantage that it should stay reasonably consistent regardless of the physical state of the coal, particularly moisture content. For convenience, we will henceforth set $Y = SiO_2/Al_2O_3$.

Two varieties of silica sand (120 kg of a coarser sand and 40 kg of a finer sand) were used for start-up. These had SiO_2 and Al_2O_3 contents of 99.28% and 0.36%; and 99.7% and 0.08% respectively. Assuming that both sands were elutriated in proportion to their mass (which is questionable but makes calculation easier), the mean SiO_2 and Al_2O_3 concentrations are 99.4% and 0.29% respectively, giving a Y value of 343 for the sand. For the coal we have two different analyses, which gives an average Y values of 4.25 (Table 2).

The parameter Y for the bed material can be obtained experimentally or calculated from the following equation using the earlier analysis results of the coal (Table 2):

$$Y = \frac{\mathrm{SiO}_{2,\mathrm{sand}}(1-X) + \mathrm{SiO}_{2,\mathrm{ash}}X}{\mathrm{Al}_2\mathrm{O}_{3,\mathrm{sand}}(1-X) + \mathrm{Al}_2\mathrm{O}_{3,\mathrm{ash}}X} \tag{4}$$

where X is the percentage of material replaced from the bed estimated from equation (3), and the characteristic time, τ_p, is 15.6 hours. The results are presented in Fig. 2.

From Table 5, it is clear that early into the run, the baghouse material was basically fuel ash derived, *e. g.*, greater than 90% at 4 hours, and the fuel ash fraction in the fly ash continued to increase as a function of time. This was consistent with the hypothesis that early in the run some fines in the bed sand were selectively removed but subsequently nearly all of the sand was selectively maintained in the primary reaction loop, *i. e.*, combustor and return leg (Fig. 1) and was only removed by direct withdrawal of solids from the bed itself.

In the case of the bed material, it is possible that there was some selective withdrawal of fuel-derived ash early in the run because Y adopted a lower experimental value than would be expected on the basis of eq. (3). However, early in the run, the value

Table 5. Silica to alumina ratio, $Y = SiO_2/Al_2O_3$ according to chemical analysis results of bed ash (BA) and fly ash (FA) samples

Time since fuel feed started, [h]	Trial #1, Obed #4		Trial #2, Obed #7		Trial #3, Obed #10		Trial #4, Obed #4		Trial #5, Obed #7	
	BA	FA	BA	FA	BA	FA	BA	FA	BA	FA
1							40.04	4.02		
2							26.05	3.98		
3					20.0	4.67	23.63	4.14	10.46	5.04
4	12.25	4.55	8.26	4.83			21.14	4.13	9.15	4.80
5					16.14	4.76	18.71	4.11		
6	9.18	4.38					18.34	4.30		
7					14.78	4.59				
8			6.80	4.80						
9					18.11	4.71				
10	8.34	4.36								
11					16.98	4.36				
12			7.81*	4.86						
13					19.58	5.25				
14	8.0	4.39	6.63	4.96						
15					21.64	4.60				
16			6.50	4.63						
17					27.17	4.53				
18	6.06									
19						5.58				
20			5.58	4.69						
21	6.37	4.21								
22			5.48	4.77						

* 50 kg of sand was added over a 30 minutes period starting at 11.0 hours since fuel feed commenced, hence the increase in SiO_2/Al_2O_3 ratio

than would be expected on the basis of eq. (3). However, early in the run, the value of *Y* was very strongly dependent on an accurate knowledge of the Al_2O_3 content of the sand. Since this was a very small number, even quite small errors in its determination results in large differences in the value of *Y*. Thus, initial values of *Y* may simply reflect inaccuracies in the analysis for Al_2O_3 concentration. However, by 10 hours, the simple model implied by eq. (3) provides a very good description of the bed composition as expressed by the ratio *Y* (taking the mean bed ash withdrawal as the actual removal rate

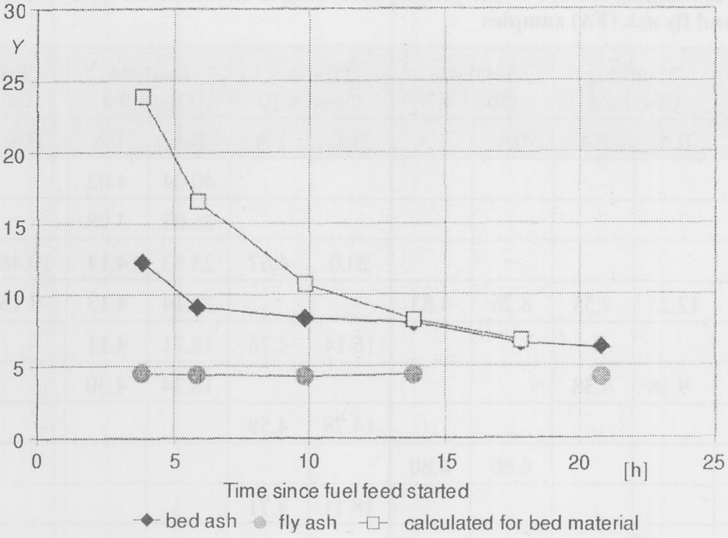

Figure 2. Silica to alumina ratio, $Y = SiO_2/Al_2O_3$, for Trial # 1 with Obed raw coal (Obed #4). The calculated Y values are based on $\tau_p = 15.6$ h as determined experimentally in the test

of material from the bed, and hence confirming that the mean bed turnover time is 15.6 hours).

Unfortunately, this bed turnover time implies that true chemical steady-state was not reached in this run. However, as this has implications primarily for sulphur capture, it should not strongly affect the other results obtained, although with other fuels this type of behaviour might be very significant. Also, since nearly all of the sulphur captured appears to be found in the baghouse ash, it may be that even the sulphur capture results are acceptable because it is reasonable to suppose that larger bed ash particles which collect in the primary reaction loop are not very effective in capturing SO_2.

During a period of several hours, bed temperatures increased by approximately 40 °C suggesting that the heating value of the fuel had changed. Otherwise, combustion conditions were essentially stable. Later in the run, limestone was added for 2.5 hours at the rate of 3.1 kg/h. This corresponds to a Ca/S molar ratio of about 2.2.

Test trial #2 (Obed #7, Jig rejects)

Trial #2 was the second nominal 24 h test attempted. Heating of the unit with gas was followed by coal feed after 3 hours. Thermal and operational steady-state conditions were judged to have been achieved 1.5 hours after coal feed started. The silica to alumina ratios for the fly ash and bed ash samples are given in Table 5. This fuel showed some variability in its heating value and it was occasionally difficult to maintain a steady bed temperature. The test was run with Jig rejects only for the first 11.5 hours and then limestone was added at a level of 6 kg/h for the remaining 8.5 hours.

The rate of bed withdrawal was about 22 kg/h. This number represents approximately twice the amount that was removed during the raw coal (Obed #4) test for a fuel with very similar ash content and identical feed rates. A mass balance for ash indicates that the jig rejects should have produced 1173 kg of ash, whereas, in actuality, 1334 kg was produced. Correcting for 50 kg sand added for bed makeup, 50 kg of limestone used (assuming limestone calcined completely) and ignoring any contribution of either carbon or sulphate addition to the overall weight of solids withdrawn from the bed, the closure was 107% which represents excellent agreement. Contribution from the carbon or sulphate components normally amounts to a small positive contribution (1 or 2%) to the net weight of solids removed from the system.

The natural silica to alumina ratio of the fuel ash was 4.63. After 4 hours the silica to alumina ratio (Y) in the fly ash was 4.83 and did not vary substantially during the rest of the run period without limestone addition. This suggested that almost all of the baghouse ash is obtained from the fuel ash. Using the silica to alumina ratio for the sand and fuel ash provides an estimate of the contribution of the bed sand to the baghouse ash at about 3%.

Unfortunately, it is not possible to draw quantitative conclusions about the change in bed ash composition as there are only 2 data points prior to sand having been added near the end of the period without limestone addition. This was done to compensate for excessive removal of bed material (see Table 5). However, it is reasonable to assume the same extremely slow replacement of the silica sand by fuel-derived ash occurred.

The duration of this run (24 hours) was sufficient for chemical steady-state to have been achieved given that the degree of sulphur capture associated with fuel ash was completely negligible. Thus, it would appear that the results from the first portion of the run (*i. e.*, without limestone addition), were representative of the entire run. It is also interesting to note that the silica to alumina ratio for the baghouse ash is very nearly constant for the entire period of limestone addition. Since the alumina content of the limestone is effectively zero and its silica content is very small we may conclude that the bulk of the limestone was carried over with the rest of the baghouse solids.

Test trial #3 (Obed #10, Jig middlings)

This particular run employed Havelock limestone to determine whether the very low sulphur capture observed with the use of Cadomin limestone was due simply to its reactivity or other factors. Havelock limestone is known to be a moderately reactive limestone [4]. In addition to altering the limestone type it was decided to examine the effect of operating at 800 °C and 900 °C on combustion performance. Thermal steady-state was achieved after 2 hours of coal firing.

In total 2672 kg of fuel was burned, and the corresponding theoretical ash production was 643 kg. Actual ash removed was 662 kg (discounting limestone and sand addition), which gives a mass closure of 103%, providing excellent agreement between expected and actual results. About 82% of the ash was found in the baghouse stream and the average bed ash production was fairly low at 7 kg/h compared with 31.5 kg/h from the baghouse. There was some evidence that more of the sand was escaping with the baghouse ashes since a total of 80 kg of sand had to be added to the bed during the test. The fluctuation in *Y* values for the bed and fly ash during the test was apparently the results of sand addition.

Test trial #4 (Obed #4 – raw coal revisited)

Having determined that longer runs did not confer significant benefits, it was decided to repeat part of the test with Obed #4 raw coal in order to help verify results, particularly those associated with sulphur capture using Cadomin limestone. The bed was run at nominal steady-state for 2 hours, and limestone addition occurred for 4 hours. This run was carried out at 800 °C because this was the temperature at which sulphur capture was shown to improve for the tests carried out on the Obed #7 and Obed #10 fuels. The bed ash was produced at a rate of 30 kg/h (189 kg total) which was significantly higher than in Trial #1. However, the reason for this was not apparent. The baghouse ash production was 23 kg/h (145 kg total). The total theoretical ash production (based on the ash content of the raw coal) should have been 306 kg. Taking limestone addition into account, this result gives a mass closure of 106% which is in agreement with previous test results.

Test trial #5 (Obed #7 – Jig rejects revisited)

This test was performed at 800 °C without limestone addition and then at 900 °C with limestone addition at Ca/S molar ratio of 5.5. The total ash collected, corrected for the presence of limestone, was 487 kg. However, the theoretical ash collection expected was only 310 kg. This suggests a significant error in the fuel analysis used in the calculation. This hypothesis would be consistent with the fact that combustion performance experienced during the run indicated that the coal composition was extremely variable. The bed ash production was 51 kg/h while that from the baghouse was 35.5 kg/h. This latter result represents an ash production of over twice that observed in the previous run (Trial #2). The reason for this discrepancy is not obvious. As with all previous runs, the baghouse stream appears to be composed almost entirely of fuel-derived ash as the average *Y* value was 4.92, compared to the natural value of *Y* for the parent fuel ash of 4.6.

Sulphur capture

As indicated in Table 4, the natural Ca/S molar ratio of all the fuels tested is relatively high, 1.74–2.86. These high levels of alkali metals versus fuel sulphur content might potentially result in a significant inherent capture, providing the calcium is present in a suitable form. Sulphur removal without limestone addition observed by CETC for

FBC combustion of Canadian fuels appears to average about 28% [5], although captures of over 90% have been observed for one Western Canadian subbituminous coal using both circulating and bubbling FBC technology [6, 7]. Similar data have been reported elsewhere, *e. g.*, inherent captures of up to 75% have been reported for some British coals [8]. However, one important difference between capture due to ash components and limestone in FBC systems is that the optimum capture temperature for ash appears to be about 700–750 °C, about 100 °C below the optimum temperature for most limestones [8–10] via reaction:

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \tag{5}$$

Several possible explanation for this phenomenon might apply. One is that fuel particle surface temperatures are typically 50 to 200 °C higher than bed temperature, so that the actual capture temperature experienced on the surface of the fuel particle may be very similar to that of the limestone [11]. An alternative explanation for low inherent sulphur capture in coals with significant pyritic sulphur is that sulphur escapes the system without being oxidized to SO_2. This is theoretically feasible because the oxidation rate of pyritic sulphur is comparable to char carbon oxidation rate [8]. Stover *et al.* [10] found for a coal with a high natural Ca/S molar ratio (4.6) and a high organic sulphur content (80%) that the fluidizing velocity did not influence the inherent sulphur capture, but the sulphur capture was still the highest at about 750 °C. Further, to the authors knowledge the only reported case in the open literature of significant amounts of unreacted sulphur being elutriated from a FBC system, and contributing to an "apparent sulphur capture", occurred with a petroleum coke burned in a pilot scale bubbling FBC [12]. However, without analysis of the sulphur forms in the baghouse ash it is impossible to eliminate the hypothesis that escape of unreacted pyritic sulphur might be contributing to the sulphur contained in ash solids and adding to the reported sulphur capture.

Finally, it is possible that ash components are reacting with available CaO binding it in the form of unreactive silicates and other components and this has been reported both for oil shale [13], and direct reactions of coal ash with limestone [14]. In practice, all of these hypotheses would lead to increasing apparent sulphur capture at lower bed temperatures, as shown by the data summarized in Table 6.

Examining the inherent sulphur capture data, it becomes immediately evident that there is a striking difference between data for Obed #4 and the other fuels tested. Obed #4 has about 74% of its sulphur present in pyritic form (Table 3) (and only 23.5% of its sulphur in organic form), which support the hypothesis that these figures do not simply represent actual chemical capture, but elutriation of pyritic sulphur compounds with the fly ash. This would be consistent with the fact that for Obed #7 and Obed #10, where pyritic sulphur composition is about 53% and 42% respectively, the inherent capture drops to about 14%. Alternatively expressed, 46% and 54% of these fuel's sulphur is present in organic form which should be easily released and converted to SO_2 and therefore one might expect sulphur capture to be relatively low if elutriated sulphur in the coal ash was contributing significantly to the "apparent sulphur capture".

Table 6. Combustion efficiency and sulphur capture data

Test and date	Bed temperature [°C]	Ca/S	Fluidizing velocity [m/s]	Sulphur capture efficiency [%]	Combustion efficiency [%]
Trial #1 (Obed #4)	850	0	5.4	26	99.0
	850	2.2 (Cadomin)	5.5	28	–
Trial #2 (Obed #7)	850	0	5.6	14	98.2
	850	4.9 (Cadomin)	5.5	32	98.9
	800	4.9 (Cadomin)	5.3	49	97.7
Trial #3 (Obed #10)	850	0	5.6	14	99.0
	850	2.8 (Havelock)	5.4	30	98.8
	800	2.8 (Havelock)	3.4	63	98.0
	900	2.8 (Havelock)	5.7	38	99.1
Trial #4 (Obed #4)	800	0	4.2	26	98.5
	800	2.7 (Cadomin)	4.2	31	98.3
Trial #5 (Obed #7)	900	5.5 (Cadomin)	5.8	44	99.0

Further to this argument it should be noted that the natural Ca/S molar ratios for Obed #7 and #10 are both high but quite different at 2.86 and 1.74 respectively (Table 4). However, their inherent capture is almost identical and low. Given these two facts, the explanation of sulphur escaping the system via elutriation of unreacted pyritic sulphur seems much more probable than that of being chemically captured by the ash. Quantitatively, therefore these data are consistent with an assumption that sulphate sulphur leaves the system unchanged, little or no organically bound sulphur is captured, and at 850 °C, about 25 to 30% of the pyritic sulphur escapes the CFBC unreacted.

These results also indicate that Cadomin limestone is relatively ineffective as a sulphur sorbent until it is present at Ca/S molar ratio levels of about 5 or more. The superior performance of Havelock limestone also supports the contention from previous TGA work that Cadomin is a relatively low reactivity limestone. However, the fact that greater than 50% sulphur capture is achieved with Cadomin at Ca/S molar ratios greater than 5 may not pose a problem because even though these levels are high by FBC standards for firing high sulphur coal, the relative amounts of limestone used are modest compared with fuel feed rates, *i. e.* only 5% of the fuel feed rate.

Combustion efficiency

The combustion efficiency data (Table 6) follow the expected trend of increasing with increasing bed temperature. No other experimental parameter over the range used in this test series seems to have a significant effect on the combustion efficiency. The variation in combustion efficiency from 97.7% to 99.1% is very small, with typical combustion efficiency being about 99% for bed temperature of 850 °C. This is what one would expect from a very reactive fuel like Obed Mountain coal and one would also expect that combustion efficiency ought to improve still further in commercial-scale equipment, with its more efficient cyclone and greater residence time.

Gas phase emission results

The mean gas phase emission results, normalized to 3% oxygen, are given in Table 7. The following are discussions for each of the pollutants.

NO_x and N_2O emissions

NO_x emissions vary from 72.7 to 187.9 ng/J, well below levels typically seen from conventional combustion and as expected increases with bed temperature. Interestingly, there appears to be no effect associated with the addition of limestone (Fig. 3). Limestone is well known to increase NO_x emissions in CFBCs due to its ability to catalyze NH_3 oxidation (from fuel volatiles) [15]. A possible explanation is that limestone is simply not present in sufficient absolute quantities to have a significant impact, despite the high Ca/S molar ratios used in this study.

NO_x in a FBC is almost entirely derived from fuel nitrogen, as the bed temperatures are too low to permit fixation of nitrogen in the air. Thus, NO_x emissions are most strongly related to the nitrogen content of the fuel. When expressed this way it becomes apparent that the NO_x results are extremely uniform for the three fuels tested, with 10 to 13% of the fuel nitrogen being converted to NO_x in all tests carried out at 850° to 900 °C, and 6 to 8% conversion for tests at 800 °C (Table 7). When the total conversion of fuel nitrogen to NO_x and N_2O is taken into account the figure becomes almost constant at 14.5%. The observation that total fuel nitrogen conversion to NO and N_2O is effectively a constant has been made before by Gavin and Dorrington [16], who noted that for their bench-scale FBC the conversion was always about 50%. Here the results are much lower but support the idea that for a given fuel and FBC system, total conversion tends to be constant.

Nitrous oxide (N_2O) is not currently regulated but it is an emission of some potential concern as it is a greenhouse gas and is also implicated in ozone destruction [17]. It is now well established that N_2O from CFBC boilers is strongly dependent on bed temperature, with decreasing N_2O emissions as bed temperature increases. The test results follow this trend with the highest levels of about 80 ppm occurring at 800 °C and the lowest values of about 20 ppm occurring at 900 °C. At 850 °C, N_2O emissions are about 40 ppm. Such levels are quite modest and appear to be unlikely to pose a problem.

Table 7. Gas emissions (corrected to 3% O_2)

Test and date	Bed temperature [°C]	CaS	NO_x, ppm [ng/J]	% fuel nitrogen converted		SO_2, ppm [ng/J]	CO [ppm]	N_2O [ppm]	CO_2 [%]
				to NO_x	to NO_x & N_2O				
Trial #1 (Obed #4)	850	0	250±8 (155.3±8.7)	10.8±0.6	14.4±2.1	433±30 (370.3±32)	99±8	42±6	16.1±0.65
	850	2.2 Cadomin	222±13 (151/8±7.7)	10.5±0.5		375±59 (354.1±54)	92±17	–	16.3±0.56
Trial #2 (Obed #7)	850	0	209±13 (149.5±10.1)	11.8±0.8	15.2	556±33 (562.5±35)	164±96	30	16.0±0.83
	850	4.9 Cadomin	222±9 (144.9±11.7)	9.9±0.8	14.4±1.0	391±74 (377.9±74)	99±4	50±3	16.1±0.59
	800	4.9 Cadomin	150±8 (100.9±5.5)	6.9±0.4	14.5	239±34 (224.1±32)	151±5	83	15.9±0.88
Trial #3 (Obed #10)	850	0	224±15 (117.8±8.6)	10.5±0.8	14.8±1.4	597±55 (422.0±69)	117±9	46±3	15.9±0.62
	850	2.8 Havelock	220±10 (107.2±5.1)	9.5±0.5	13.3	464±43 (313.5±25)	102±5	44	16.1±0.44
	800	2.8 Havelock	180±25 (72.7±8)	6.5±0.7		342±33 (185.7±18)	134±12	–	16.1±0.59
	900	2.8 Havelock	271±9 (135.1±4.1)	12.0±0.4		561±40 (395.2±24)	66±2	–	16.2±0.54
Trial #4 (Obed #4)	800	0	154±8 (103.6±10.4)	7.2±0.1		335±20 (316.8±66)	228±28	–	15.7±0.3
	800	2.7 Cadomin	138±8 (97.6±10.4)	6.8±0.1		264±48 (264.3±62)	207±22	–	15.8±0.43
Trial #5 (Obed #7)	800	0	185±10 (113.2±14.7)	7.8±0.1		281±49 (218.4±14.7)	178±9	–	17.2±0.38
	900	5.5 Cadomin	302±8 (187.9±4.9)	12.9±0.03	14.9	468±56 (403.7±50)	78±4	24	16.3±0.74

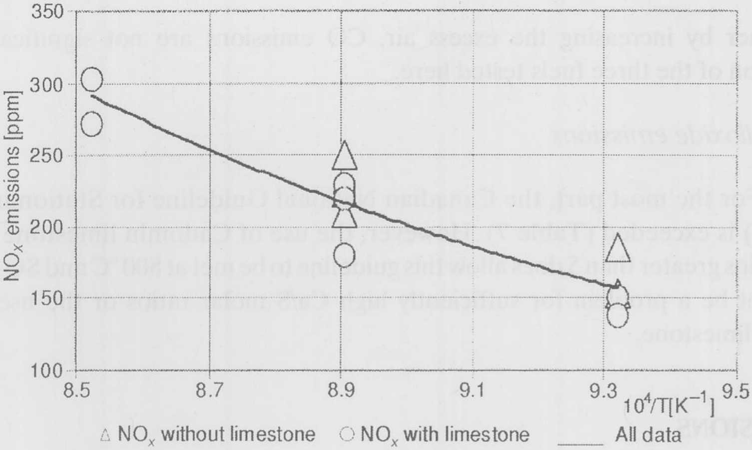

Figure 3. NO_X emissions versus bed temperature

CO emissions

As expected, CO emissions decreases with increasing temperature, essentially the reverse behaviour of NO_x, given that this is a very reactive fuel it is reasonable to assume that reduction of NO_x by CO over char is not occurring to a significant extent and that temperature is the most important variable here. There was also a small, but definite effect due to limestone addition, with CO falling in the presence of limestone, presumably due to a catalytic effect, as previously reported by Leckner and co-workers [18]. Figure 4 shows the relationship between NO_x and CO, and clearly demonstrates the effect of limestone in reducing CO emissions. While these emissions could probably be reduced

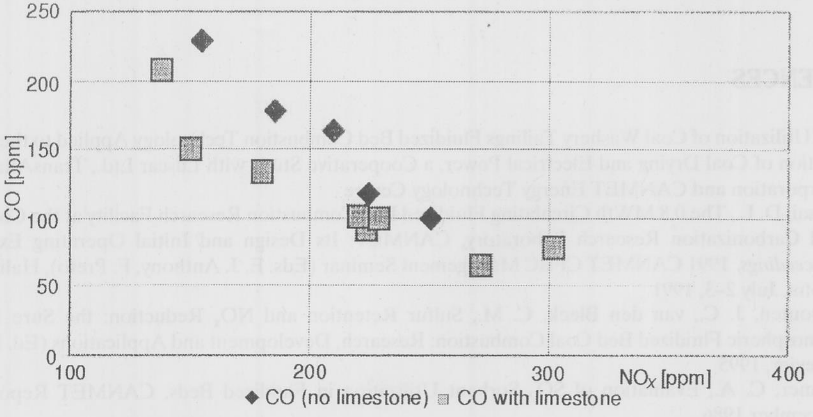

Figure 4. NO_X versus CO with and without limestone addition

still further by increasing the excess air, CO emissions are not significant for the combustion of the three fuels tested here.

Sulphur dioxide emissions

For the most part, the Canadian National Guideline for Stationary Sources (258 ng/J) is exceeded (Table 7). However, the use of Cadomin limestone with Ca/S molar ratios greater than 5 does allow this guideline to be met at 800 °C and SO_2 emissions should not be a problem for sufficiently high Ca/S molar ratios or the use of higher reactivity limestone.

CONCLUSIONS

Three fuels, Obed #4, Obed #7 and Obed #10, have been burned in a CFBC combustor. These fuels are highly reactive and at typical CFBC operating conditions (850 °C and 3% O_2), it appears that combustion efficiency (based on unburned carbon loss) is 99.0% which is typical of very reactive fuels. Inherent sulphur capture was shown to be small and to decrease with bed temperature, and appeared to be directly related to the degree of pyritic sulphur content in the fuel, suggesting that the low 'apparent capture' is due to carryover of unreacted pyritic sulphur. Cadomin limestone is only likely to be effective in achieving emission guidelines when it is used at Ca/S molar ratios greater than 5. NO_x emissions are all below the current guidelines. Other emissions such as CO and N_2O appear to be low and are unlikely to pose problems. CO and N_2O emissions decrease with increasing bed temperatures as expected and interestingly, limestone appears to have a small positive effect in reducing CO levels. CFBC appears to be an entirely satisfactory technology for burning these fuels and based on these results would have no problem in achieving good combustion performance and low emissions.

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