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COMBUSTION PERFORMANCE, SULPHUR CAPTURE AND VANADIUM BALANCE TRIALS WITH SYNCRUDE PETROLEUM COKE IN A CIRCULATING FLUIDIZED BED COMBUSTOR

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- D. L. Dessi
CANMET, Energy Mines and Resources Canada
Ottawa, Canada
- F. Engstrom
Pyropower Corporation
San Diego, California
- W. B. Alderton
Polymath Energy Consultants Ltd.
Vancouver, British Columbia
- S. H. Vayda
Consultant, Poway
San Diego, California
- C. E. Wood
Polymath Energy Consultants Ltd.
Vancouver, British Columbia
- F. D. Friedrich
CANMET, Energy Mines and Resources Canada
Ottawa, Canada

ABSTRACT

Syncrude coke is a byproduct from Canada's largest tar sands upgrading plant. The coke has high calorific value but due to its high sulphur and vanadium content, very low volatiles and some less reactive carbon forms, it is not suitable for conventional combustion technology. A comprehensive test program was carried out with Syn crude petroleum coke in a pilot scale circulating fluidized bed combustor at the Hans Ahlstrom Laboratory in Finland.

Three tests were carried out without limestone to establish the baseline SO₂ emissions. A total of 16 tests were conducted with Fort McMurray limestone for sulphur capture at maximum, minimum and intermediate loads with and without baghouse ash recycle. The superficial fluidizing velocity was varied from 2.8 to 6.9 m/s and combustor temperature was varied from 830°C to 960°C. The baghouse ash recycle rate was 80% for six tests and 67% for an optimum condition test.

Test results indicated that high combustion efficiencies of over 99% are achievable. Sulphur capture of over 90% was achieved with a Ca/S molar ratio of 1.7 or less except in three initial runs when it was up to 2.26:1. The baghouse ash recycle improved the performance of limestone slightly and reduced the Ca/S molar ratio by about 10%. A combustor temperature of about 900°C optimized combustion efficiency at about 99% and sulphur capture at about 90%.

The NO_x concentrations varied from 54 to 450 ppm whereas CO concentrations varied from 10 to 120 ppm in runs with limestone. Most of the vanadium and nickel were captured in the various ash streams. Sulphur, calcium, vanadium and nickel balances are also given.

INTRODUCTION

Canada's largest tar sands extraction plant, operated by Syncrude Canada Ltd. employs fluid coking units to upgrade the bitumen to produce a

synthetic crude transportable and usable by existing pipelines and refineries. The plant has an output of 125,000 b/d of synthetic crude and produces about 2500 t/d of coke as byproduct.

Syn crude coke has a high calorific value but because it has high sulphur, low volatiles and contains carbon forms which are less reactive, it is not suitable for process steam generation by conventional combustion technology and is currently stockpiled. It also contains high concentrations of vanadium and nickel.

In 1981 the Canada Centre for Mineral and Energy Technology (CANMET) sponsored a short series of exploratory tests with Syn crude coke in a circulating fluidized bed combustor (CFBC) test facility at the Hans Ahlstrom Laboratory in Finland using a Swedish limestone for sulphur capture (1). The results were very encouraging, giving high combustion efficiency and over 90% sulphur capture with a Ca/S molar ratio of less than 2. In light of this, CANMET decided to carry out a comprehensive test program with Syn crude coke utilizing local Fort McMurray limestone. A contract was awarded to Polymath Energy Consultants Ltd. to carry out the desired program, again using the pilot scale CFBC at the Hans Ahlstrom Laboratory. Fifty tonnes of coke and thirty tonnes of limestone were shipped to Finland. The test program and results are described in this report. The test objectives were:

1. To establish the baseline emissions of SO₂ when burning without limestone.
2. To establish the effect of bed temperature, superficial gas velocity and baghouse ash recycle on combustion efficiency and sulphur capture, in terms of the Ca/S molar ratio required for 90% sulphur capture.
3. To establish optimum conditions in terms of combustor temperature, superficial gas velocity and baghouse ash recycle for combustion efficiency and sulphur capture.
4. To determine the fate of vanadium and nickel in the coke.
5. To generate a database for optimizing the design of a commercial CFB boiler.

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PILOT SCALE TEST FACILITY

The pilot scale CFBC at the Hans Ahlstrom Laboratory has a thermal input rating of approximately 1.5 MW. Its main components are combustor, hot cyclone and recirculation loop-seal, boiler, baghouse and coal and limestone feed systems. The test facility is shown schematically in Fig. 1.

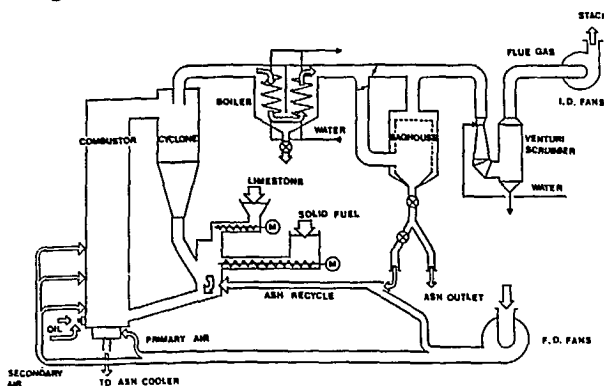


Fig. 1 Schematic of Ahlstrom pilot scale circulating fluidized bed combustor

The refractory lined combustor is 8.5 m high with an inside diameter of 0.6 m and a bed area of 0.28 m². At the base of the combustor are the distributor plate and windbox through which the primary air is supplied from two centrifugal fans connected in series. Secondary combustion air can be supplied from the same fans through diametrically opposite air nozzles at five levels above the distributor. The combustor temperature is controlled by variable lengths of bayonet water-cooled tubes inserted vertically through the top of the combustor. For startup, combustor is heated to the ignition temperature of fuel by an oil/gas preheat burner. The bed ash is removed via a fluidized bed ash cooler, collected in a weighed bin, then transferred pneumatically to an ash silo.

The fuel is fed from a weighed hopper via a screw conveyor and rotary air-lock valve into the loop-seal for recirculation of cyclone solids to the combustor. The sulphur sorbent is fed from a hopper into the loop-seal via an impact plate metering device and a calibrated screw conveyor.

The solids elutriated with the flue gases from the combustor pass into a refractory lined hot cyclone with an inside diameter of 0.6 m. Most of the elutriated solids are captured by the cyclone and are recirculated to the combustor through a non-mechanical loop-seal arrangement to improve combustion efficiency and sorbent utilization.

The hot flue gases from the cyclone pass through a hot water boiler (gas/water cooler). The solids collected in the boiler are discharged into a weighed bin, then transferred to an ash silo. The flue gases are cooled to about 200°C in the boiler before exiting to the baghouse.

The baghouse has two compartments with NOMEX type fabric bags suitable for continuous operation at 220°C and a maximum of 300°C. It removes (with air pulse cleaning) the fine particulates from the flue gas. The baghouse catch can be collected in a weighed bin and then transferred to the ash silo, or it can be pneumatically recycled to the combustor through a rotary valve. The ash recycle rate is controlled by varying the open/close frequency and timing of air operated ball valves, located in the

recycle line.

The venturi scrubber between the baghouse and the induced draft fan is used to remove fine particulates during startup and when there are problems with the baghouse. It is bypassed at other times. The cleaned flue gases are discharged into the atmosphere via the induced draft fan and a stack.

Ash samples for chemical and sieve analysis are collected from the combustor, boiler, baghouse, and, when it is in use, the venturi scrubber. The particulate samples downstream from the baghouse are collected by an isokinetic sampling system.

Flue gas is continuously analyzed and monitored for SO₂, CO, NO_x and O₂. Various flowrates, temperatures and pressures are measured and monitored throughout the rig. An ALCONT control and data acquisition system is employed to control, measure, record and process data.

COKE AND LIMESTONE CHARACTERISTICS

Table 1. Analytical data for Syncrude coke

Proximate analysis: (wt %) dry basis	A	B	C		
volatiles	5.6	6.72			
ash	9.5	7.96	8.44		
fixed carbon	84.9	85.32			
Ultimate analysis (wt % in dry solids)					
C	79.6	79.93			
H	1.3	1.61			
N	1.4	2.01			
S	6.6	6.74			
ash	9.5	7.96	8.44		
O (by difference)	1.6	2.08			
Higher heating value, MJ/kg (dry basis)	28.56	29.99			
moisture wt %	3.41	2.82			
V in coke wt % dry basis	0.209	0.1624*	0.1522		
		(0.1423)**			
Ni in coke wt % dry basis	0.0665	0.0541	0.0598		
Ash analysis (wt %)					
SiO ₂	45.60	TiO ₂	2.30	K ₂ O	1.87
Al ₂ O ₃	22.00	MnO	0.24	P ₂ O ₅	0.17
Fe ₂ O ₃	8.74	Ni	0.68	SO ₃	5.78
CaO	4.50	V	1.71		
MgO	1.75	Na ₂ O	1.38		
Ash fusion temperature (°C)		Oxidizing	Reducing		
Initial deformation		1270	1250		
Fluid		1390	1340		
Coke particle size distribution (single composite sample)					
Sieve size (mm)		Passing sieve (wt %)			
2.0 (0.18)		99.5	(29.4)		
1.0 (0.125)		99.2	(6.7)		
0.5 (0.063)		98.2	(0.1)		
0.35		96.5			
0.25		66.8			

- A Technical Research Centre of Finland, Finland
 B Chemex Lab Ltd., Vancouver, Canada * by Neutron activation method ** by atomic absorption method.
 C Energy Research Laboratories, CANMET, EMR Canada

The chemical analysis of Syncrude coke is fairly consistent and the analytical data from three sources are given in Table 1. They include proximate, ultimate and vanadium and nickel analyses on a bulk coke sample and sieve analysis on a composite sample taken by the Technical Research Centre of Finland; more comprehensive analyses including ash analysis, sulphur forms and ash fusion temperatures obtained by Chemex Lab Ltd. of Vancouver; and vanadium and nickel determinations by CANMET on samples from three runs.

Also, for each combustion test a representative coke sample was collected and analyzed for C, S, Ca, V, Ni, moisture and ash contents. The moisture, ash, S and V contents varied as follows:

Moisture 2.5 to 4.4% Sulphur 6.6 to 6.9%
Ash 6.7 to 9.4% Vanadium 0.19 to 0.215%

The sulphur and vanadium contents of the coke are high. The size consist of the Syncrude coke is fine with over 99% less than 2 mm and over 50% less than 0.2 mm.

The Fort McMurray limestone, used as sulphur sorbent, contained about 75% CaCO₃. The analytical data are given in Table 2. Also, samples were taken

for each test and analyzed for Ca, Na, K, V, and Ni. Sieve analysis of the limestone indicates that over 98% was smaller than 2 mm and over 50% was less than 0.30 mm. It also contains about 1 to 2% of alkaline compounds which appeared to concentrate in the fly ash making it sticky and prone to agglomerate.

TEST PROGRAM

The test program consisted of 19 separate test runs: Test 0 was a scoping test to establish the range of reliable operating values for the system. Test 1, 2, and 3 were baseline runs, without limestone addition and without baghouse ash recycle, at 823°C, 890°C and 940°C, to establish baseline SO₂ emissions. Tests 4 to 16 were with addition of Fort McMurray limestone.

The limestone runs were conducted at maximum, minimum and intermediate loads at nominal temperatures of 850°C, 900°C and 950°C with and without baghouse recycle, adjusting the Ca/S molar ratio to achieve 90% sulphur capture. The duration of these tests at steady state conditions was from 3.5 to 17 h. One test, at optimum conditions, was

Table 2. Analytical data for Fort McMurray limestone

1. OVERALL SAMPLES

Sample	Ca	Mg	CO ₃	C	S	Na	K	Cl	Moisture %	Loss on ign. %	Part. size 50% less than mm
	% in dry solids										
A	31.4	0.60	48.3	9.13	0.18	0.19	0.87	0.27	0.07	34.47	0.35
B	31.3	0.57	54.8	9.21	0.16	0.25	0.90	0.33	0.06	34.59	0.28
C	31.0	0.61	54.7	9.19	0.16	0.23	0.89	0.26	0.06	34.59	0.31

2. SAMPLES OF EACH TEST RUN

Test	Ca in dry solids %	Part. size 50% less than mm	Na in dry solids, %	K in dry solids, %	V in dry solids, mg/kg	Ni in dry solids, mg/kg
4	29.0	0.25	0.39	1.0	0	0
5	29.8		0.35	1.0	0	0
6	31.0	0.66	0.39	0.70	0	0
7a	28.0	0.36	0.35	0.70	0	0
8a	28.8	0.42	0.38	0.80	0	0
7b	29.8	0.31	0.36	0.60	0	0
8b	31.0	0.42	0.44	0.86	0	0
9	29.0		0.43	1.0	0	0
10	29.0	0.32	0.35	0.95	0	0
11	29.0	0.35	0.40	0.93	0	0
12	27.5	0.50	0.37	0.89	0	0
13	30.0	0.30	0.42	0.80	0	0
14	31.6	0.35	0.42	0.76	0	0
15	31.0		0.41	1.3	0	0
16	30.1	0.34	0.37	0.78	0	0

3. LIMESTONE PARTICLE SIZE DISTRIBUTION (single composite sample)

Sieve size (mm)	Passing sieve (wt %)
2.0	97.9
1.0	84.2
0.5	60.8
0.35	54.6
	41.3
	34.9
	24.9
	19.6

conducted for 25 h to confirm overall performance in prolonged operation. The superficial fluidizing velocities for the test series were varied from 2.8 m/s to 6.9 m/s while the nominal excess air was 20%. The superficial velocity is defined as the flue gas velocity in m/s in the combustor free board at combustor temperature (without considering the area of internals). Up to 80% of baghouse ash was recycled to the combustor in six tests to study the effect on combustion efficiency and sulphur capture.

TEST RESULTS AND DISCUSSIONS

Summary of Test Data

Mean input and output conditions and measurements are given in Table 3, including calculated values such as superficial fluidizing velocity, Ca/S molar ratio and sulphur capture. The coke feed rate is given on the "as fired" basis. The higher heating value (HHV) of coke was corrected for each test to account for variations in ash content.

$$\text{The correction factor } K_1 = \frac{100 - W_{\text{ash}}}{100 - 9.5}$$

where W_{ash} = % ash content of coke for a given test and 9.5 is the per cent ash content from the bulk sample. The corrected HHV = $K_1 \times \text{HHV}$ of bulk sample. Similarly, concentrations of N, H and O in the coke were corrected to account for variations in ash and sulphur content for each test.

$$\text{The correction factor } K_2 = \frac{100 - W_{\text{ash}} - W_s}{100 - 9.5 - 6.6}$$

where W_{ash} = % ash content and W_s = % sulphur content of coke for a given test and 9.5 & 6.6 are % ash content and % sulphur content respectively for the bulk sample. The corrected value = $K_2 \times$ the value from bulk sample analysis.

The weight of bed solids in the combustor at the beginning and end of steady state for each test is estimated from the calibration of weight of material in bed versus the pressure under the distributor grid. Bed variation is the difference in bed inventory during the steady state period of each test and is positive or negative depending upon

Table 3. Mean values of input and output conditions and results

Test	Coke kg/h	Lime-stone kg/h	Total air kg/h	Fluid vel. m/s	Mean combustor temp °C	Primary air, per cent total air	O ₂ %	CO ppm	NO _x ppm	SO ₂ ppm	Ca/S mol/mol	S capture %	Bag-house ash recycle %
0	111.6	-	1224	4.6	896	62.9	3.5	150	220	-	-	-	0
1	125.6	-	1350	4.7	823	62.9	3.6	650	100	4300	-	19.7	0
2	115.6	-	1274	4.7	890	64.1	3.2	110	150	4800	-	10.4	0
3	131.0	-	1530	5.9	940	64.0	3.8	80	520	5000	-	0.0	0
4	124.6	72.4	1562	6.1	937	62.0	4.7	50	310	480	2.04	89.9	0
5	132.8	55.4	1526	5.6	881	63.0	3.2	70	130	500	1.54	90.2	0
6	130.7	76.7	1476	5.3	854	59.0	3.4	90	200	480	2.26	90.7	0
7A	118.8	73.4	1379	4.9	833	63.2	3.5	120	160	460	2.11	91.0	80
8A	126.4	60.8	1559	5.3	884	63.0	4.5	40	120	490	1.71	89.6	0
7B	117.4	52.9	1483	5.3	842	61.9	5.0	30	175	470	1.64	90.0	0
8B	123.5	54.0	1516	5.6	896	62.0	4.3	45	185	480	1.65	90.1	80
9	130.0	63.4	1490	5.8	938	62.1	3.2	40	254	490	1.72	90.6	80
10	140.0	69.5	1624	6.3	947	62.1	3.5	20	240	470	1.73	90.9	0
11	147.2	72.7	1739	6.9	960	62.1	4.0	5	450	430	1.76	91.4	80
12	88.2	35.6	1091	4.0	883	59.1	4.8	20	70	490	1.34	89.9	80
13	83.5	32.4	1044	3.8	882	60.0	5.0	10	65	440	1.41	90.8	0
14	73.4	23.0	860	3.1	862	51.9	3.6	45	54	580	1.21	88.6	0
15	67.0	18.0	756	2.8	875	51.9	3.2	50	52	520	1.03	90.0	80
16	124.9	52.9	1480	5.5	900	62.0	4.0	10	220	480	1.53	90.5	67

an increase or a decrease in bed inventory. There were difficulties in obtaining accurate ash weights from various ash streams. The errors ranged from 0.5 to 16.5% with limestone runs and up to 26% without limestone runs. The ash balances are given in Table 4 where the ash quantity is the sum of the ash in the coke feed, the limestone residue (after ignition), and the unburnt carbon in the ash streams (as given in Table 5). The CaO is the residual unreacted CaO from the limestone. The CaSO₄ is calculated from the amount of CaO converted to CaSO₄, as determined from the sulphur capture for each test (Table 3).

It was assumed that steady state had been achieved when thermal equilibrium was reached and SO₂ concentrations in the flue gases were steady.

Combustion Efficiency

High combustion efficiencies were achieved, ranging from 97.4 to 99.4% over all the test conditions except for Test 0 when combustion efficiency was 96.4%. As this was a scoping test to establish combustor operating conditions, efficiency was not a major concern.

The combustion efficiency was calculated in two ways, based on carbon losses and energy losses. The carbon losses were calculated in two ways, based on carbon losses and energy losses. The carbon losses were calculated from the average carbon content and mass flow rate of each of the bed drain, boiler and baghouse ash streams, plus the carbon loss in CO. The carbon combustion efficiency was then obtained by subtracting the total carbon losses from the carbon in the coke.

The energy losses due to unburned carbon and CO were calculated as follows:

Energy loss due to unburned carbon: 33.73 MJ/Kg C

Energy loss due to unburned CO: 0.283 MJ/mole CO

The combustion efficiency based on energy losses was then obtained by subtracting the energy losses from the energy in the coke, HHV basis. The carbon losses and respective combustion efficiencies by both methods are given in Table 5 and are in agreement.

The test results also indicate that as the test program progressed and more operating

Table 4. Ash balance

Test	Ash kg/h	CaO kg/h	CaSO ₄ kg/h	Input total kg/h	Bottom ash kg/h	Boiler ash kg/h	Baghouse* ash kg/h	Bed variation kg/h	Accumulation error kg/h
0	10.8	-	-	10.8	-	9.0	6.6	-2.9	-1.9
1	19.1	-	-	19.1	-	4.7	5.1	7.2	2.1
2	12.2	-	-	12.2	-	3.6	9.0	-3.6	3.2
3	11.2	-	-	11.2	-	2.2	9.7	-2.2	1.5
4	28.4	16.6	31.3	76.3	33.5	4.0	39.3	2.9	-3.4
5	23.8	9.7	32.8	66.3	38.2	1.8	22.1	-1.0	5.3
6	28.4	19.8	32.8	81.0	52.9	2.5	19.4	8.3	-2.1
7A	29.2	16.2	30.2	75.6	38.9	5.0	27.7	-2.2	6.2
8A	25.6	11.9	31.0	68.5	42.8	2.9	17.6	10.4	-5.4
7B	22.0	9.7	29.5	61.2	52.6	6.5	9.8	-3.2	-4.5
8B	21.6	10.8	31.0	63.4	37.8	11.5	5.8	2.2	6.1
9	25.2	12.2	33.1	70.5	35.3	12.6	25.7	-1.1	-2
9	25.2	12.2	33.1	70.5	35.3	12.6	25.7	-1.1	-2
10	29.2	13.3	36.4	78.9	56.5	4.0	20.6	-8.6	-6.4
11	31.3	14.0	37.4	82.7	37.4	9.0	14.5	10.8	11.0
12	17.3	4.7	22.3	44.3	30.2	6.5	6.9	-2.9	3.6
13	15.1	5.0	21.2	41.3	20.2	3.6	4.7	6.1	6.7
14	10.8	2.9	18.0	31.7	3.2	2.2	6.1	18.0	2.2
15	9.7	1.1	16.6	27.4	21.6	4.0	9.7	-8.6	0.7
16	23.0	9.0	32.0	64.0	32.4	15.8	14.0	2.2	-0.4

* Includes particulates escaping the baghouse, measured by isokinetic sampling.

experience was gained with burning the Syncrude coke, the combustion efficiency improved, ranging from 98.6 to 99.4% for the last eight tests. The freeboard and cyclone temperatures indicate that a small amount of combustion occurred in the cyclone, equivalent to a maximum of 0.4% carbon input.

Regression analysis was used to calculate the effect on combustion efficiency of the following variables:

- average reactor temperature (°C)
- superficial gas velocity in the freeboard (m/s)
- excess O₂ in dry flue gas (%)

- primary air as per cent of total combustion air
- bag house ash recirculation (%)

Results indicate that the per cent primary air has the greatest effect on combustion efficiency, which improves as primary air is decreased and secondary air is increased. Baghouse ash recirculation to the combustor improves the combustion efficiency slightly. The combustor temperature and excess O₂, in the operating range explored, have minor effects on combustion efficiency. The combination of primary air, temperature and excess O₂ gives the smallest

Table 5. Combustion efficiency

Test	Carbon in bottom ash		Carbon in boiler ash		Carbon in baghouse ash		CO		Energy input kW	Combustion efficiency %		Baghouse ash recycle %
	%	kW	%	kW	%	kW	ppm	kW		A	B	
0	-	-	22.5	19.0	21.3	12.9	150	0.5	858	96.2	95.8	0
1	-	-	26.1	11.4	23.7	11.2	650	2.4	953	97.4	97.1	0
2	-	-	19.3	6.5	*16.1	13.6	110	0.4	900	97.7	97.5	0
3	-	-	10.9	2.2	*11.1	10.1	80	0.3	1026	98.8	98.7	0
4	0.6	1.9	4.5	1.7	4.0	14.5	50	0.2	987	98.1	97.9	0
5	0.8	2.9	6.4	1.1	5.5	11.4	70	0.3	1057	98.5	98.3	0
6	0.9	4.5	8.8	2.1	8.3	15.2	90	0.4	1028	97.8	97.6	0
7a	1.1	4.0	5.8	2.7	4.8	12.4	120	0.5	946	97.9	97.7	0
8a	0.8	3.1	6.2	1.7	6.0	9.9	40	0.2	998	98.5	98.3	0
7b	2.4	11.7	6.4	3.9	3.5	3.2	30	0.1	926	98.0	97.8	80
8b	1.0	3.5	4.4	4.7	2.0	1.1	45	0.2	974	99.0	98.9	80
9	0.5	1.7	3.0	3.5	1.8	4.4	40	0.2	1030	99.0	99.0	80
10	1.9	6.9	3.8	1.4	3.8	7.3	20	0.1	1099	98.6	98.5	0
11	1.9	6.7	3.0	2.5	3.1	4.2	5	0.0	1146	98.8	98.7	80
12	1.0	2.9	3.3	2.8	1.6	1.0	20	0.1	685	99.0	98.9	80
13	0.9	1.7	4.9	1.6	1.8	0.8	10	0.0	646	99.4	99.3	0
14	0.8	0.2	5.8	1.2	3.0	1.7	45	0.1	581	99.4	99.4	0
15	0.9	1.8	5.2	1.9	1.2	1.1	50	0.1	520	99.1	99.0	80
16	1.3	4.1	3.9	5.7	2.9	3.7	10	0.0	976	98.6	98.5	67

* Measured from particulate samples, baghouse bypassed

A - based on higher heating value B - based on carbon only

standard deviation, however the variation for different variables is small and no conclusive relationship is obtained.

Sulphur Capture

The baseline tests without addition of limestone indicate that ash constituents of coke captured 19.7%, 10.4% and 0% sulphur at 823°C, 890°C and 940°C respectively. This clearly shows that, in the range of temperatures employed, sulphur capture by coke ash constituents is maximum at about 820°C and decreases as combustor temperature increases.

Sixteen tests were conducted with the addition of Fort McMurray limestone, adjusting Ca/S molar ratio to achieve 90% SO₂ reduction. As shown in Fig. 2, sulphur retention varied from 88.6 to 91.4%, and in general, a sulphur retention of 90% was achieved with a Ca/S molar ratio of less than 1.7, except for runs early in the program (Tests 4, 6 and 7A) when Ca/S molar ratios of up to 2.26 were required.

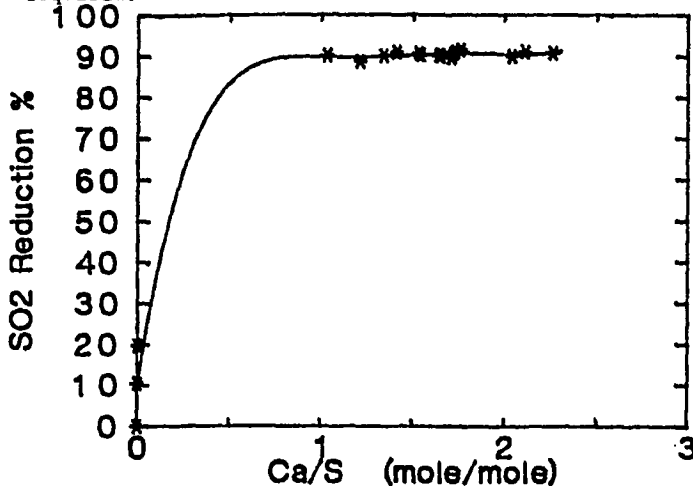


Fig.2 Sulphur capture vs Ca/S ratio

The following input parameters were analyzed by linear regression analysis to determine their influence on sulphur retention:

- Ca/S molar ratio
- average reactor temperature (°C)
- superficial gas velocity in the freeboard (m/s)
- O₂ content of the flue gas (%)
- primary air as a percentage of total combustion air (%)
- baghouse ash recirculation (%)

The analysis showed that sulphur capture increased with increasing Ca/S molar ratio as expected. However, because 90% SO₂ reduction was a target parameter for this test program the effect of differing Ca/S molar ratios on sulphur capture is masked and detailed exploration of this phenomenon is not possible.

The effect of average combustor temperature on Ca/S molar for about 90% sulphur capture ratio is shown in Fig. 3. The optimum temperature range appears to be from 860°C to 900°C. At temperatures lower than 860°C and higher than about 900°C slightly higher Ca/S molar ratios are required for a given sulphur capture.

The effect of temperature on Ca/S molar ratio can be expressed as:

(within the operating temperature range for this test program)

$$\text{Ca/S} = 128.45 - 0.2833T + (1.5811E-4)T^2$$

for tests without baghouse ash recycle and:

$$\text{Ca/S} = 67.938 - 0.15126T + (8.5958E-5)T^2$$

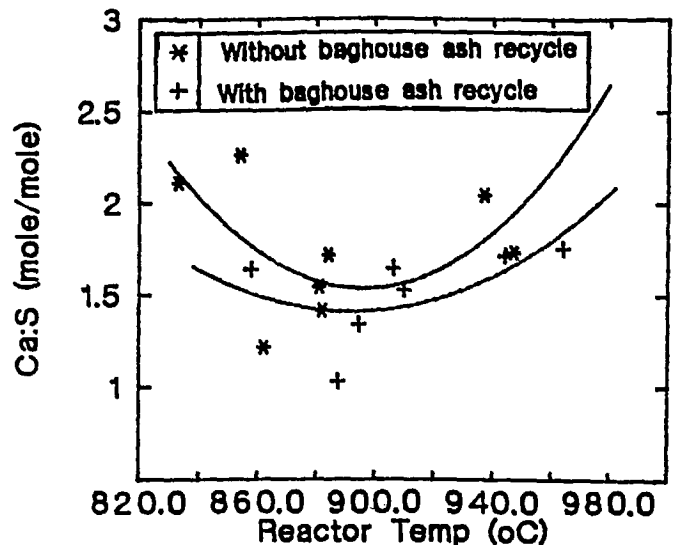


Fig.3 Ca/S molar ratio as a function of reactor (combustor) temperature

for tests with baghouse ash recycle. In both cases, T is the combustor temperature in °C.

Baghouse ash recirculation appears to reduce the required Ca/S molar ratio for 90% sulphur capture, by about 10% for temperatures over 900°C and by up to 20% for temperatures between 840°C and 880°C.

At lower superficial gas velocity the sulphur capture appears to be slightly more efficient due to increased residence time at low loads. Increase in the primary air also marginally improves sulphur retention.

Calcium utilization was high, ranging from 40 to 65%, and for Tests 14 and 15 it was 73 and 87% respectively. Average calcium utilization was about 57%.

NO_x Emissions

The NO_x emissions in the flue gas, reported in Table 3, varied from 54 to 520 ppm (on a dry gas basis) corresponding to 0.035 to 0.341 mg NO₂/kJ heat input.

The following parameters were studied by linear regression analysis to determine their effect on NO₂ emissions:

- primary air as a percentage of total combustion air (%)
- mean combustor temperature (°C)
- superficial fluidizing velocity (m/s)
- CO content in dry flue gas (%)
- O₂ in dry flue gas (%)
- baghouse ash recirculation (%)

Over the range investigated, it seems that increasing the percentage of primary air increases the NO_x level, doubtless due to the increased amount of oxygen available for reaction in the lower part of the combustor. NO_x increases as the temperature increases for the tests with and without limestone as shown in Fig. 4. For the range of test conditions employed, a combustor temperature of 900°C seems to be the optimum for NO_x emissions as well as for combustion efficiency and sulphur capture. Excess O₂, CO concentration, baghouse ash recirculation and sulphur capture have very little influence on NO_x emissions.

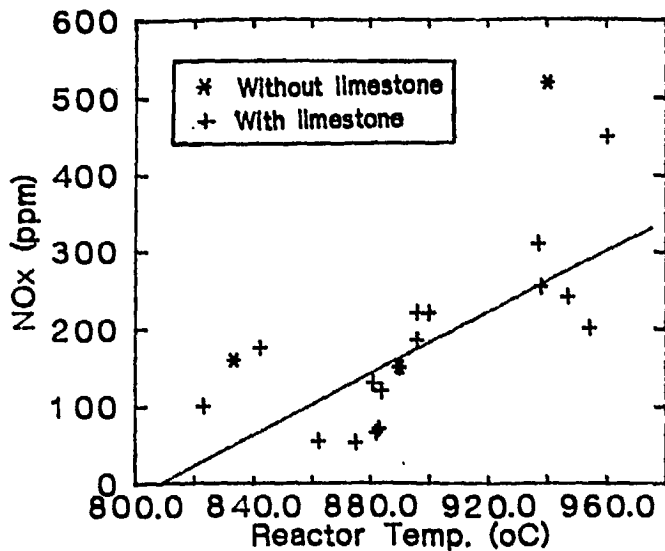


Fig.4 NO_x emissions as a function of reactor (combustor) temperature

Nitrogen conversion to NO_x varied from a low of 3% to 10% except for the three high temperature runs when it was up to 21%.

It was observed that NO_x increases with increasing superficial fluidizing velocity, as shown in Fig. 5. This probably is due to a residence time effect; with increased velocity NO_x does not have sufficient time to convert back to nitrogen (2,3).

It appears that NO_x levels of less than 100 ppm can be achieved by proper selection of operating conditions, but it should be noted that

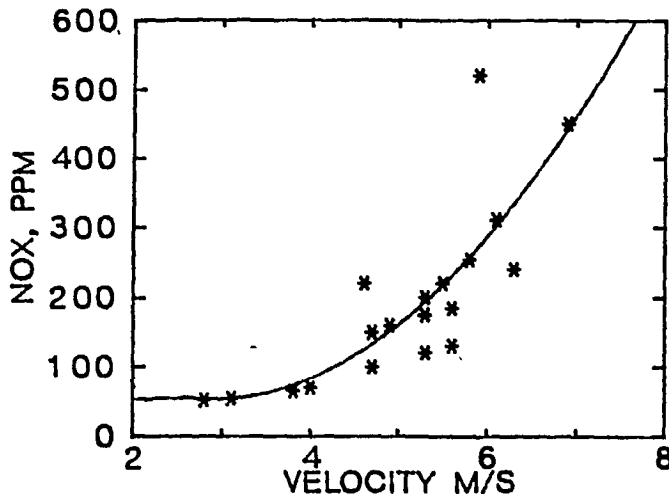


Fig.5 NO_x emissions vs superficial velocity

investigating the parameters affecting NO_x formation was not a primary objective of the program.

Emissions of CO in the flue gases were quite low, ranging from 5 to 90 ppm for all runs with limestone addition, hence CO losses were minimal. No attempt has been made to correlate CO with any of the test parameters. It appears that at higher temperatures CO is slightly lower.

Particulate Emissions

The particulate emissions were measured between the baghouse and the venturi scrubber by an isokinetic sampling method. They ranged from 6 mg/MJ to 41 mg/MJ except for two runs when they were high because the baghouse was bypassed due to mechanical problems. These emissions are well within the guideline of 86.2 mg/MJ (0.216lb/MBTU). Analysis of particulate samples indicates that after the baghouse and venturi scrubber less than 1% of total vanadium, nickel, calcium and sodium was emitted to the stack during tests with limestone addition.

SULPHUR, CALCIUM, VANADIUM AND NICKEL BALANCE

Procedure

The mass balance of a given element was determined from its rate of mass input with coke and limestone and its total mass output in the bottom, boiler and baghouse ash streams during the steady state period of each test. The elements in the particulates leaving the baghouse are included in the baghouse ash total.

The other important factor included in the mass balance is the variation in mass and element concentrations in bed inventory from the beginning to the end of the steady state period for each run.

From the initial and final masses of the material in the combustor, as determined by calibration of windbox pressure, and initial and final concentration of an element from analysis, the change in bed inventory for a given element is given by:

$$\text{Change in inventory } e = M_1 \times C_1 - M_2 \times C_2$$

where M_1 = initial bed mass

M_2 = final bed mass

C_1 = initial bed concentration of a given element

C_2 = final bed concentration of a given element

Since the solid inventory and concentration for a given element may increase (+ve) or decrease (-ve) during a test, the bed elemental variations may be +ve or -ve.

The "accumulation error" is due to difficulties in obtaining accurate weights of ash streams and representative samples. Ash holdup in the system due to sticky depositions may also be partially responsible for the error.

Sulphur and Calcium Balance

The sulphur balance data are given in Table 6. For the tests with limestone addition about 50% of sulphur was captured by the bottom ash except for Test 14 during which very little bottom ash was drained and the change in bed inventory was large. About 2 to 16% of sulphur was captured in the boiler ash and about 4 to 28% of sulphur was retained in the baghouse ash. The sulphur variation in the bed was from -12 to 24% except for Test 14 when it was 101%. The accumulation error varied from -27 to 31%.

Data for the calcium balance indicate that calcium distribution follows trends similar to sulphur distribution. On the average over 50% calcium was found in bottom ash, 2 to 25% in boiler ash and 6 to 33% in baghouse ash.

Table 6. Sulphur balance

T e s t	S in bottom ash	S in boiler ash	S in baghouse ash	S variation in bed	S in flue gas	Accu- mula- ting + error
	% of input					
0	-	-	-	-	-	-
1	-	2	2	1	80	15
2	-	1	3	0	90	6
3	-	0	3	0	100	-3
4	21	4	28	16	10	21
5	49	2	16	8	10	15
6	52	3	13	24	9	-1
7a	56	5	23	-12	9	19
8a	63	3	15	19	10	-10
7b	61	7	8	-3	10	17
8b	54	11	4	12	10	9
9	48	12	20	8	9	3
10	69	3	14	-9	9	14
11	41	7	9	5	9	29
12	45	9	7	-4	10	33
13	36	5	5	11	9	34
14	4	3	8	101	11	-27
15	37	7	15	1	10	30
16	39	16	10	1	9	25

Vanadium Balance

The average vanadium content of Syncrude coke is relatively high, about 0.2% by weight as per analysis by the Technical Research Centre of Finland. By comparison the average values for samples from two runs, analyzed by Chemex Lab Ltd. of Vancouver, are 0.1624% (by neutron activation) and 0.14% (by atomic absorption and inductively coupled plasma spectrometry (ICP), while CANMET measured 0.1522% V in the sample from a third run, using ICP. The results presented in Table 7 and Fig. 6 are based on analyses from Finland.

This high concentration of vanadium in coke can be a potential of boiler tube corrosion at high metal temperatures (4,5,6). On the positive side it raises the possibility of recovery of vanadium on a commercial scale.

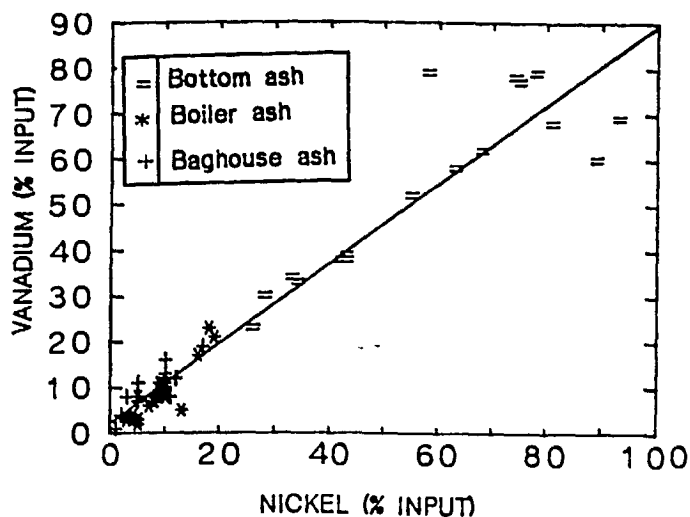


Fig.6 Vanadium vs nickel as % input in ash streams

In conventional combustion processes it has been found that vanadium corrosion can be suppressed by adding small amounts of magnesium oxide, but small amounts of calcium oxide are not significantly effective. Syncrude coke contains about 0.074% magnesium and the Fort McMurray limestone used for sulphur capture has about 0.6% magnesium in addition to 30% calcium. Magnesium and/or calcium in high concentrations may tend to capture the vanadium in the coke by forming refractory vanadium compounds.

For baseline runs without addition of limestone, the Mg/V ratio was about 0.36. For runs with limestone addition, the Mg/V ratio varied from

Table 7. Vanadium capture and nickel balance data in ash streams

Test	V input g/h	Bottom ash		Boiler ash		Baghouse ash		Variation in		Accumulation						
		V g/h	% of input	Ni % of input	V g/h	% of input	Ni % of input	V g/h	% of input	Ni % of input	% of input					
0	211	-	-	-	31.0	14	17	117	55	66	0.0	0	-2	64.1	31	19
1	238	-	-	-	19.1	8	9	90.7	30	28	9.0	4	5	119	50	58
2	224	-	-	-	14.8	-7	8	153	68	81	1.4	1	-4	54.4	24	15
3	265	-	-	-	8.6	3	5	165	62	68	-5.8	-2	-2	97.2	37	29
4	250	17.3	7	5	7.6	3	5	208	83	119	-1.1	0	28	18.4	7	-1
5	263	11.5	4	2	4.3	2	5	206	79	58	3.6	1	2	37.1	14	33
6	271	22.7	8	8	6.8	3	4	190	70	78	6.5	2	5	44.6	17	5
7A	249	28.8	12	10	12.6	5	13	194	78	74	-2.9	-1	-1	16.6	6	4
8A	233	25.6	11	5	6.5	3	3	136	58	63	13.7	6	7	51.8	22	22
7B	233	44.3	19	17	17.6	8	5	76.6	34	33	21.6	9	9	69.8	30	36
8B	243	28.4	12	12	56.5	23	18	55.4	23	26	1.4	1	0	102	41	44
9	252	17.6	7	31	42.8	17	16	194	77	75	1.4	1	-8	-4.3	-2	-14
10	260	33.8	13	10	10.1	4	4	156	60	89	-10.4	-4	-15	70.6	27	12
11	281	22.3	8	3	29.9	11	9	108	38	42	-2.2	-1	29	123	44	17
12	168	18.0	11	5	30	8	10	65.5	39	43	5.0	3	-9	66.2	39	51
13	156	17.6	11	10	15.1	10	10	51.5	33	34	7.6	5	0	63.7	39	46
14	139	1.4	1	1	8.6	6	7	53.3	38	43	36.4	26	30	38.9	29	19
15	126	19.8	10	10	10.8	9	9	86.4	69	93	0.7	1	8	8.3	5	-20
16	236	19.4	8	11	49.0	21	19	123	52	55	0.4	0	0	43.9	19	15

1.22 to 2.13 when taking into account magnesium from the coke as well as the limestone. The Mg/V ratio ranged from 0.84 to 1.76 when magnesium from the limestone only was considered. In general, magnesium appears to influence vanadium capture; however, the large amount of calcium present in the limestone may also be responsible for the vanadium capture. Further work is needed to clarify the relative effects of magnesium and calcium on the vanadium capture phenomenon in CFBC.

The vanadium balance data in Table 7 indicate that baghouse ash captures the highest amount of vanadium, ranging from 23 to 83% of input. The vanadium content in the boiler ash varies from 2 to 23% whereas in the bottom ash it varies from about 4 to 19%. The total vanadium capture varies from about 56 to 100% with an accumulation error ranging from 0 to 44% for runs with limestone. It appears, from the results, that vanadium and its compounds tend to concentrate in the smaller particle stream, hence the large proportion found in the baghouse ash. The variations in vanadium concentration from 23 to 83% in the baghouse may be due to the accumulation of ash in the boiler section and errors in weights and sampling. The vanadium concentration in the particulates after the baghouse for most of the runs is less than 0.5% of the total input.

If the lower values of 0.1624 and 0.1522% vanadium in the coke, as determined by the Chemex and CANMET labs, are assumed to be accurate, then the accumulation error decreases and the vanadium balance improves to some extent, except for Tests 4, 7A, 9 and 15, in which the accumulation errors increase up to -34%. Assuming 0.1624 and 0.1522% V in the coke, the ranges of errors are respectively 39 to -25% and from 35 to -32%.

The effects of temperature, baghouse ash recycle, and superficial gas velocity on vanadium capture do not indicate any clear trends.

Nickel can be used as a tracer, assuming it to be inert, for vanadium in ash streams. It can be observed from Table 7 and Fig. 6 that concentrations of vanadium in the various ash streams closely follow the distribution of nickel. Concentrations of both nickel and vanadium are much higher in baghouse ash than in boiler and bottom ash.

The Fort McMurray limestone, containing from 0.35 to 0.44% sodium, contributes 80 to 90% of the sodium input. Syncrude coke has about 0.02 to 0.05% sodium except for Run 16 when it was 0.16%. Approximately 40% of sodium was captured in the bottom ash, 10% in the boiler ash and 40% in the baghouse ash.

BOILER DESIGN CONSIDERATIONS

One of the objectives of the test program was to generate data useful for optimizing the design of a commercial scale boiler. In light of this, the results have been analyzed with respect to their impact on the design of a commercial CFB boiler utilizing the subject fuel and limestone.

Combustor Operating Temperature

From the test program results, a combustor temperature of 900°C was found to achieve optimum combustion efficiency, sulphur capture and NO_x emissions. The low-volatile Syncrude coke can be burned in a CFBC with high combustion efficiency, 97.4 to 99.4%.

The tests indicate that the combustion is carried over slightly into the cyclone but this is not expected to be of significant concern in a

commercial CFB boiler. Although Syncrude coke is low in volatiles and contains some less reactive carbon forms, the coke burns well in the lower portion of the combustor.

SO₂ Emissions and Ca/S Molar Ratio

Fort McMurray limestone added at a Ca/S molar ratio of 1.7 or less appears to be adequate to achieve the requirement of 90% sulphur capture, although higher Ca/S molar ratios of up to 2.26 were required for three runs early in the program. The calcium utilization was high, with an average value of 57%. This information can also be useful in design of limestone storage, handling and feeding systems. It is important to bear in mind that the lower Ca/S molar ratio was achieved with limestone sized at 100% smaller than 2 mm and 50% smaller than 0.3 mm. Coarser limestone may need a higher Ca/S ratio while a very fine size may increase elutriation and need a more efficient cyclone system.

Primary and Secondary Air

The test work indicated that 60% primary air and 40% secondary air provided a good balance between higher combustion efficiency and lower NO_x emissions. Although the low volatiles in the coke require more primary air than for some other fuels, and therefore NO_x control is compromised to some extent, NO_x emissions are still well within the applicable limits.

Ash Split

The distribution of bottom ash and fly ash with limestone runs is about 50/50. This can be useful in designing and sizing the bottom ash handling system and baghouse or electrostatic precipitator.

Slagging/Fouling and Corrosion/Erosion

The test results showed that the ash, with limestone runs, is alkaline, slightly sticky and easily agglomerated. This suggests that the spacing between convection and superheater surfaces should be slightly larger than normal to minimize ash deposition. Also, sootblowers will be required. The tests were of insufficient duration to directly study corrosion and erosion of tubes and surfaces, but results indicate that most of the vanadium will be captured in various ash streams, and that corrosion from fused ash will not be a significant problem. The ash fusion temperatures are fairly high (1250-1270°C) and the operating temperature of 900°C to 950°C will not cause any slagging problems.

CONCLUSIONS

1. Syncrude coke containing about 6.75% sulphur, low volatiles and less reactive carbon forms can be burned efficiently and in an environmentally acceptable manner in a CFBC. High combustion efficiencies ranging from 97.4 to 99.4% were achieved.
2. Fort McMurray limestone proved to be fairly effective in sulphur capture and on the average, with a Ca/S molar ratio of 1.7% or less, about 90% sulphur capture was readily achieved.
3. The optimum conditions offering the best compromise between sulphur capture and combustion efficiency were found to be 900°C with 67% baghouse ash recycle and 60% primary and 40% secondary air.
4. Baghouse ash recycle to the combustor improves the combustion efficiency slightly and decreases

the Ca/S molar ratio by about 10% for temperatures about or greater than 900°C and by about 20% between 840°C and 880°C.

5. NO_x emissions varied from 54 to 450 ppm (0.035 - 0.295 mg/kJ) in runs with limestone. NO_x level increases as the combustor temperature increases. NO_x also increases with increase in superficial fluidizing velocity. CO emissions were quite low, ranging from 5 to 120 ppm.
6. It seems that most of the vanadium in the coke is captured by small amounts of MgO in the coke ash and/or large amounts of CaO provided for sulphur capture. Corrosion due to vanadium is not expected to be a problem.

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