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REDUCTION OF SULPHUR EMISSIONS BY COAGGLOMERATING COAL WITH LIMESTONE

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1. ABSTRACT

A novel technique is described whereby sulphur dioxide adsorbents can be incorporated directly into coal or coke agglomerates during liquid phase agglomeration using bitumen or heavy oil as the binder. This technique allows the advantageous use of very small and more active sulphur adsorbent particles in fluid bed combustion by binding them tightly within larger coal agglomerates, thereby reducing the possibility of their elutriation from the bed. As a result, higher adsorbent utilization efficiencies can be obtained for the coagglomerated fuel, compared to those systems in which a coarser adsorbent is added separately to the fluid bed.

In this investigation we have attempted the coagglomeration of a Nova Scotia coal with limestone to reduce sulphur emissions during combustion. Static combustion tests at 850°C were carried out in a muffle furnace and compared to results found for a bench scale fluidized bed unit at the same temperature. In both cases sulpher capture of over 60% was obtained at a calsium to sulphur molar ratio of 1:1.

2. INTRODUCTION

The increasing concern about the environment, in particular, the gaseous emissions from coal-fired power stations and their associated link to the formation of acid rain with its detrimental effects of the ecosystem, has resulted in considerable research into both flue gas cleaning techniques and methods of sulphur reduction in coal (1). Physical cleaning methods can only remove inorganic forms of sulphur, leaving the organic sulphur in the coal matrix. Therefore, in addition to precombustion cleaning, sulphur emission control after combustion may also be necessary.

In some previous work (2-5) by the authors, it has been demonstrated that sulphur dioxide sorbents can be incorporated directly into coal or coke agglomerates during liquid phase agglomeration to recove bitumen or heavy oil from waste sludges. The bitumen acts as a binder for both coal and sorbent.

This technique allows the advantageous use of very small and more active sulphur sorbent particles in fluid bed combustion by binding them tightly within larger coal agglomerates. This approach reduces the possibility of elutriation of the sorbent particles from the bed and consequently higher sorbent utilization efficiencies can be obtained for the coagglomerated fuel when compared to those systems in which a coarser sorbent is added separately to the fluid box.

The objective of the present investigation was to study the feasibility of coagglomerating sulphur capture agents such as limestone with a Nova Scotia coal as a means of reducing sulpher dioxide emissions during combustion. In this study, coagglomeration with limestone has been tested using coal samples freshly beneficiated, as well as material which had been previously beneficiated and stored for an extended period of time. Static combustion tests at 850°C were carried out in a muffle furnace and compared to the results found for a bench scale fluidized bed unit at the same temperature.

3. EXPERIMENTAL SECTION

The coal used in this study was a bituminous thermal coal from the Prince Mine, Cape Breton Island, Nova Scotia. It was dry pulverized to approximately 80% minus 200 mesh prior to suspension in water for the beneficiation tests. Initial ash content was 19 wt % with a total sulphur level of 3.8 wt % and pyritic sulpher content of 1.5 wt %.

In addition, tests were carried out on this same coal after beneficiation by agglomerating with ≈ 2 wt % No. 4 fuel oil and storage in a drum for a period of about 2 months. The former coal is here referred to as the "untreated" coal, while the latter is referred to as "preagglomerated" or as "aged agglomerated coal."

3.1 COAGGLOMERATION WITH LIMESTONE

Freshly beneficiated coal was coagglomerated with limestone using the liquid phase agglomeration procedure described elsewhere (2-5). The previously-beneficiated, aged, agglomerated coal did not coagglomerate satisfactorily using this procedure.

As an alternative, this coal was pressure compacted with limestone, using bitumen as a binder. Pellets were prepared in a 1.25 cm diameter die fitted with dual pistons to allow more uniform compaction. After loading, the die was placed in a hydraulic press and subjected to a pressure of 7 MPa to give a final pellet thickness of approximately 0.5 cm.

3.2 COMBUSTION TEST

Combustion tests were carried out in both a muffle furnace and a bench scale fluidized bed reactor at 850°C (4,6). The SO_2 concentrations in the combustion gas from the fluidized bed reactor were measured with a Beckman model 865 SO_2 infrared analyzer. Tests were also carried out with blank samples containing no sorbent. The percentage retention of SO_2 by the sorbent, called "Sulphur Capture," was calculated by comparison of the results from the two tests. Corrections were made for the different sulphur contents of the agglomerates used as a blank and those containing sorbent.

For the combustion experiments in a muffle furnace, the sulphur content in the ash residue was determined by x-ray flourescence spectrometry. The sulphur fized in the ash during combustion was the expressed as a percentage of the total sulphur in the original sample to give the "Sulphur Capture." In addition, "Calcium Utilization" was calculated as the amount of calcium fixed as $CaSO_4$ in the ash as a percentage of the total calcium present in the feed agglomerates.

4. RESULTS AND DISCUSSION

In previous work (2-5), it was demonstrated that the desulphurization of petroleum cokes could be effectively achieved by coagglomeration with sulphur sorbents; this lead to greater sorbent utilization, compared with systems where the sorbent was added separately (3). This advantage results from two factors: firstly, the agglomeration step allows use of much finer sulphur sorbent particles in a fluid bed system [it is well known that finer particles will give increased SO_2 adsorption (7)]; secondly, agglomeration provides intimate contact between the sorbent and fuel particles.

During burning, sulphur dioxide, formed within the agglomerates, is not subject to the flushing action of the fluidizing gas and consequently there is a longer period of contact with the sorbent compared to the case for physical mixtures. If the agglomerates break down, this advantage is lost.

4.1 BENEFICIATION OF UNTREATED COAL AND COAGGLOMERATION WITH LIMESTONE

Our earlier work was based on the coagglomeration of petroleum cokes, whereas the present study deals with the coagglomeration/beneficiation of coal from the Pince Mine in Nova Scotia. Previously, Athabasca oil sands bitumen was found to be not only an excellent conditioner for limestone, but also a good binder for both the coke and the limestone.

However, initial tests with the Prince Coal showed that it did not respond to a single step coagglomeration with limestone, when the same procedure used for the petroleum cokes was applied. This may be due to the relatively high ash content of the coal which resulted in a different surface wetting character towards the bitumen-limestone combination. Consequently, the coal was first beneficiated with a minor amount of No. 4 fuel oil and these agglomerates were then coagglomerated with limestone using the bitumen as binder. Combustion tests on coal-sorbent agglomerates were carried out in both a bench scale fluidized bed apparatus and a muffle furnace at 850°C. The results are given in Table 1.

It is obvious from these results that the efficiency of sulphur capture is a function of the calcium-to-sulphur molar ratio in the agglomerates. Up to a Ca:S ratio of 0.7, the results from fluidized bed combustion did not differ significantly from those obtained in the muffle furnace tests. Beyond this point, for equivalent Ca:S molar ratios, a considerable higher sulphur capture was achieved from combustion in the fluidized bed compared with the static bed.

Table 1 also illustrates the effect of Ca:S molar ratio on the percent calcium utilization for the muffle furnace tests. Calcium utilization progressively increases with increases in Ca:S mole ratio until it reaches a plateau at around Ca:S ratio of 0.7, when it starts to decrease. These results were consistent with our previous findings for cokes (4).

4.2 THE EFFECT OF CONDITIONING AGENTS ON SULPHUR DIOXIDE CAPTURE BY LIMESTONE

In our previous work, we demonstrated that certain conditioning agents improved coagglomeration of the components, which resulted in the use of smaller quantities of oil, especially at high Ca:S molar ratios (3). This effect results from the improved wettability of the components towards the bridging oil. However, the combustion data for the soke-sorbent agglomerates, prepared with or without a conditioning agent, showed little difference in sulphur capture efficiency.

These effects were also investigated for the coal-limestone system. Conditioning agents used in the present investigation included: sodium silicate, oleic acid, sodium oleate, sodium hydroxide, Accol 4433 (a hydrocarbon surfactant mixture from Cynamide) and Witco TRS/10-80 (a petroleum sulfonate). All of the conditioning agents, except sodium silicate, improved coagglomeration of the components.

The combustion data for coal-limestone agglomerates, prepared with and without conditioning agents, are listed in Table 2. These results showed that, as found in earlier work (2), the sulphur capture efficiency of limestone in the coal-limestone agglomerates was not affected by any of the conditioning agents used.

4.3 SULPHUR CAPTURE EFFICIENCY OF LIMESTONE IN COAL-LIMESTONE COMPACTS

Attempts to coagglomerate pretreated, aged coal with limestone were unsuccessful. It appeared likely that weathering had rendered the coal surface less hydrophobic. The presence of hydrophilic limestone would further reduce the oleophilicity of the material which in turn would have a deleterious effect on the oil agglomeration characteristics of the coal. The relative oleophilic/hydrophilic nature of coal surfaces has been reported to be extremely important to the oil agglomeration process (8-10). Because of their hydrophobic nature, unoxidized or mildly oxidized coals are readily wetted by the bridging oil and may be agglomerated with considerably smaller quantities of bridging liquid than oxidized or low rank hydrophilic coals.

As the preagglomerated, weathered coal could not be coagglomerated with limestone, it was compacted instead into pellets with varying proportions of limestone. Combustion tests on thes pellets were carried out in a muffle furnace at 850°C. The results are given in Table 3.

The data in Table 3 for compacted pellets show that the efficiency of sulphur capture is again a function of the calcium to sulphur molar ratio in the pellets. These results also showed that the type and amount of oil used did not affect the sulphur retention capacity of the sorbent. It should also be noted that beyond a Ca:S molar ratio of 0.9, sorbent utilization for the compacts was essentially constant at 48% ± 2.5% and did not indicate the downward trend at high Ca:S ratios noted in Table 1.

In Figure 1 the sulphur capture efficiencies for the two types of agglomerates are compared as a function of the Ca:S molar ratio for tests in a static bed muffle furnace. (The compacted pellets were not of a size suitable for fluidized bed combustion). This plot indicates similar sulphur

retention results for the two types of agglomerates, suggesting that they withstood the combustion conditions equally well, producing intimate contact between the SO_2 and sorbent with similar degrees of SO_2 escape through fissures and breakdown of the agglomerates.

4.4 COMPARATIVE SULPHUR CAPTURE EFFICIENCIES

Figure 2 is a plot showing the levels of SO_2 emission obtained for both blank and lime containing agglomerates of Prince coal, Suncor and Syncrude cokes. U.S.A. and Canadian SO_2 emission standards are also shown on this plot. This Figure clearly illustrates that a Sulphur Capture capacity of more than 80% may be needed to burn these fuels to meet SO_2 emission standards. The data for coal/coke lime agglomerates plotted in Figure 2 shows that coagglomeration of fine sulphur sorbents in amounts representing a Ca:S molar ratio in the range of 1 to 2.0 could result in the reduced SO_2 emissions necessary to meet proposed standards.

5. CONCLUSIONS

5.1 Freshly ground Prince coal was successfully coagglomerated with varying amounts of limestone as a means of reducing sulphur emissions during combustion. Sulphur capture of over 60% was achieved at a calcium to sulphur molar ratio of 1:1.

5.2 Surface active agents such as oleic acid and Accoal 4433 facilitated coagglomeration of the coal with sulphur sorbents, but had no effect on the extent of sulphur retention by the sorbent.

5.3 Weathered Prince coal did not respond to coagglomeration with limestone and was dry compacted to yield pellets for combustion testing at various calcium to sulphur molar ratios. Results for sulphur retention during combustion in a muffle furnace were comparable to those for the coagglomerates made with the fresh coal.

5.4 Intimate mixing of fine sulphur adsorbents into the agglomerate matrix for coal and coke has produced the reduced SO_2 emission results in Figure 2. That is, the U.S. and Canadian emission standards can be met with Ca:S molar ratios in the range of 1 to 2.0, much below the 2.5 to 3 levels often reported for comparable SO_2 retention using coarser adsorbents mixed in the combustion system.

6. ACKNOWLEDGEMENTS

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TABLE 1 - SO_2 Capture by Limestone Fluidized-bed vs Static-bed Combustion*

Exp. #	Ca:S	Sulphur Capture (as w/w% of total sulphur)		Ca Utilization (w/w% of total Ca)***
		FBC	MF**	MF
Blank	0.15	-	6	40
1	0.35	26	30	86
2	0.50	37	36	72
3	0.60	59	43	72
4	0.65	57	51	79
5	0.65	46	55	85
6	0.70	44	52	74
7	0.70	66	53	76
8	0.80	-	57	71
9	1.10	84	64	58
10	1.80	-	66	37

* Untreated Prince coal, Agglomeration procedure: The coal was first agglomerated into microagglomerates using No. 4 fuel oil and then coagglomerated with conditioned limestone using bitumen. All experiments were carried out in the presence of Accoal 4433. Combustion conditions: Temperature 850°C, Air flow rate in the fluidized bed reactor: 15 liters per minute. FBC = Fluidized bed combustion; MF = Muffle furnace.

** Reference 3.

*** Calculated as $\frac{\text{Ca in } CaSO_4}{\text{Total Ca}} \times 100$; from the analysis of ash obtained after the combustion of coal-limestone agglomerates in a muffle furnace.

Table 2 The Effect of Conditioning Agents on the Retention of Sulphur by Limestone*

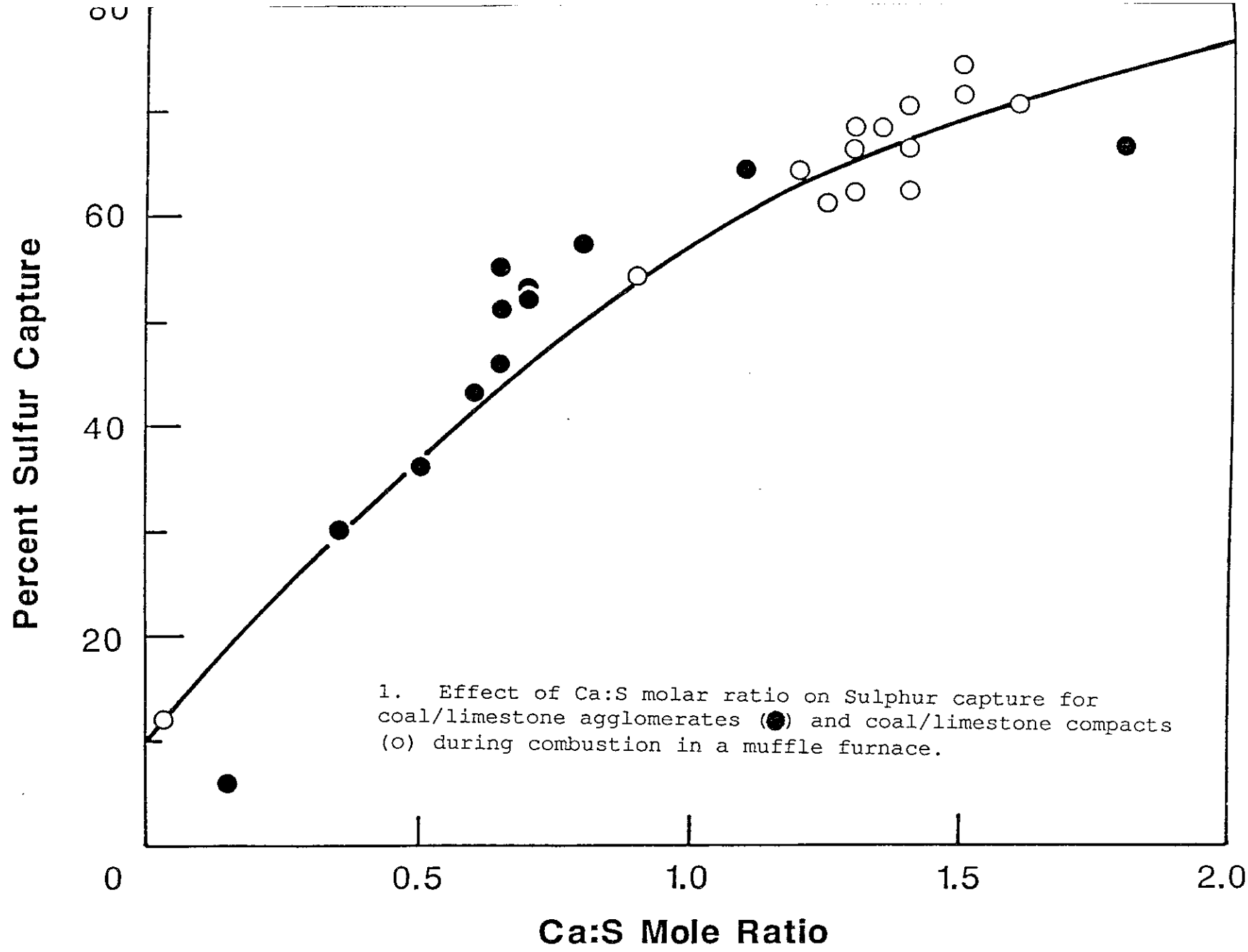
Exp. #	Conditioning Agent; concentration	Ca:S	Sulphur Capture (as w/w% of total sulphur)	Ca Utilization (w/w% of total Ca)
1	-	0.25	21	84
2	Sodium Silicate; 0.02%	0.25	19	76
3	-	0.55	40	73
4	Witco TRS/10-80; 0.05%	0.55	40	73
5	-	0.80	54	68
6	Accoal, 1 drop/20g coal	0.80	57	71
7	Accoal, 2 drop/20g coal	0.85	59	69
8	-	1.0	64	64
9	Oleic Acid; 1 drop/20g coal	1.0	67	67
10	Oleic Acid; 1 drop/20g coal	1.0	64	64
11	-	1.25	71	57
12	NaOH, 0.05%	1.25	54	43
13	Na-Oleate, 0.05%	1.3	72	55

* Experimental conditions same as in Table 1. Untreated prince coal was used in all experiments except # 12 where preagglomerated coal was used with 14% bitumen as agglomerating agent. Sulphur capture and Ca utilization calculated as in Table 1.

Table 3 Sulphur Capture by Limestone from the Combustion of Coal/Limestone Compacted Pellets in a Static bed*

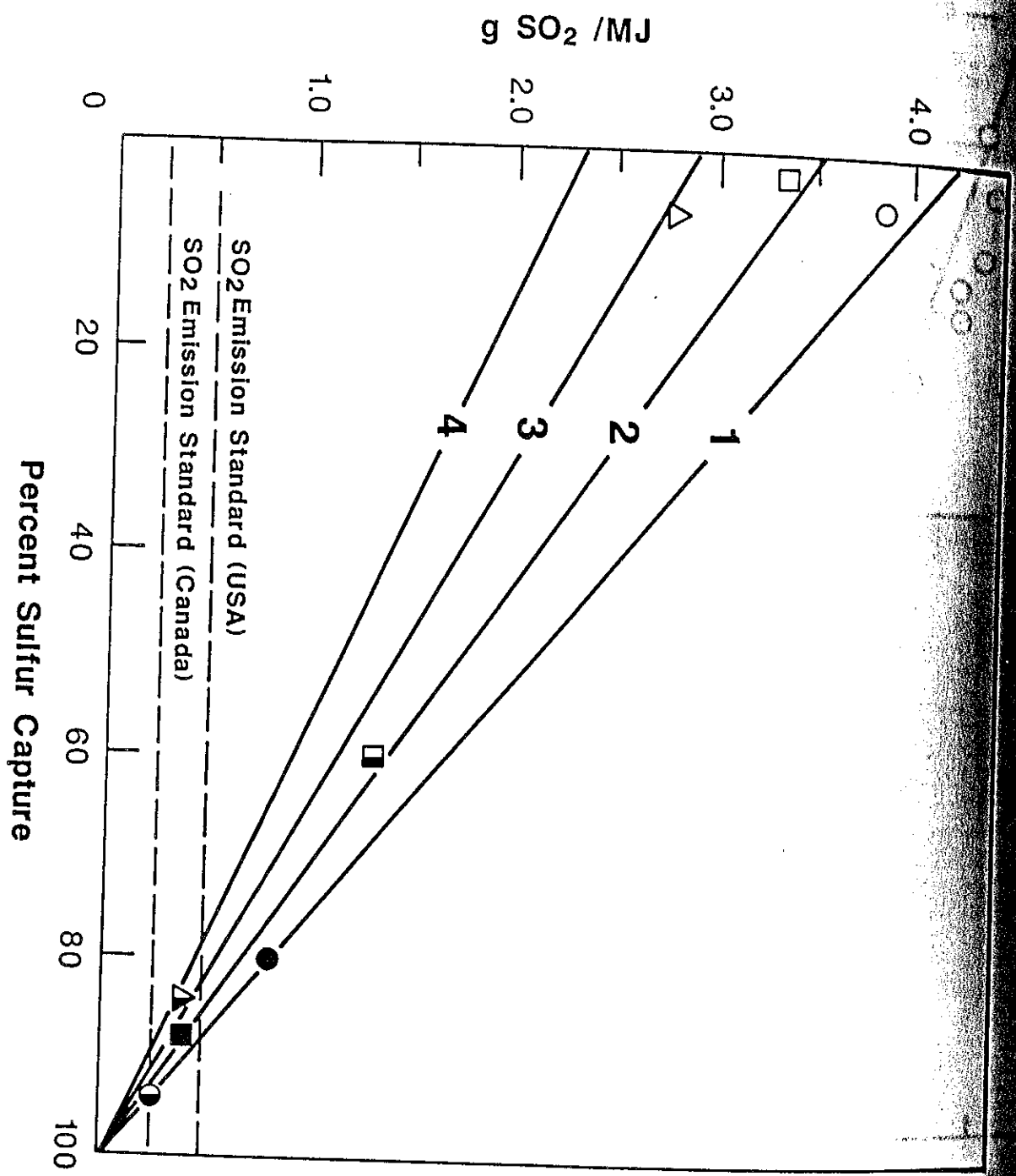
Exp. #	Binder and Amount	Ca:S	Sulphur Capture (as wt.% of total sulphur)	Ca Utilization (wt.% of total Ca)
Blank	-	0.03	12	100
1	Bitumen, 10%	0.9	54	60
2	Fuel Oil No.4, 10%	1.25	61	49
3	Bitumen, 10%	1.30	62	48
4	Fuel oil No.4, 5%	1.30	68	52
5	Fuel oil No.4, 5%	1.35	68	50
6	Fuel oil No.4, 5%	1.40	66	47
7	Fuel oil No.4, 1%	1.40	62	44
8	Fuel oil No.4, 1%	1.40	70	50
9	Fuel oil No.4, 10%	1.50	71	47
10	Fuel oil No.4, 5%	1.5	74	49
11	Bitumen, 10%	1.6	70	44

* Using preagglomerated prince coal



1. Effect of Ca:S molar ratio on Sulphur capture for coal/limestone agglomerates (●) and coal/limestone compacts (o) during combustion in a muffle furnace.

2. Levels of SO_2 emission obtained for blank (open symbols) and fuel-lime agglomerates (half closed symbols static-bed results, closed symbols, FBC). Syncrude coke, o,1; Suncor coke, □,2; prince coal, Δ,3; Athabasca Bitumen, plot #4. Ca:S molar ratios, Syncrude coke, 2.0; Prince coal, 1.1 and Suncor coke, 1.5 static-bed; 2.0 FBC.



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