

Agglomeration of Athabasca Petroleum Cokes in the Presence of Various Additives as a means of Reducing Sulfur Emissions during Combustion.

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The relatively high sulfur content of coke produced during the upgrading of Athabasca bitumen, makes it environmentally unsuitable as a fuel. We have attempted to coagglomerate these cokes with sulphur dioxide capture agents such as: lime, hydrated lime and limestone in an attempt to reduce emissions during combustion. By providing an environment where there is intimate contact between fuel and sorbent it was hoped that greater utilisation of the sorbent could be achieved, compared to fluid bed combustion, where the sorbent is added separately to the bed. Cokes from both Suncor and Syncrude operations were used in this investigation. The effect of conditioning agents such as sodium hydroxide, sodium oleate, and a petroleum sulfonate on the formation of coke oil agglomerates as well as on the efficiency of sulfur dioxide capture was also investigated. Sulfur dioxide capture was found to depend mainly on the calcium to sulfur mole ratio in the agglomerates, the combustion temperature, partial pressure of oxygen, and the type of coke and sorbent. The efficiency of the three capture agents in the reduction of sulfur dioxide emissions, has been compared.

Upgrading of Athabasca oil sands bitumen to form a synthetic crude oil produces a solid carbonaceous material, known as "Coke". The two commercial oil sands plants operating in Alberta produce approximately 4,000 tons of coke per day [1]. This coke contains 6-8% sulfur almost entirely in the form of organic sulfur compounds such as thiophenes, sulfides, disulfides and thiols [2]. Due to serious environmental and corrosion problems associated with the combustion of this coke, its use as a boiler fuel is limited and a significant portion of the coke is being stockpiled as a waste product. However, oil sands coke with a calorific value of about 33 MJ/Kg [3] would be an attractive boiler fuel if it could be desulfurized economically.

Although considerable work has been done on various methods of desulfurizing coal and coal chars, comparatively few studies appear in the literature on the desulfurization of petroleum coke, particularly coke derived from Athabasca oil sand bitumen. There have been some attempts at desulfurization of these cokes employing such methods as hydrodesulfurization, combustion with limestone addition, impregnation with high base loadings followed by calcination in an inert atmosphere and subsequent leaching, chemical oxidation, and solvent extraction [2-5]. However, most of these methods are said to be uneconomical [1]. Fluidized-bed combustion of coal in the presence of limestone is emerging as a promising technology that can achieve high combustion efficiency with significantly reduced sulfur dioxide emissions [6]. The disadvantage of the process is the high calcium to sulfur mole ratios required for acceptable reductions in sulfur dioxide emissions. For example, using limestone as a sulfur sorbent in a fluidized bed for Suncor delayed coking coke, a Ca/S ratio of 3:1 was required to achieve 80% reduction in SO₂ emissions [5].

The objective of this investigation was to develop an economically attractive method by which the oil sands coke may be utilized directly as a boiler fuel without serious environmental damage. To the best of our knowledge there are no reports regarding the coagglomeration of coal, coke or char with sulfur sorbents. The present program was designed to study the feasibility of co-agglomerating sulfur capture agents such as limestone, lime and slaked lime with oil sands bitumen coke as a means of increasing the utilisation of these agents during sulfur dioxide removal on combustion.

Experimental Methods

Materials. Suncor delayed coking coke and Syncrude fluid coke samples were obtained from the Alberta Research Council sample bank. The coke was ground to 150 μm size using a Brinkman ZM-1 Centrifugal Grinding Mill. The composition and Calorific value of these samples are listed in Table I.

TABLE I
Composition and Physical Data for Cokes

	Suncor Delayed Coke	Syncrude Fluid Coke
Proximate Analysis* (Dry Basis)		
Ash	6.0	8.7
Volatile Matter	11.6	7.3
Fixed Carbon	82.4	84.0
Ultimate Analysis (Dry Basis)		
Carbon	83.0	76.8
Hydrogen	3.4	1.6
Nitrogen	1.5	1.5
Sulfur	5.9	6.9
Oxygen	2.9	4.4
Ash	3.4	8.0
Calorific Value* MJ/Kg	33.4	32.6

* Alberta Research Council (Fuel Sciences Division)

Bridging liquid used for agglomeration of coke particles was a sample of bitumen obtained from the Alberta Research Council sample bank. This was a sample of coker feed bitumen from Suncor, prepared for use in a round robin study of bitumen analyses [7].

A number of sulfur dioxide capture agents were tried including: limestone, lime and slaked lime. The sample of limestone used was pulverized agricultural limestone (Domtar). It contained approximately 97% CaCO_3 . A partial size distribution of this sample is given in Table II. Lime was a laboratory grade CaO sample. Various samples of slaked lime were prepared as shown in Table III.

Petroleum sulfonate (TRS-10-80), used as a conditioning agent, was obtained from Witco Chemicals Corporation.

TABLE II
Size Distribution of Limestone

Sieve Size (μm)	Cumulative Weight Percent Passing
44	67.0
53	74.7
74	91.8

Procedure. 20 g of coke was mixed with known amounts of sorbent and the mixture dispersed in 100 ml of tap water contained in a Waring Blendor. An appropriate amount of a conditioning agent was then added and the contents agitated at 250 rps for 15 seconds. At this stage the blending speed was lowered to 120 rps. Bitumen was added slowly while continuing blending until discrete agglomerates or a unitary phase was obtained (5-15 minutes). Coke oil agglomerates/oil phase were then separated from the aqueous phase by screening. A portion of the agglomerates were used for analysis of bitumen, coke and ash content using a procedure described elsewhere [8]. The second portion of the agglomerates was dried at 100°C to a constant weight.

TABLE III
Experimental Conditions for Various Hydrated Lime Sample Preparation

Sample #	Experimental Conditions
1.	Laboratory grade CaO was mixed with distilled water in the ratio of 1:4 and then air dried at 90°C.
2.	20 g of CaO was mixed with 80 g of distilled water and 740 ml of isopropyl alcohol. The slurry was then dried at 90°C on a rotary evaporator under vacuum.
3.	Same as above, except the excess liquid was removed under atmospheric pressure at 90°C.
4.	10 g of CaO was mixed with 40 g of 0.5% aqueous solution of sodium sulfonate (Witco TRS-10-80) and 370 ml of isopropyl alcohol. Contents were mixed into a slurry and then dried on a rotary evaporator at 90°C under vacuum.
5.	Same as above, except the excess liquid was removed under atmospheric pressure at 90°C.
6.	Same as sample 1 except that the sample was freeze dried.
7.	Same as sample 1 except that the sample was dried in a vacuum oven at 90°C.

Combustion of Oil Agglomerates/Oil Phase. Before combustion wet agglomerates were first dried in an oven at 100°C to a constant weight to facilitate analytical calculations. However, because of the economic advantage in burning wet agglomerates, a separate investigation involving the combustion of wet agglomerates is in progress. The results of this study will be reported elsewhere. Two procedures were used for the ashing of dried coke-oil agglomerates/oil phase. The first procedure involved weighing an agglomerate sample into a porcelain crucible, and placing it directly into a muffle furnace preset at the desired temperature. This technique has been referred to as combustion with limited air. The second procedure involved burning the sample over a bunsen burner in the open air followed by completion of the ashing process in the muffle furnace at an appropriate temperature. This has been referred to as combustion with excess air.

Sulfur Analysis. Attempts were made to measure the sulfur dioxide emissions from coke-oil agglomerates by burning ~ 1.0 g of the sample in a porcelain boat placed inside a quartz tube contained in a tube furnace (ASTM method D4239-83). This method is specifically designed for the determination of sulfur in coke and coal. Sulfur dioxide in the combustion gases was absorbed by 1% hydrogen peroxide solution and the resulting sulfuric acid titrated against 0.05N-NaOH solution to pH 5.0, see equation [1].



The sulfur content of the coke, coke-oil agglomerates and coke-sorbent-oil agglomerates was also determined independently using a Leco sulfur analyzer and by x-ray fluorescence spectrometry. Excellent agreement between the results for sulfur content for coke and coke-oil agglomerates was obtained by the three methods. However, each method gave a different result for the sulfur content of coke-sorbent-oil agglomerates. Reproducibility was extremely poor for these samples when using the ASTM method. Results from the Leco sulfur analyzer were reproducible within ±5% but gave significantly lower sulfur contents than x-ray fluorescence spectrometry. Results from x-ray fluorescence spectrometry were much closer to the expected values than the results from the other two methods. Total sulfur in the ash obtained from the combustion of coke-oil and coke-sorbent-oil agglomerates was also determined using x-ray

fluorescence spectrometry.

The sulfur fixed in the ash during combustion is expressed as a percentage of the total sulfur in the original coke. It was calculated from the equation:

$$\text{Percentage sulfur fixed} = \frac{\text{wt. of sulfur in ash from } y \text{ g of agglomerates}}{\text{wt. of sulfur in } y \text{ g of agglomerates}} \times 100 \quad (2)$$

$$\text{wt. of sulfur in ash} = \frac{\text{wt. ash} \times \% \text{ sulfur in ash}}{100}$$

$$\text{wt. of sulfur in agglomerates} = \frac{\text{wt. agglomerates} \times \% \text{ sulfur in agglomerates}}{100}$$

Results and Discussion

Sulfur Determination. Sulfur contents of coke and coke agglomerates as determined by: ASTM method D4239-83, Leco sulfur analyzer and x-ray fluorescence spectrometry are listed in Table IV. The three methods gave similar results for coke and coke oil agglomerates, but each method gave a different result for coke-limestone-oil agglomerates with the most scatter being obtained with the ASTM method. The reproducibility of the other two methods was similar. However, the Leco sulfur analyzer gave lower sulfur values compared with the x-ray fluorescence method. Sulfur content, determined using x-ray fluorescence spectrometry, was much closer to the expected values. Hence, all the results discussed in this report are based on the x-ray fluorescence spectrometry method.

TABLE IV
Comparison of Sulfur Results Obtained Using Different Methods.

Sample	Total oxidisable sulfur (SO ₂ emitted) by ASTM Method				Total sulfur (as w/w% of agglomerates)		Total oxidisable sulfur from ash* analysis	
	460°C	750°C	840°C	1000°C	x-ray method	Leco method	460°C	1000°C
Suncor Coke	5.5±0.1 (4)	5.3±0.2 (3)	-	-	5.9±0.2 (4)	5.8±0.1 (4)	-	-
Suncor Coke-Bitumen Agglomerates	5.8±0.1 (2)	5.9±0.2 (2)	-	5.6±0.2 (2)	5.7	5.9±0.1 (3)	5.8	5.7
Suncor Coke-Limestone-Bitumen Agglomerates Ca:S Mole ratio 0.6	3.2±0.7 (3)	2.8±0.7 (3)	3.3±0.1 (2)	4.1±0 (2)	4.75±0.3	3.7±0.2 (3)	3.2	1.3
" Ca:S Mole ratio 0.8	1.8	2.9	-	3.1	4.2±0.3	3.5±0.4 (3)	3.2	1.3
" Ca:S Mole ratio 2.6	1.40±0.1 (2)	3.0±0.5 (3)	1.3	2.1±1.0 (2)	3.5±0.3	2.6±0.1 (10)	2.2	0.9

* by x-ray fluorescence spectrometry.

Values in parenthesis are number of determinations.

Sulfur Retention by the Ash from Suncor Coke-Oil Agglomerates.

Tests on several lignites at various laboratories have shown that with no limestone injection, highly variable sulfur retention by the ash is achieved during combustion in a fluidized bed. In some cases the retention of sulfur by the ash alone have been quite significant [9]. Mineral composition of the ash is said to be important in determining the extent of sulfur retention. Iron in particular has been

reported to catalyze the sulfation reaction between CaO(s) and $\text{SO}_2(\text{g})$ [10]. Ash analyses of the Suncor delayed coking coke and Syncrude fluid coke are presented in Table V below:

TABLE V
Ash analyses of the Cokes (w/w% of Ash)

Component	Suncor delayed Coking Coke	Syncrude Fluid Coke
Total Ash	3.4	8.0
SiO_2	42	41
Al_2O_3	19	22
Fe_2O_3	23	12
NiO	2	1
V_2O_5	5	3
TiO_2	2	3
CaO	3	5
MgO	2	2
Na_2O	1	2
K_2O	2	2

As Fe_2O_3 is one of the major components of the ash from both cokes, significant amounts of sulfur retention by the ash from these cokes might be expected. However, no significant sulfur retention by the ash from either coke was observed. Sulfur retention by the ash from Suncor coke ranges from 1-3% and for Syncrude coke it is in the 3-5% range. Although the Fe_2O_3 content of the ash from Suncor coke is about double that of the Syncrude coke, its sulfur retention is only half that of the Syncrude coke ash. This appears to be more consistent with the CaO content of the two ashes and suggests that CaO is the only reactive ingredient for sulfur retention in the coke ash.

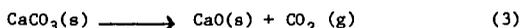
Conditioning agents used did not affect the retention of sulfur by ash. However, conditioning agents were found to facilitate agglomeration, probably by increasing the wettability of the coke particles with respect to the bridging oil. The effect was more pronounced for Syncrude coke than for Suncor coke. This was evident from the lower amount of bridging liquid required to agglomerate Syncrude coke in the presence of conditioning agents, in particular oleic acid and sodium oleate. This is consistent with the fact that Suncor delayed coke is more hydrophobic than Syncrude fluid coke because of the presence of a small amount (0.4% by weight) of a benzene extractable material [11].

Coagglomeration of Limestone with Suncor Coke in the absence of a conditioning Agent.

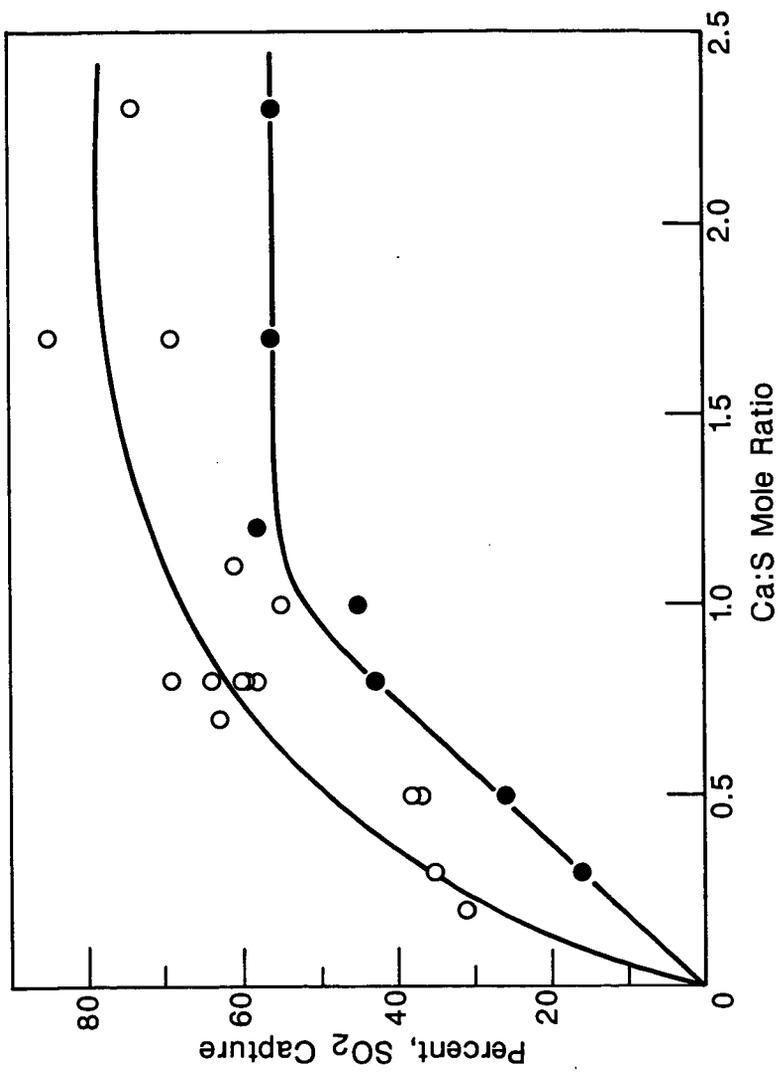
Suncor coke can be easily coagglomerated with limestone. However, individual agglomerates were only obtained when the Ca to sulfur ratio was < 1.2 ; beyond this ratio a unitary phase resulted.

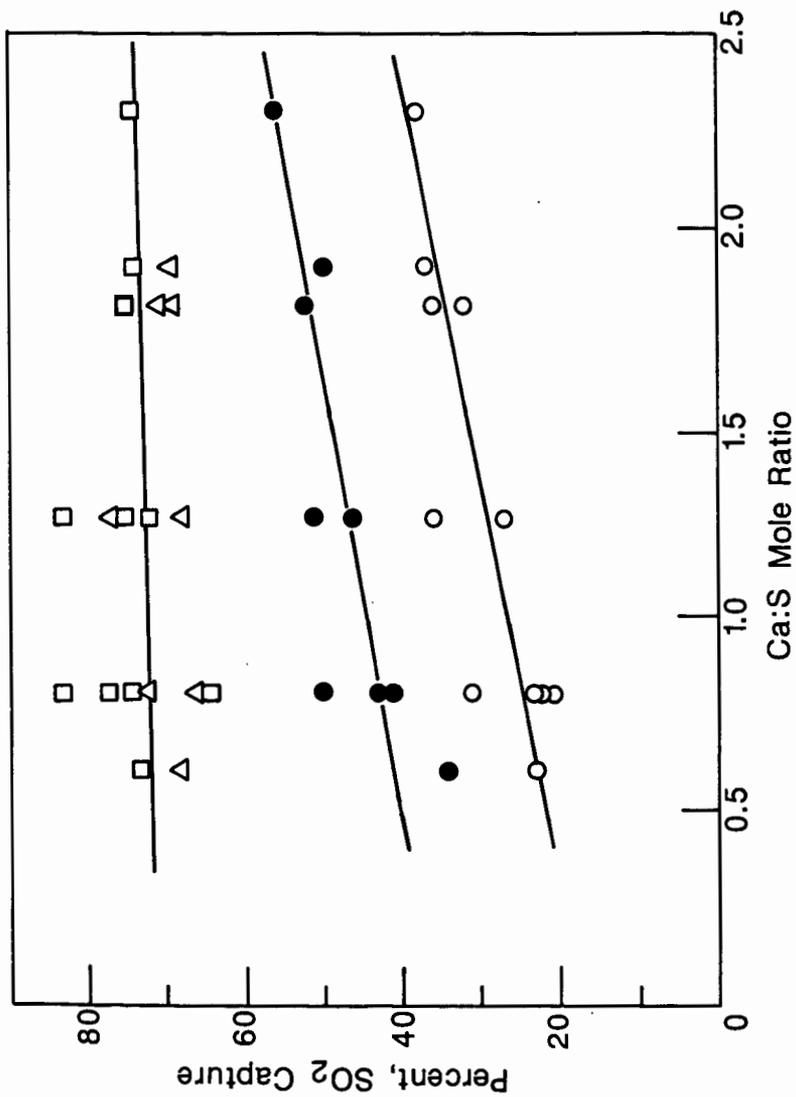
Figure 1, is a plot of the percentage of the sulfur retention versus calcium to sulfur molar ratio. It is obvious from these plots that the efficiency of sulfur dioxide capture mainly depends on the calcium to sulfur mole ratio in the agglomerates, and the combustion temperature. Considerably more sulfur dioxide retention was obtained at 1000°C than at 460°C . This is consistent with various published reports [9,12-15]. This greater reactivity of limestone at higher temperatures has been explained on the basis of several mechanisms [9].

The detailed kinetic mechanism of the reaction between carbonate rock and sulfur dioxide is not well understood [16-17]. However it is generally accepted that the reaction involves two steps. The first step is the decomposition of calcium carbonate (calcination) to carbon dioxide and calcium oxide:



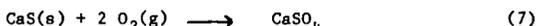
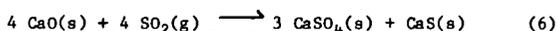
The second step is the reaction of sulfur dioxide and calcium oxide. In the presence of excess air this reaction produces $\text{CaSO}_4(\text{s})$:







However, with limited amounts or no air present the preferred product was temperature dependent [12]. At lower temperatures CaSO_3 was formed whereas the more thermodynamically stable $\text{CaSO}_4 \cdot \text{CaS}$ was formed at higher temperatures as shown in reactions 5-7 below.



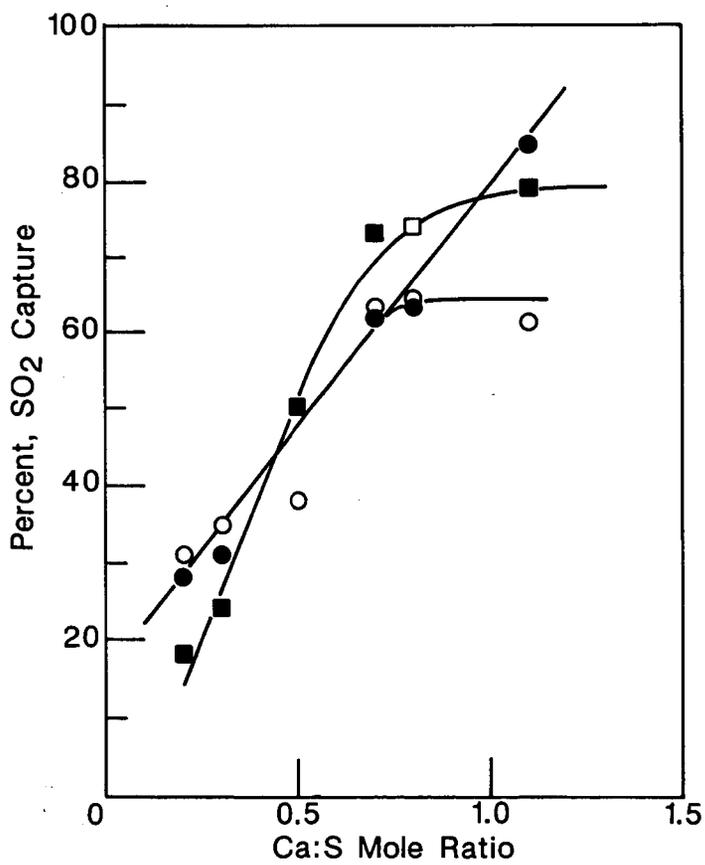
The capacity of limestone to react with SO_2 in a fixed bed reactor has been studied by various workers [9,12-15]. It has been found that the calcination reaction is the controlling step at low temperatures, and the sulfation reaction is the controlling step at high temperatures. At low temperatures calcination is slow and hence overall conversion of limestone to CaSO_4 will be low. As the temperature is raised the calcination rate will increase [18]. At the optimum temperature the rate of calcination is so fast that the rate of sulfation dominates the overall reaction resulting in higher utilisation of sorbent.

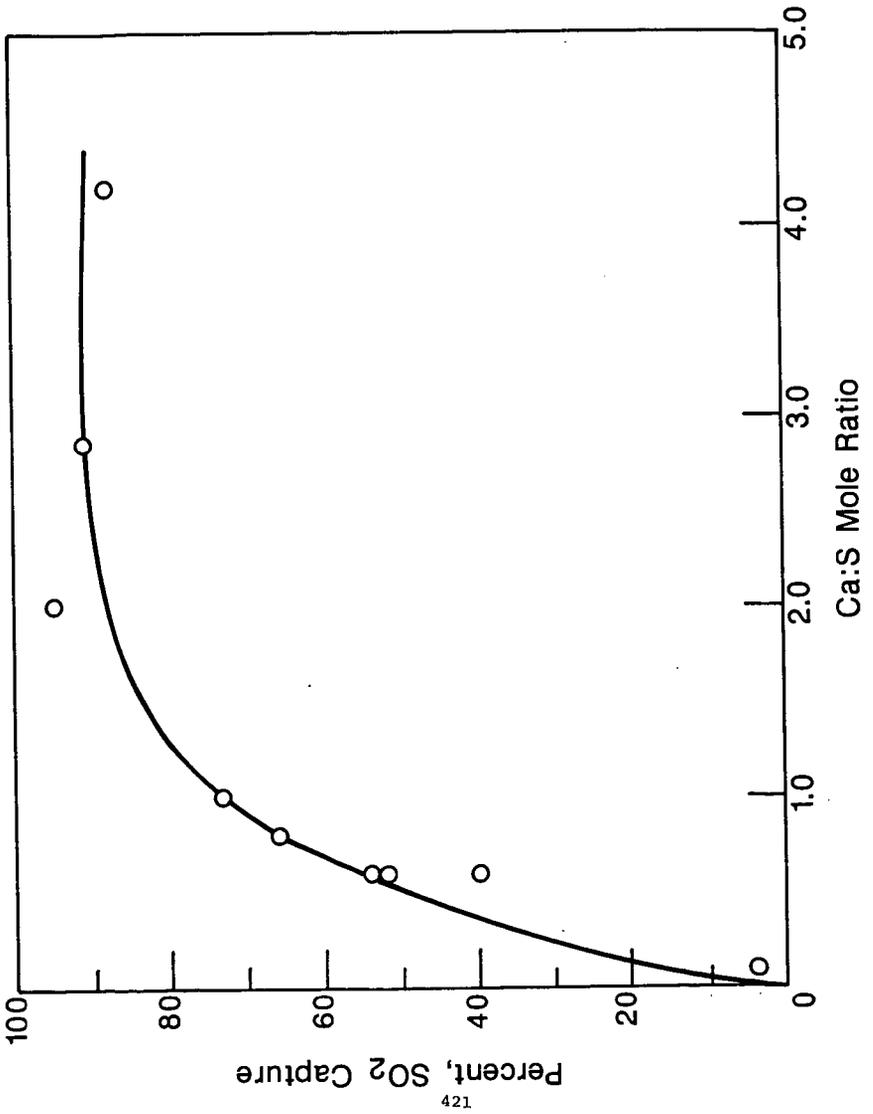
Results summarized in Figure 1 demonstrate that as the limestone content of the agglomerates is increased a corresponding decrease in sulfur dioxide emissions during combustion of Suncor coke is achieved. For small values of the calcium to sulfur ratio there appears to be a linear correlation between sulfur dioxide capture and the calcium to sulfur mole ratio. This is consistent with the fluidized bed combustion studies of coals in presence of limestone. In this range, sulfur retention has been found to be related to the capacity of the stone and not its reactivity [6].

It has been suggested that the rate of reaction between sulfur dioxide and limestone is strongly affected by the diffusion of the gaseous reactants [16,17]. Because calcium sulfate has a molar volume about 3 times larger than that of calcium oxide, the accumulation of reaction product causes the sorbent porosity to decrease and the diffusional resistance to increase. When the pore mouths are filled with the reaction product, a considerable percentage of the interior of the pores become inaccessible to the gaseous reactants and the reaction stops. In addition it has been shown that the pore size distribution is affected by the temperature and CO_2 partial pressure during calcination [14]. At higher temperatures and under higher partial pressures of CO_2 , higher rates of reactions between SO_2 and CaO have been reported [19]. This is consistent with the observed lower degree of sulfur fixation at 460°C than at 1000°C .

The sulfur retention by limestone was also found to be affected by the oxygen partial pressure during combustion at a particular temperature. Much higher sulfur retention values were obtained under excess air than under limited air at the same combustion temperature (460°C). This is because at lower temperatures, in the presence of excess air CaSO_4 is formed which is thermodynamically more stable than the CaSO_3 preferentially formed in the presence of limited air. However, it is noteworthy that the results under discussion were obtained from two stage combustion as described in the experimental section. The initial combustion was carried out on a bunsen burner where the effective combustion temperature could have been considerably higher than 460°C , the temperature of the furnace for second stage of combustion. Hence, the effect noted above could be due to a combination of excess air and higher initial combustion temperature.

With increasing amounts of limestone, greater quantities of bitumen were required for agglomeration. However, the ratio of coke to bitumen does not affect the extent of sulfur retention by limestone. This suggests that limestone is a good sorbent for sulfur emissions from both bitumen and coke.



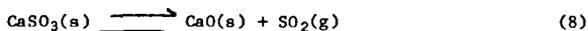


The Effect of Combustion Temperature on the Retention of SO₂ by Ash from Suncor Coke-Limestone Agglomerates.

As discussed above, the capture of sulfur dioxide by the sorbent is affected by the combustion temperature. The samples of coke agglomerates containing limestone were ashed at 460°C, 750°C and 1000°C in order to find the optimum combustion temperature for maximum sulfur retention. Results are summarized in Figure 2. These results are different from the results shown in Figure 1 in that these were obtained using sodium hydroxide as a conditioning agent. It is obvious from these results that maximum retention is achieved around 750°C to 1000°C. However, an ashing temperature of 1000°C was selected for subsequent work because this is closer to the temperatures used in actual combustion equipment.

At higher temperature sulfur retention is almost independent of the calcium to sulfur mole ratio in the range investigated. Almost 70% sulfur retention can be achieved with a Ca to sulfur mole ratio of 0.6. This can be explained on the basis of much faster rates of reactions for both calcination and sulfation as well as pore plugging at higher temperatures as discussed above [14,16-17,19]. For lower temperatures, sulfur retention is proportional to the Ca to S mole ratio. This could have been due to the greater thermal stability of CaSO₄ at lower temperatures.

At 460°C, for a particular Ca to S mole ratio the extent of sulfur retention was much higher in excess air than in limited air. The effect of oxygen partial pressure at higher temperatures was insignificant. This can be explained on the basis of the formation of thermodynamically more stable CaSO₄ in excess air at low temperature and under any conditions at higher temperatures as against thermodynamically less stable CaSO₃ obtained at low temperatures in limited air. Calcium sulfite will decompose above 400°C according to the equation:



The Effect of Conditioning Agents on Sulfur Dioxide Capture by Limestone.

In a recent publication it has been reported that when sodium was deposited on CaO, there was a significant increase in SO₂ adsorption, and adsorption increased with increasing sodium deposition [20]. The presence of sodium was suggested to have activated the CaO surface for SO₂ adsorption due to the formation of Na-O-Ca species. In order to investigate the effect of sodium on SO₂ capture by limestone, Suncor coke was coagglomerated with limestone in the presence of various concentrations of sodium hydroxide, sodium oleate and a sodium salt of a petroleum sulfonate (Witco TRS 10/30). The effect of these additives on the retention of sulfur dioxide by limestone has been illustrated in Figure 3.

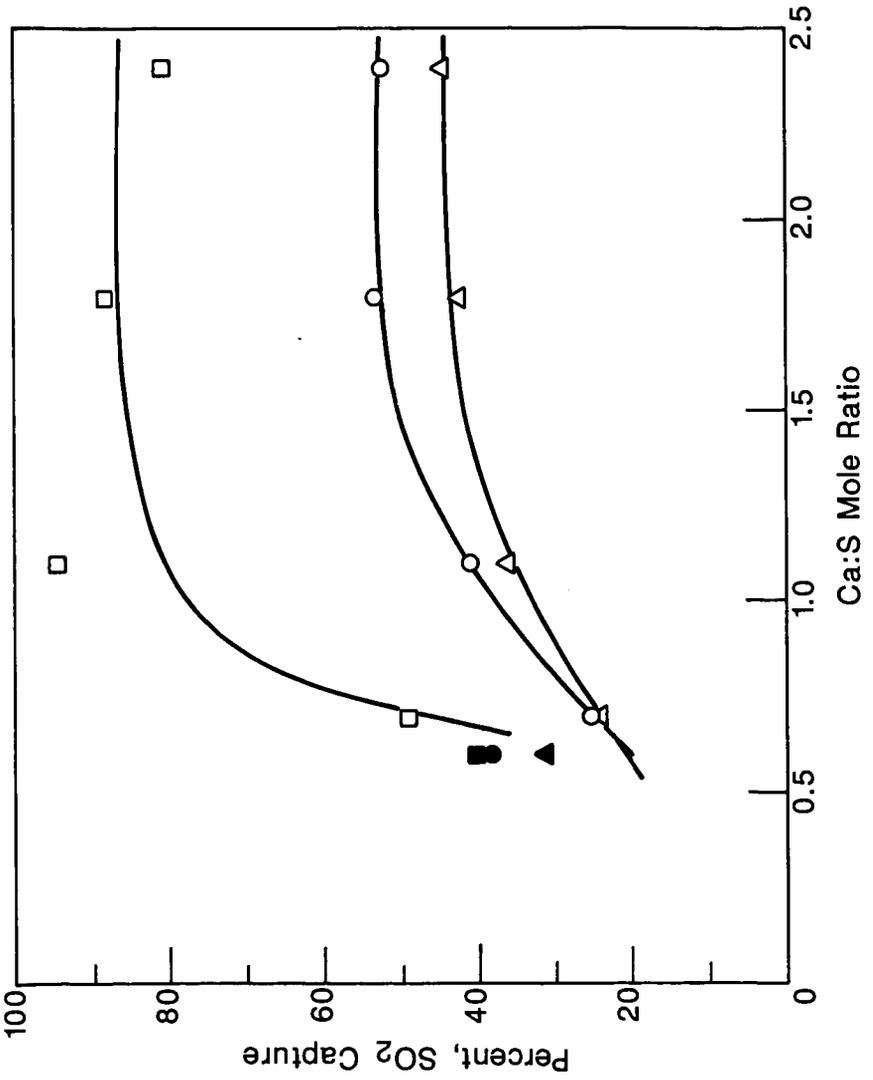
The addition of all three conditioning agents improved the coagglomeration of the components, resulting in the use of smaller quantities of bitumen, especially at higher Ca to sulfur mole ratios. This could have been due to the improved wettability of the components towards the bridging oil as a result of the use of surfactants or by in situ formation of surfactants by reaction between the alkali and certain bitumen components.

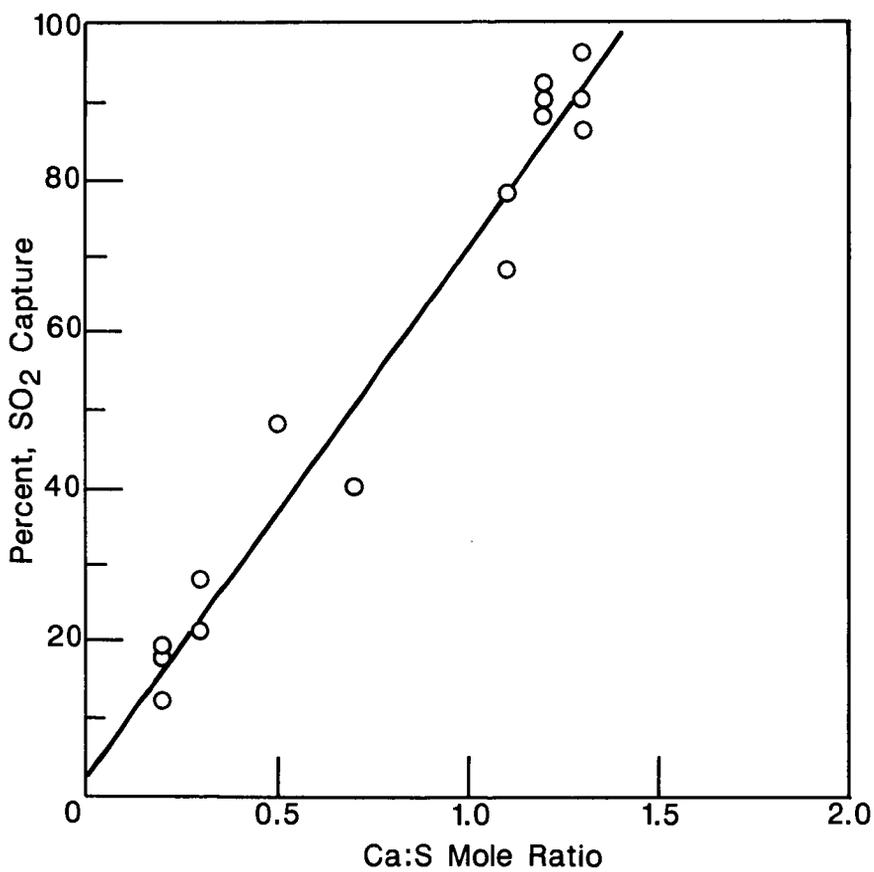
As can be seen from the plots in Figure 3, better sulfur capture was achieved when the agglomerates were prepared in the presence of these additives. This effect was more pronounced for the higher Ca to sulfur ratios. The relative effectiveness of the three additives was essentially identical. As all three additives were sodium salts it is possible that the observed improvement was owing to sodium activation of calcined limestone [20].

It is also apparent that there is a reduced scatter in the data points for experiments carried out in the presence of additives, compared with the blank experiments. It appears that the three additives all have the ability to distribute limestone uniformly within the agglomerates. Overall sulfur capture by limestone was independent of the concentration of the various additives. This is consistent with the presumed catalytic nature of these additives.

Coagglomeration of Suncor Coke with Lime.

Coagglomeration of Suncor coke with lime was also attempted. This procedure was considerably more difficult than with limestone, resulting in a unitary phase in most cases. Certain bitumen components (carboxylic acids) are known to interact





strongly with calcium ions. For limestone, chemisorption of these components to calcium atoms at the solid surface appears to occur readily. This results in a hydrophobic surface easily wettable by the oil, allowing co-agglomeration with the naturally hydrophobic coke. Lime, however, reacts strongly with water and this reaction probably occurs in preference to interaction with the acidic bitumen components. Thus, the lime surface does not become properly conditioned by the bitumen and co-agglomeration does not readily occur.

The effect of calcium to sulfur mole ratio on the retention of sulfur dioxide by lime is illustrated in Figure 4. As is evident the degree of sulfur dioxide retention increases with increasing amounts of lime in the agglomerates up to about 90% at a calcium to sulfur mole ratio of about 2. Relatively low data scatter in Figure 4 suggests a uniform distribution of lime within the agglomerates.

Figure 5 demonstrates the effect of combustion temperature and amount of excess air on the retention of sulfur by lime. Again, considerably higher sulfur retentions were achieved at 1000°C than at 460°C. This effect is identical to the one noted for limestone. It is also consistent with the published results for the fluidized bed combustion studies with similar systems [9,12-15]. However, contrary to the limestone case, where sulfur capture was found to be independent of the calcium to sulfur mole ratio in the higher ratio range, sulfur capture by lime is dependent on the calcium to sulfur mole ratio at a combustion temperature of 1000°C. This could be partly due to the difference in the reactivities of uncalcined and precalcined limestone at higher temperatures [13]. It has been found that the capacity of uncalcined limestone to react with $\text{SO}_2(\text{g})$ reached an optimum near 900°C while the capacity of precalcined limestone decreased with increasing temperature above 700°C. Higher reactivity of uncalcined limestone at higher temperatures is said to be due to the higher partial pressure of $\text{CO}_2(\text{g})$ produced from the calcination reaction [21].

The temperature effect for sulfur dioxide retention by lime is more pronounced for the Syncrude fluid coke-lime system than for the Suncor delayed coking coke-lime system. This reflects the differences in the conditions during formation of the cokes. During fluid coking (FC), more volatile matter is removed from the bitumen feed than during delayed coking (DC) [22]. As a result DC coke may require lower combustion temperatures than the FC coke.

Another important observation relating to the temperature effect is that maximum sulfur dioxide retention was obtained near 750°C for lime in contrast to a value of 1000°C for limestone. This is consistent with the published data of various authors who found that the optimum sulfation temperature for uncalcined particles is generally higher than that for calcined particles of the same material [9,13].

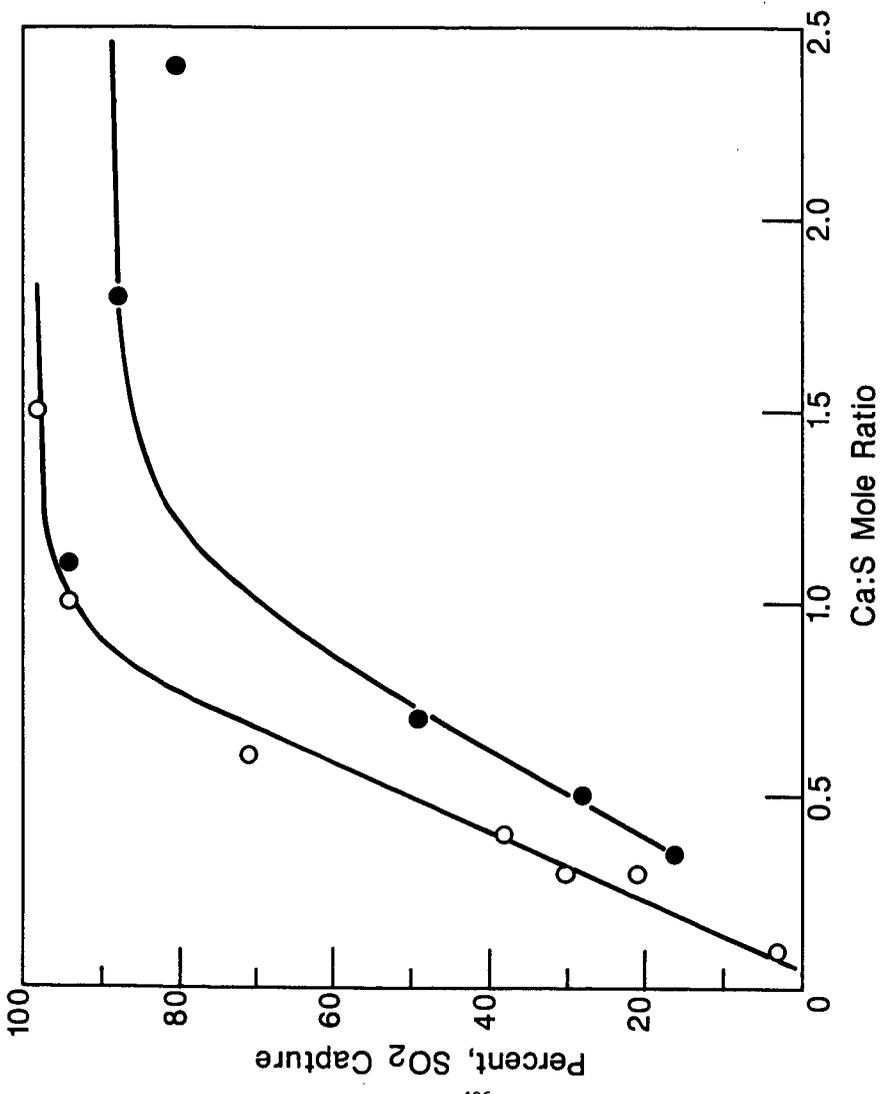
Excess air had a negative effect on the retention of sulfur dioxide by lime at a combustion temperature of 460°C. This is contrary to the effect noted for limestone. The presence of excess air will lead to the formation of thermodynamically stable CaSO_4 in both cases. However, the rate of sulfation reaction will decrease with the extent of reaction due to pore plugging [16-17]. It is probable that this pore plugging is slower in the presence of CO_2 produced from the calcination of limestone.

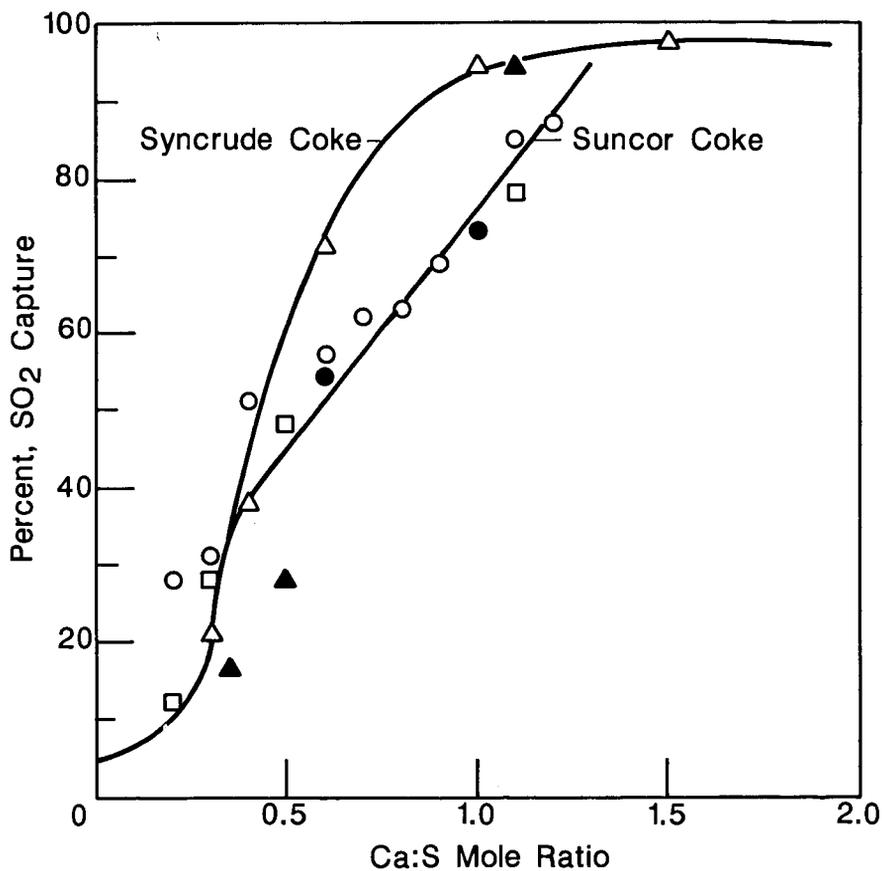
Coagglomeration of Suncor Coke with Hydrated Lime.

It was relatively easy to coagglomerate the samples of hydrated lime prepared in the laboratory under different conditions as listed in Table III, compared with the reagent grade $\text{Ca}(\text{OH})_2$. The results for the retention of sulfur dioxide from Suncor coke by hydrated lime lead to various observations.

As with lime maximum sulfur dioxide retention was achieved near 750°C for reagent grade $\text{Ca}(\text{OH})_2$ in contrast to the maximum near 1000°C for the laboratory prepared samples of hydrated lime. The reason for this difference in behavior of the same sorbent obtained from different sources is not well understood. However, this behavior is consistent with the fluidized bed combustion studies of sulfur retention by limestone and dolomite. It has been reported that the maximum in sulfur retention in fluidized bed combustion depends on the specific limestone or dolomite employed [23].

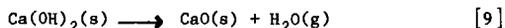
Whereas sodium oleate was found to be beneficial in the agglomeration of laboratory prepared samples of hydrated lime, none of the additives affected either the retention of SO_2 or agglomeration of the reagent grade $\text{Ca}(\text{OH})_2$. This suggests





that reagent grade Ca(OH)_2 is the least hydrophobic among the sorbents investigated in this work.

Also, decomposition of Ca(OH)_2 possibly produced reactive CaO



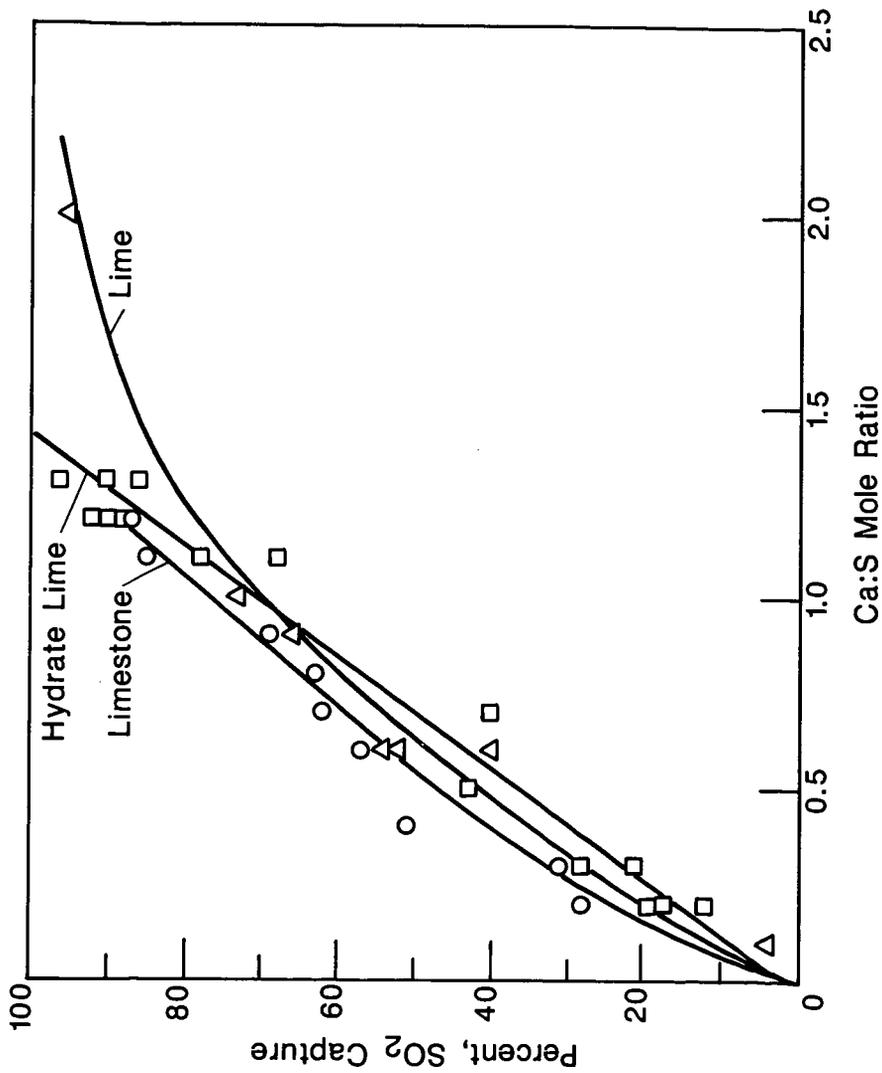
Water vapour and oxygen have been found to show a similar effect on the oxidation rate of CaSO_3 to CaSO_4 [24]. Figure 6 is a graphic representation of these results. There is a linear correlation between the amount of sulfur retention and the mole ratio of calcium to sulfur in the agglomerates. About 90% sulfur retention can be achieved with a calcium to sulfur mole ratio of 1.2. Coke to bitumen ratio does not appear to affect the reactivity or capacity of hydrated lime for SO_2 capture. This suggests that hydrated lime is an effective sorbent for sulfur dioxide from bitumen as well as from coke.

The presence of excess air does not have any significant effect on the overall retention of sulfur dioxide by hydrated lime. This is contrary to the effect noted for CaO and limestone. Since water vapor and oxygen have a similar effect on the oxidation rate of CaSO_3 to CaSO_4 [24], the need for additional air will be eliminated. Also, it could be possible that water vapor prevents the pore plugging that produced a negative effect for CaO in the presence of excess air, leading to almost stoichiometric utilisation of the sorbent. This will also explain the linear relationship between the extent of sulfur dioxide retention and the amount of hydrated lime in the agglomerates.

Coagglomeration of Syncrude Fluid Coke with Lime/Limestone.

In order to assess the efficiency of this process for controlling sulfur dioxide emissions from the combustion of various types of cokes, coagglomeration of Syncrude fluid coke with lime or limestone was also attempted. The results were essentially identical to those observed for Suncor coke. The efficiencies of sulfur dioxide retention from the combustion of Syncrude coke by limestone and lime can be compared with the results presented in Figure 7. Although, both curves follow essentially the same trend, it is obvious from the results that limestone is a more efficient sorbent, compared with lime, over the entire range of calcium to sulfur ratios. This could be attributed to the higher porosity and reactivity produced by the in situ calcination reaction [16,17]. The effect of pore size is known to be significant in determining the rate as well as the extent of reaction between SO_2 and CaO . It has been found that small pores in the calcines resulted in high rates of reactions and low overall conversions due to pore plugging, while large pores caused lower rates of reaction with higher conversions [17,21,25]. It is probable that the freshly calcined limestone particles have bigger pores than the CaO used. This is a very important result as the ability to use a cheap and readily available material in its natural form has a considerable economic significance. The cost ratio of lime to limestone on a molar basis may vary from 2 to 4 depending on the transportation distance [26]. Even the costs for transportation and handling of limestone tends to be lower than for lime since it can be transported in open trucks.

Results discussed so far have demonstrated that coagglomerating cokes with such sulfur capture agents as limestone, lime and hydrated lime could be an effective way for controlling sulfur dioxide emissions from the combustion of these cokes. In Figure 8 a comparison of the efficiency of this process in terms of sulfur retention by the ash has been made for the two cokes investigated. It is obvious from the plots that although this process is effective for both cokes it is slightly more efficient for Syncrude coke compared with Suncor coke specially at higher calcium to sulfur ratios. Thus, at a calcium to sulfur mole ratio of about 1:1 over 90% sulfur retention can be achieved for Syncrude coke compared with over 80% sulfur retention for Suncor coke. This difference may be due to the reportedly higher bulk gasification reactivity of Syncrude fluid coking coke compared with that of Suncor delayed coking coke [22]. Higher reactivity of fluid coke, compared with delayed coke, is surprising as the former was subjected to more severe treatment in the coking process. However, no reason for this reactivity difference has been suggested.



Comparative efficiencies of the three sorbents investigated; lime, hydrated lime and limestone have been illustrated in the plots shown in Figure 9. These results were obtained in the presence of conditioning agents that activate the sorbent as discussed above. It is obvious from these plots that activated limestone is the most efficient in its capacity to retain SO_2 . Lime and hydrated lime both have comparable efficiencies for low calcium to sulfur ratios (up to " 1.0). However, in the range of Ca to S ratios beyond 1, hydrated lime appears to be more efficient than lime, approaching in efficiency to that observed for activated limestone. The observed higher efficiency of activated limestone for SO_2 retention is of considerable significance because of its already mentioned economic advantage over the other sorbents.

According to the findings of Schneider and George [27] calcium has a beneficial effect on the leaching of nickel and vanadium from coke ash using hydrochloric acid. Hence, coagglomeration of coke with calcium compounds will have the added advantage that the ash from these agglomerates would be more suitable for mild acid leaching than the ash from coke alone.

In a fluidized bed combustion of coal the amount of sorbent required to achieve a given reduction in sulfur dioxide emissions mainly depends on the gas retention time in the bed and consequently the flow rate of air. However, in the present case, where there is intimate contact between fuel and sorbent within an agglomerate matrix, sulfur dioxide has to diffuse out through the agglomerate pores, contacting sorbent during its passage, before coming in contact with the fluidizing air. Hence, one might expect greater utilization of the sorbent in this latter case compared to fluidized bed combustion where sorbent is added separately to the bed. A comparison of the results from this investigation with the data from some preliminary experiments on the simulated fluidized bed combustion of Suncor coke does suggest a greater efficiency for coagglomerated sorbents compared to a simple mixture of components. Details of these findings will be presented elsewhere.

Conclusions

- (1) There is no significant sulfur retention by the original ash from the Athabasca bitumen cokes.
- (2) Cokes produced during the upgrading of Athabasca bitumen can be successfully coagglomerated with sulfur dioxide capture agents such as: lime, hydrated lime and limestone as a means of reducing sulfur emissions. On combustion, most of the sulfur remains in the recovered ash from these agglomerates instead of escaping to the atmosphere as SO_2 .
- (3) ASTM method D 4239-83 is not satisfactory for measuring the sulfur dioxide emissions from the combustion of coke-limestone agglomerates.
- (4) Decrease in the sulfur dioxide emitted on combustion of the coke-sorbent agglomerates depends on such variables as the calcium to sulfur mole ratio, combustion temperature, partial pressure of oxygen, conditioning agents and the type of coke and sorbent.
- (5) The quantity of the sulfur dioxide capture agents required for coagglomeration with coke depends on the degree of sulfur removal desired. The decrease in the sulfur dioxide formed on combustion increases with increasing quantities of additive, until further additive confers no additional benefit. Thus over 80-90% reductions in sulfur dioxide emissions can be achieved with a calcium to sulfur mole ratio of approximately 1:1.
- (6) Combustion temperature had a profound effect on the retention of sulfur dioxide by sorbents. In general, at higher temperatures more sulfur dioxide retention was achieved than at lower temperatures. However, the optimum temperature at which maximum sulfur retention could be obtained varies with the type of sorbent.
- (7) At lower combustion temperatures, the presence of excess air had a beneficial effect on the retention of sulfur in the coke-limestone system, and a negative effect in the coke-lime system. For the coke-hydrated lime, presence of excess air does not affect the overall conversion.
- (8) Conditioning agents such as sodium hydroxide, sodium oleate and a petroleum sulfonate had a beneficial effect both on agglomeration and on the extent of sulfur dioxide capture.

- (9) Coagglomeration of Athabasca bitumen cokes with lime, hydrated lime or limestone is an effective desulfurization method. However, Syncrude fluid coke gave slightly better results than Suncor delayed coke.
- (10) Activated limestone is a slightly more efficient sorbent than lime. This has an economic advantage as limestone is 2-4 times cheaper than lime.

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Figure Captions.

- Figure 1. Calcium to sulfur ratio effect on SO₂ capture by limestone ● Ashing temperature 460°C in excess air; ○ Ashing temperature 1000°C in limited air.
- Figure 2. The effect of ashing temperature on SO₂ capture by limestone. ○ 460°C, limited air, ● 460°C, excess air, △ 750°C, excess air and □ 1000°C limited air.

- Figure 3. The effect of various conditioning agents on the retention of sulfur dioxide by limestone.
 ○, blank; ●, NaOH; □, sodium oleate and ■, TRS 10/80.
- Figure 4. Calcium to sulfur ratio effects on the retention of sulfur dioxide by lime.
- Figure 5. The effect of ashing temperature on SO₂ capture by lime. ○, ●, 460°C limited air; △, ▲, 460°C, excess air and □, ■, 1000°C limited air. Open symbols for Syncrude coke; close symbols, Suncor coke.
- Figure 6. Calcium to sulfur ratio effect on SO₂ capture by hydrated lime.
- Figure 7. The SO₂ capture efficiencies of limestone vs lime ○, limestone; ● Lime; from Syncrude coke.
- Figure 8. Efficiency of SO₂ capture; Suncor coke vs Syncrude coke. ○, △, limestone; ●, ▲, lime; □, hydrated lime; △, ▲, Syncrude coke; ○, ●, □, Suncor coke.
- Figure 9. Comparative SO₂ capture efficiencies of various sorbents for Suncor coke. ○, limestone; △, lime; □, hydrated lime.