

ALKALI-ALUMINA SORBENTS FOR REGENERABLE SO<sub>2</sub>  
REMOVAL IN FLUIDIZED-COAL COMBUSTION

by

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ABSTRACT

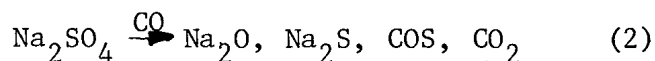
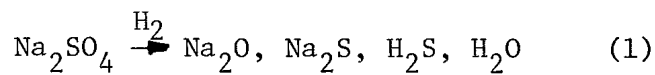
Sodium and sodium-lithium oxides supported on porous alumina have been investigated as regenerable SO<sub>2</sub> sorbents for fluidized coal combustion. In adsorption the oxides are converted to sulfates. In regeneration, carried out by reduction with CO, the sulfates are converted back to oxides while sulfur is removed in elemental form (S<sub>2</sub>), SO<sub>2</sub> and COS. The transient composition of sorbent and gaseous products was measured in a thermogravimetric analyzer and a packed-bed microreactor in order to delineate the basic chemistry of regeneration and determine conditions that maximize the yield of elemental sulfur.

INTRODUCTION

Among various possibilities for improving current fluidized coal combustion (FCC) technology, the use of regenerable sorbents has received relatively little attention. Although regenerable sorbents would eliminate the consumption and disposal of large amounts of throw-away sorbents like limestone, the anticipated high cost of regeneration has generally discouraged research in this direction.

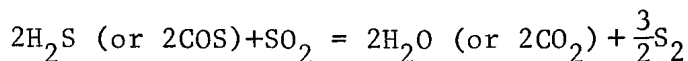
The limited work performed on regenerable sorbents has focused on limestone or dolomite (Hammons and Skopp 1972, Chen and Yang 1979, Yang and Shen 1979) and alkalized alumina (Town et al. 1970). Alkalized alumina has also been studied relative to flue gas desulfurization for oil-fired or pulverized-coal fired boilers (Newell 1969, Schlesinger and Illig 1971) at 100-350°C. In either case regeneration

would be carried out by reduction at 600-700°C with CO or hydrogen—from natural gas reforming. The reduction processes can be summarized as follows:



Conditions that maximize the yield of oxide versus sulfide are clearly desirable. In any case further processing would be required to convert H<sub>2</sub>S or COS to elemental sulfur for final disposal. The final sulfur recovery adds significantly to the overall cost.

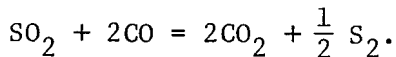
A careful look at the chemistry of regeneration will reveal a very complex mechanism in which the alumina substrate plays a vital role. It is known, for example, that alumina is a catalyst for the Claus reaction



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and for SO<sub>2</sub> reduction (Khalafalla et al. 1971, Khalafalla and Haas 1972, Querido and Short (1973)



Both reactions involve the production of elemental sulfur which raises the possibility of combining SO<sub>2</sub> removal and sulfur recovery by means of the alumina or alkali-alumina sorbent-catalyst. One such FCC scheme is shown in Figure 1.

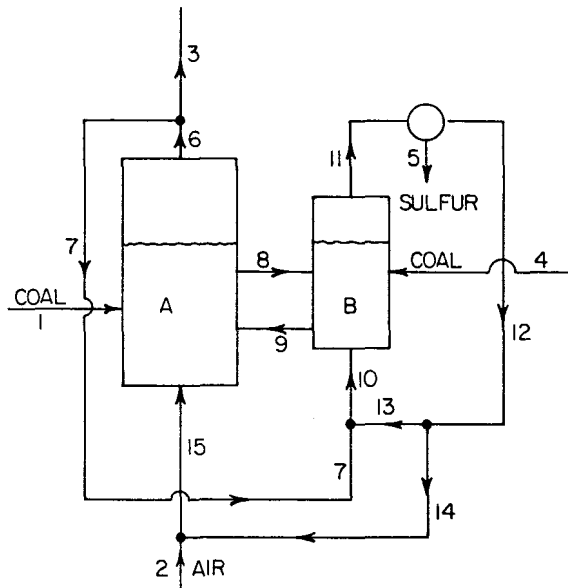


Figure 1. Schematic of a Fluidized Combustion-Regenerator System

Coal combustion and SO<sub>2</sub> removal take place in fluid bed A. The exhaust stream 6 is essentially free of SO<sub>2</sub>. Sorbent regeneration takes place in fluid bed B under reducing conditions. Sulfated sorbent and regenerated sorbent are exchanged between the two beds by means of streams 8, 9. The regenerator offgas 11 is cooled to remove liquid sulfur (stream 5) and recycled to the regenerator B and reactor A. The reactions in the regenerator include sulfate and SO<sub>2</sub> reduction by COS and CO with production of elemental sulfur. The recycle stream 14 is necessary in order to remove nitrogen. A small stream 7 from the reactor to the regenerator serves to balance the loss of material with streams 14 and 5. Heat exchangers for recovery from stream 11 and fans for maintaining the various flows are not shown. Likewise, boiler

tubes and recycle streams of carbon fines are omitted.

The scheme of Figure 1 achieves sulfur removal and recovery in an integrated fashion. However, the cost of the cleaning process increases with increasing recycle ratios. These ratios are determined by the composition of stream 11 and hence by the chemistry of regeneration.

This work was addressed to the basic chemistry of regeneration rather than the process as a whole. Hence, rather than using a fluidized bed reactor, the regeneration reactions were studied using a thermogravimetric analyzer (TGA) and a packed-bed microreactor. Potential difficulties due to sorbent attrition and contamination by flyash were not examined.

## EXPERIMENTAL

### Sorbents

The sorbents investigated are listed in Table 1. They were prepared as sodium sulfate or sodium-lithium sulfate supported on porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>. The two alkali sulfates differ primarily in their phase behavior at reaction temperatures of 700-800°C. Sodium sulfate is solid in this temperature range, while the sodium-lithium sulfate mixture is molten.

Table 1. Sorbent Composition and Properties

Sorbent	Na (m mols/g)	Li	Melting point (°C)	Surface area of support (m <sup>2</sup> /g)
Na <sub>2</sub> SO <sub>4</sub> /αAl <sub>2</sub> O <sub>3</sub>	1.18	0	884	4
Na-LiSO <sub>4</sub> /αAl <sub>2</sub> O <sub>3</sub>	1.04	.68	630	4
Na-LiSO <sub>4</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	1.00	.66	630	89
Na-LiSO <sub>4</sub> /ZrO <sub>2</sub>	1.05	.72	630	20
Na <sub>2</sub> SO <sub>4</sub> /SiO <sub>2</sub>	1.45	.91	630	288

### Apparatus

The reduction reactions were investigated thermogravimetrically and by a flow microreactor. The thermogravimetric apparatus consisted of a DuPont 951 thermogravimetric analyzer and a Varian series 3700 gas chromatograph equipped

with a flame photometric detector. A 30 to 40 milligram sample of sorbent material was used. Because of the small sample size, the amount of elemental sulfur produced was too small to be measured gravimetrically. During reduction the concentration of  $\text{SO}_2$  and  $\text{COS}$  were measured by the gas chromatograph. Under these conditions the analysis of each sample required approximately 4 minutes. At the beginning of the reduction period, the gas concentrations in the product gas were found to change rapidly within the 4 minute time span of a gas chromatogram. Therefore, a multiport valve which allowed the collection of up to 9 samples was installed. At the beginning of the reduction period, samples were collected every 15 to 30 seconds, using this multiport valve. During the remainder of the period samples were injected on-line. The collected samples were analyzed at the conclusion of the reduction period.

The thermogravimetric experiments were run at 700-800°C and atmospheric pressure. The reducing gas used was 1-10%  $\text{CO}$ , 0.5%  $\text{CO}_2$  in nitrogen. The  $\text{CO}_2$  was added to prevent carbon deposition on the sorbent.

The flow microreactor consisted of a .8 cm ID quartz tube mounted vertically in an electric tube furnace. The bed of 1.5 to 2 grams of sample was held in place by a quartz frit and quartz wool. The temperature of the bed was monitored using a type K thermocouple inserted within .3 cm OD quartz thermal well which was inbedded in the solid sample. Reduction was carried out at 700-800°C and pressure slightly above atmospheric. The composition of the reducing gas was 10%  $\text{CO}$ , .55%  $\text{CO}_2$  in  $\text{N}_2$  or 1.1%  $\text{CO}$ , .2%  $\text{CO}_2$  in  $\text{N}_2$ .

## RESULTS

### Thermogravimetric Experiments

The reduction of sorbent materials at 700 and 800°C was followed by observing the weight loss and the  $\text{COS}$  and  $\text{SO}_2$  concentration in the product gas as shown in Figures 2-4. The  $\text{COS}$  and  $\text{SO}_2$  production is shown as moles of product per

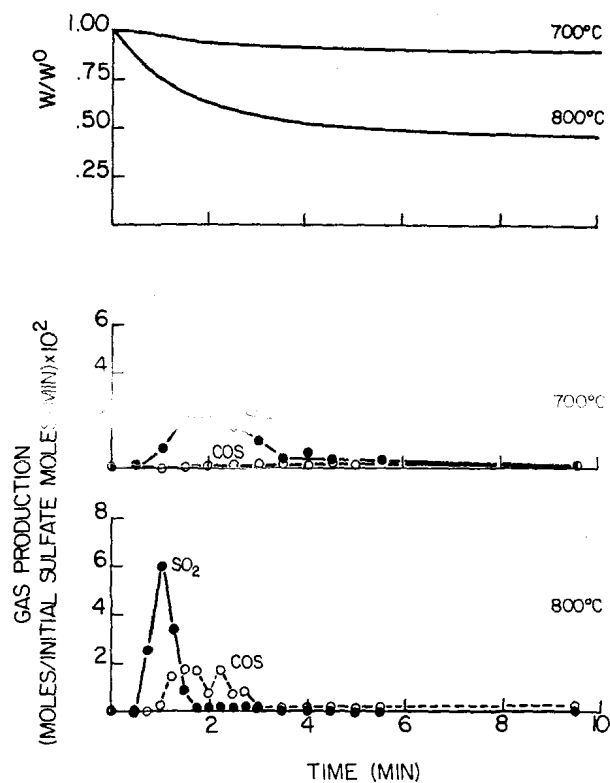


Figure 2. Weight loss and gas production in the reduction of  $\text{Na}_2\text{SO}_4/\alpha\text{Al}_2\text{O}_3$ .

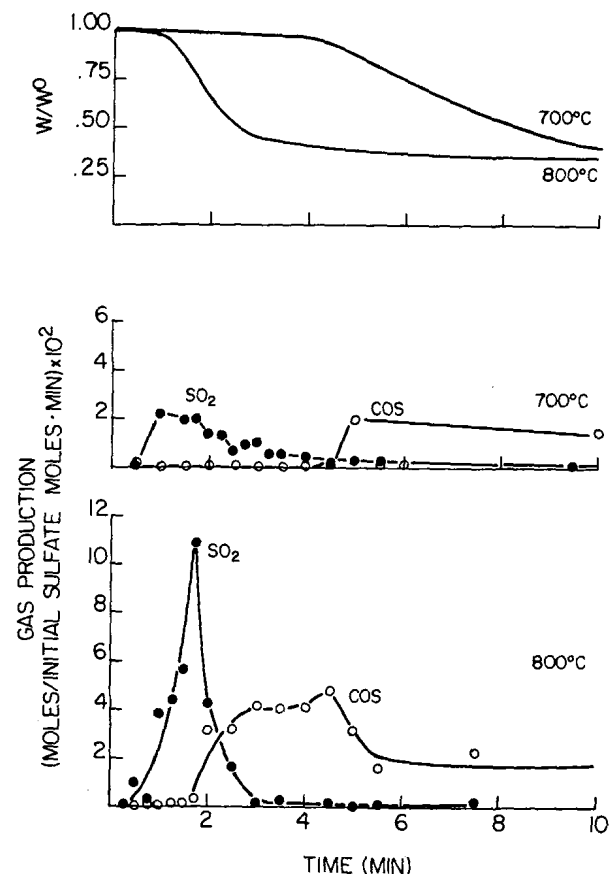


Figure 3. Weight loss and gas production in the reduction of  $\text{NaHSO}_4/\alpha\text{Al}_2\text{O}_3$ .

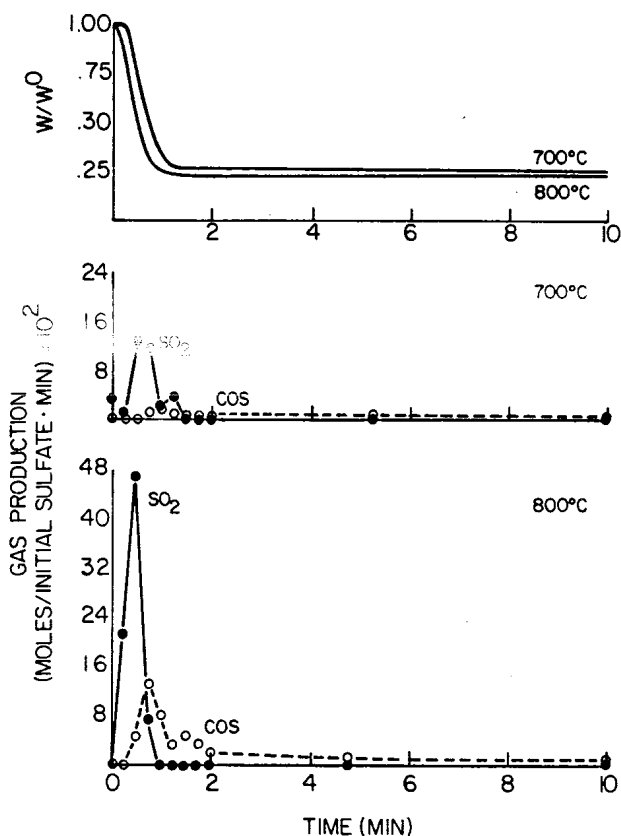


Figure 4. Weight loss and gas production in the reduction of Na-LiSO<sub>4</sub>/γ-Al<sub>2</sub>O<sub>3</sub>.

mole of initial sulfate per minute. An increase in weight loss with increasing temperature is seen with all sorbents but is more pronounced with the sodium sorbent. The sodium-lithium sorbent exhibits an initial period of slow weight loss which is significantly longer at 700°C. No such period is evidenced in the reduction of the sodium sorbent material at either 700 or 800°C. The rate of weight loss is much higher on the γ-Al<sub>2</sub>O<sub>3</sub> support than on the α-Al<sub>2</sub>O<sub>3</sub>.

With the exception of the Na<sub>2</sub>SO<sub>4</sub>/αAl<sub>2</sub>O<sub>3</sub> reduced at 700°C, the concentrations of SO<sub>2</sub> and COS in the product gas followed the same general pattern. Initially the major gas product was SO<sub>2</sub>. After an initial period which varied with temperature the major gas product switched from SO<sub>2</sub> to COS.

#### Sorbent Composition Experiments

Weight loss is a relatively crude measure of the extent of sorbent regeneration. To further probe the state of

the sorbent, the thermogravimetric analyzer system was used to follow the changes in total sulfur and total oxygen contents of the sorbent. The sulfur and oxygen contents were determined through a series of experiments, each experiment giving the composition of the sorbent at the end of a reduction period of specified duration. The sorbent was reduced for a specified period, after which it was exposed to oxygen. All oxygen deficient sulfur species present after reduction were thus oxidized to sulfate. The sorbent was then fully regenerated by exposure to SO<sub>2</sub> and air. Another experiment with a different reduction interval was then performed.

Analysis of the results from these experiments requires assumptions about the nature of the compounds not containing sulfur. Oxide is unstable in the presence of either alumina or carbon dioxide, therefore during reduction it is converted either to aluminate or to carbonate. For the analysis of total oxygen and sulfur, it is unnecessary to distinguish between oxide and aluminate, as there is no weight change in the formation of aluminate from oxide and alumina. The amount of carbonate present must be known, however.

The amount of carbonate and aluminate present depends on the extent of reaction between carbonate and alumina to form aluminate. Equilibrium calculations predict complete conversion to aluminate under reaction conditions. To estimate the extent of reaction between carbonate and alumina during the reaction period, the thermogravimetric behavior of alumina impregnated with sodium carbonate and sodium-lithium carbonate was studied in the presence of the reducing gas. Sodium-lithium carbonate begins reaction with alumina at temperatures near its melting point of 496°C. When heated at a rate of 50°C per minute, the sodium lithium carbonate was completely converted upon reaching 750°C, thirty percent of the conversion being achieved during the period in which the temperature was raised from 700 to 750°C. Molten carbonate, therefore reacts with alumina to form aluminate at a rate comparable to the rate at

which carbonate would be formed during reduction. When a molten phase was present during reduction ( $\text{NaLiSO}_4$  at 700 and 800°C) any carbonate formed would rapidly react to form aluminate. Therefore, the assumption that all carbonate had been converted to aluminate was used to analyze the results of these experiments, except for the  $\text{Na}_2\text{SO}_4/\alpha\text{Al}_2\text{O}_3$  sorbent.

The results for the Na-Li/ $\alpha\text{Al}_2\text{O}_3$  sorbent at 700 and 800°C are shown in Figure 5. At 800°C, reduction consists of an initial period in which the majority of oxygen is lost along with some sulfur, and a second period during which the oxygen content remains constant or decreases very slowly, but sulfur continues to be lost at a steady rate.

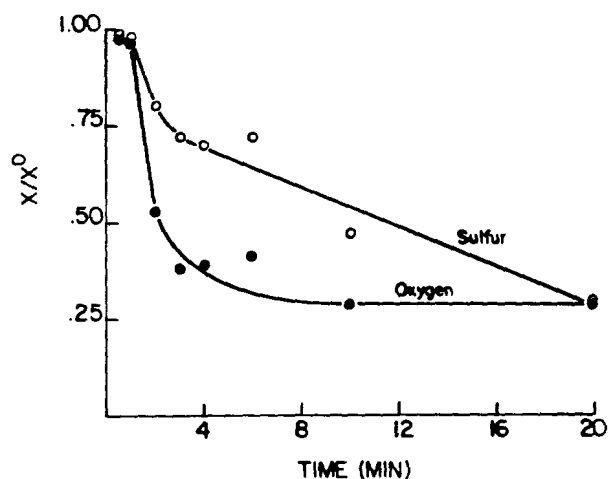


Figure 5. Sorbent composition during the reduction of  $\text{NaLiSO}_4/\alpha\text{Al}_2\text{O}_3$  at 800°C.

At 700°C the oxygen and the sulfur contents appear to approach constant values after periods of rapid loss, as compared to the behavior at 800°C when only the oxygen content approaches a steady value. Similar experiments with the  $\text{Na}_2\text{SO}_4/\alpha\text{Al}_2\text{O}_3$  material at 800°C showed oxygen loss in excess of 50% but sulfur loss limited to 25%. At 700°C this sorbent showed very little loss of either oxygen or sulfur.

Table 2 provides the distribution of sulfur products,  $\text{SO}_2$ ,  $\text{COS}$  and elemental sulfur  $\text{S}_2$  for various sorbents reduced in the TGA. The yield of elemental sulfur was estimated by subtracting the cumulative  $\text{SO}_2$ ,  $\text{COS}$  and the sulfur

remaining in the sorbent from the initial amount of sulfur in the sorbent and is subject to greater uncertainty than the directly measured quantities. At 800°C the sodium sorbent has better selectivity towards elemental sulfur compared to the sodium-lithium sorbent. The opposite occurred at 700°C when the sodium sorbent produced virtually no elemental sulfur.

Table 2. Yield of Products in TGA Experiments

Sorbent	Temp	Time (min)	$\text{SO}_2$	$\text{COS}$	S	$\text{S}_{\text{in sorbent}}$
$\text{Na}_2\text{SO}_4/\alpha\text{-Al}_2\text{O}_3$	800	20	.045	.067	.214	.674
$\text{Na}_2\text{SO}_4/\alpha\text{-Al}_2\text{O}_3$	700	20	.042	.015	0	.943
$\text{Na-LiSO}_4/\alpha\text{-Al}_2\text{O}_3$	800	20	.109	.355	.251	.285
$\text{Na-LiSO}_4/\alpha\text{-Al}_2\text{O}_3$	700	20	.061	.171	.229	.539
$\text{Na-LiSO}_4/\gamma\text{-Al}_2\text{O}_3$	800	20	.175	.238	.237	.350
$\text{Na-LiSO}_4/\gamma\text{-Al}_2\text{O}_3$	700	20	.087	.071	.312	.530

### Microreactor Experiments

Parallel experiments to those conducted in the TGA system were conducted in the packed-bed microreactor. Representative gas production curves for  $\text{SO}_2$  and  $\text{COS}$  are shown in Figure 6. For the purpose

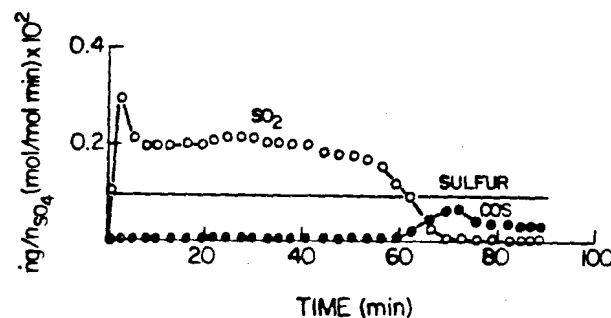


Figure 6. Gas production during the reduction of  $\text{Na}_2\text{SO}_4/\text{alumina}$  at 800°C with 1%  $\text{CO}$ .

of presentation the cumulative amount of sulfur measured at the end of the experiment is reported in the form of an average rate, constant throughout the reduction period. The gas production is reported in terms of moles per mole of initial sulfate per minute. Table 3 shows the total amount of  $\text{SO}_2$  and  $\text{COS}$  produced, as obtained by integration of the  $\text{SO}_2$  and  $\text{COS}$  production curves, the amount of sulfur produced during reduction, and the amount of sulfur produced during a nitrogen purge immediately following the reduction period. Significant amounts of sulfur were produced

Table 3. Yield of Products in Microreactor Experiments  
(t = 90 min).

Sorbent	T(°C)	CO (%)	Products (mol/mol SO <sub>4</sub> )				
			SO <sub>2</sub>	COS	S	S <sub>purge</sub>	S <sub>in sorbent</sub>
Na <sub>2</sub> SO <sub>4</sub> /αAl <sub>2</sub> O <sub>3</sub>	800	10	.0356	.177	.054	.146	.59
Na <sub>2</sub> SO <sub>4</sub> /αAl <sub>2</sub> O <sub>3</sub>	800	1	.122	.016	.085	.060	.72
NaLiSO <sub>4</sub> /αAl <sub>2</sub> O <sub>3</sub>	800	10	.097	.269	.113	.132	.39
NaLiSO <sub>4</sub> /αAl <sub>2</sub> O <sub>3</sub>	800	1	.316	.034	.122	.080	.45
NaLiSO <sub>4</sub> /αAl <sub>2</sub> O <sub>3</sub>	700	10	.006	.151	0	.661	.18
NaLiSO <sub>4</sub> /αAl <sub>2</sub> O <sub>3</sub>	700	1	.014	.097	.079	.241	.57
NaLiSO <sub>4</sub> /ZrO <sub>2</sub>	800	10	.177	.045	.016	.252	.51
NaLiSO <sub>4</sub> /ZrO <sub>2</sub>	700	10	.003	.267	.057	.040	.63
NaLiSO <sub>4</sub> /SiO <sub>2</sub>	800	10	.156	.006	.035	.014	.79

during this nitrogen purge. Although the rate of product generation is slower compared to the TGA runs, the sequence of products is similar to that in the thermogravimetric experiments. The major gas product switches from SO<sub>2</sub> to COS and the switch-over time varies with temperature and CO concentration.

The fraction of COS in the product gas was higher in the microreactor than the thermogravimetric experiments. This can be attributed to secondary reactions more prevalent in the microreactor. One such reaction is the formation of COS from CO and elemental sulfur. The effect is most dramatic in the reduction of the sodium-lithium sorbent at 700°C with 10% CO, during which no elemental sulfur is produced. Lowering the concentration of CO from 10% to 1% lowers the fraction of COS and raises the fraction of sulfur in the product gas. It also greatly increases the amount of SO<sub>2</sub> in the product gas.

The total gas production during reduction, i.e. the sum of COS, SO<sub>2</sub>, and elemental sulfur, is higher for the sodium-lithium sorbent than for the sodium sorbent at 800°C. The total gas production from the reduction of the sodium-lithium sorbent is reduced greatly when the temperature decreased to 700°C.

If the sulfur, SO<sub>2</sub>, and COS produced during reduction and the sulfur produced during the nitrogen purge are totaled, the amount of sulfur which remains in the sorbent can be calculated. This

number is shown in the last column of Table 3. As in the TGA experiments, the sodium sorbent retains more sulfur than the sodium-lithium sorbent. Experiments were also carried out with sodium-lithium supported on zirconia and silica. Zirconia exhibits catalytic properties similar to those alumina. Silica has negligible catalytic activity and, in addition, is not regenerable forming stable alkali silicates.

## DISCUSSION

### Phase Behavior of the Alkali

The differences in the reduction behavior between Na and Na-Li seem to be closely related to the phase behavior of the alkali components in each material. Sodium-lithium sulfate is molten at the onset of reduction at both 700 and 800°C. Sodium sulfate, on the other hand, is solid at the onset of reduction at both 700 and 800°C. Sodium sulfate and its reduction product sulfide form an eutectic melt at 740°C. Therefore, the active component of the sodium sorbent will melt at some point during reduction at 800°C. At 700°C the sodium sorbent remains solid throughout the reduction period.

A significant effect of the phase behavior of the alkali sorbent is seen in the weight loss measurements. Thus at 700°C the solid sodium sorbent is reduced much more slowly than the molten sodium-lithium sorbent. At 800°C the reduction of the two sorbents proceeds at comparable rates as both sorbents are at least partially molten. The sorbent composition experiments indicate that rates of sulfur and oxygen loss differ substantially only in the initial period of reduction during which the sodium sorbent is largely in the solid form.

### Support Effects

Alumina is known to catalyze the reduction of SO<sub>2</sub> with CO to produce sulfur and COS (Lepsoe 1940, Khalafalla and Haas 1972). However, comparison of Figures 3 and 4 indicates that alumina also catalyzes the initial reduction of sulfate to SO<sub>2</sub> since γ-Al<sub>2</sub>O<sub>3</sub> (89 m<sup>2</sup>/g)

is much more active than  $\alpha\text{-Al}_2\text{O}_3$  relative to rate of weight loss. The catalytic effects of alumina are much more pronounced in the microreactor experiments where readsorption of product gases is extensive in their chromatographic progression through the sorbent bed. The catalytic activity of alumina is modified by the formation of alkali aluminate during reduction. The incorporation of sodium into alumina Claus catalysts has been found to increase their activity (George 1975). Sodium hydroxide treatment of alumina affects the nature of  $\text{SO}_2$  adsorption (Deo et al. 1971).

#### Possible Reaction Mechanism

The experimental results can be qualitatively explained by the reaction network shown in Figure 7. The first step is the reduction of sulfate to sulfite, followed by the decomposition of sulfite to oxide, or aluminate, and dissolved sulfur dioxide. The dissolved sulfur dioxide will either desorb to the gas phase or chemisorb on the alumina or aluminate surface where it is reduced to elemental sulfur. Sulfur may desorb from the surface to the melt and to the gas phase or react further either with CO to form COS or with sulfide ion to produce polysulfide ions  $\text{S}_x^{2-}$ . Thus, elemental sulfur can be strongly retained in the sorbent either as species chemisorbed on the alumina or as polysulfide ions. In either case the desorption of this sulfur to the gas phase is accelerated by increasing the temperature.

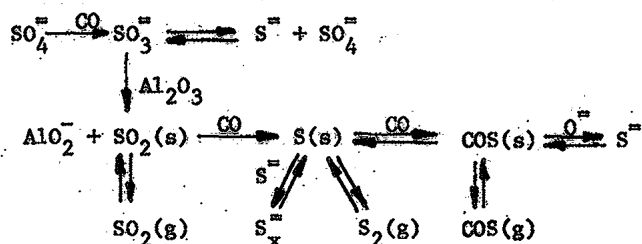


Figure 7. Reaction Network for  $\text{SO}_4^{2-}$  Reduction.

In view of the sequential formation of  $\text{SO}_2$ , elemental sulfur and COS, the yield of these products depends quite strongly on CO concentration. Low CO concentra-

tions favor  $\text{SO}_2$  production while high CO concentrations favor COS production. The yield of elemental sulfur is maximum at some intermediate CO concentration. The product yield is also strongly influenced by the contacting pattern with significant differences observed between the TGA and the packed-bed reactor. The fluid-bed reactor will be intermediate between those two, in terms of contacting pattern and effect of secondary reactions.

#### CONCLUSIONS

- Alkali salts supported on porous alumina particles are potentially attractive regenerable sorbents for in-situ  $\text{SO}_2$  removal in fluidized coal combustion. The role of the alkali is to provide capacity for  $\text{SO}_2$  absorption, while the role of alumina is to disperse the alkali and catalyze the regeneration reactions.
- The phase behavior of the alkali salts influences the rate and product distribution in sorbent regeneration. Using Na-Li mixtures which are molten at reaction temperatures allows more rapid and extensive regeneration.
- The yield of elemental sulfur depends quite strongly on CO concentration, temperature, and sorbent composition. The sulfur yield can be maximized by suitable choice of CO concentration and contacting pattern.

#### ACKNOWLEDGEMENT

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