

R. J. Sappok  
and P. L. Walker, Jr.  
The Pennsylvania State University

# Removal of SO<sub>2</sub> From Flue Gases Using Carbon At Elevated Temperatures

The interaction of a typical flue gas with active charcoal and bituminous coal char at temperatures between 600 and 800°C and atmospheric pressure has been studied. The SO<sub>2</sub> in the flue gas interacts with the carbon to form primarily H<sub>2</sub>S, COS, and a carbon-sulfur surface complex. H<sub>2</sub>S and COS break through the carbon bed much in advance of SO<sub>2</sub>. At 800°C, sulfur retention on the bed exceeds at least 11% before SO<sub>2</sub> breakthrough occurs. The reaction of H<sub>2</sub>S and COS with O<sub>2</sub> over active charcoal at 100-140°C to produce sulfur, which deposits on the carbon, has also been studied and found to be feasible. As a result of this study, a new process is outlined for the removal of SO<sub>2</sub> from flue gas, with the ultimate conversion of the SO<sub>2</sub> to elemental sulfur.

Most of the processes for the removal of SO<sub>2</sub> from stack gases recover either SO<sub>2</sub>, sulfuric acid, or ammonium sulfate. Elemental sulfur is a more desirable product because of its ease in handling and storage and greater value. To produce elemental sulfur, SO<sub>2</sub> can be reduced. A cheap material available for the reduction of SO<sub>2</sub> is carbon in the form of coke, anthracite, or char from coal gasification processes.<sup>1</sup> Coal and coke have been widely used in reducing SO<sub>2</sub> in smelter gases,<sup>2</sup> but these materials have not been applied, to the authors' knowledge, to removal of SO<sub>2</sub> from flue gas. Smelter gases have, in comparison to flue gases, a much higher SO<sub>2</sub> content and only a small amount of water. Optimum conditions in the case of the flue gas-carbon system would thus be expected to be different than that used to clean smelter gases. Therefore, an investigation of this system, with respect to a possible application in the desulfurization of flue gases, has been studied.

One important parameter in such a process is the reaction temperature. A brief look at the literature pertinent to the subject gives an idea of the most promising range. At temperatures below 300°C, SO<sub>2</sub> reacts with carbon in the absence of air and water only slightly. About 1% of the total BET surface area is covered with chemisorbed SO<sub>2</sub>, as was shown recently by Stacy and co-workers.<sup>3</sup> In the presence of water and oxygen, as in the case of

flue gas, the carbon catalyzes the oxidation of SO<sub>2</sub> to SO<sub>3</sub> and then to H<sub>2</sub>SO<sub>4</sub> at temperatures of about 100 to 150°C.<sup>4-7</sup> This reaction is the basis of the Reinluft process. The chemical and technical problems have been investigated recently by Dratwa and Jungten.<sup>8,9</sup> At temperatures around 200°C the sulfuric acid formed reacts with the carbon giving CO, CO<sub>2</sub>, H<sub>2</sub>O, and SO<sub>2</sub> (regeneration of the carbon in the Reinluft process). The continuous reduction of SO<sub>2</sub> to elemental sulfur over active carbon, in the absence of other gases, is only possible at temperatures higher than 500°C.<sup>3</sup> Therefore, it seemed reasonable to study the flue gas-carbon interaction in the temperature range from 500 to 800°C.

## Experimental

The interaction of a simulated flue gas with different carbons was studied in a flow system. A quartz tube with an outer diameter of 2.5 cm was used as a reactor vessel. It was connected on the inlet side to the gas storage tank. The outlet led directly to an analyzer unit. The flue gas was passed through the carbon bed at volume flow rates ranging from 280 to 300 cc/min (NTP). Residence times were recorded for the various runs. The system was equipped with calibrated rotameters to measure the gas flow before and after the reactor tube.

A mass spectrometer (CEC gas analyzer type 21-610) was used for analysis of the different compounds in the gas mixture. The spectrometer was furnished with a capillary inlet system, thus making possible a continuous recording of gas composition. Pure gases were used to calibrate the instrument for quantitative analysis.

The simulated flue gas mixture has

the following composition: 0.35% SO<sub>2</sub>, 2.3% H<sub>2</sub>O, 3.2% O<sub>2</sub>, 15.8% CO<sub>2</sub> in He. Helium was used instead of N<sub>2</sub> to simplify analysis of CO. Both N<sub>2</sub> and He are inert gases in the process.

## Results and Discussion

### Reaction of Flue Gas with Medium Activated Coconut Shell Charcoal

Though coconut shell charcoal will probably not be of practical use in the high-temperature desulfurization of stack gases (because it is too expensive to be consumed in large amounts), it was selected to study the basic features of the interaction. The high reactivity of this material made it possible to obtain accurate results. Some characteristics of the charcoal used are summarized in Table I.

For each run about 6g of the charcoal were placed in the reactor tube. The sample was degassed for 2 hr at 950°C in a He stream. Physically adsorbed water was desorbed and the surface was freed from most of the surface oxides. The sample was then cooled to reaction temperature in He, and the reaction with the flue gas started. At the beginning of the reaction, the bed length was about 4.5 cm. The reaction was followed over a period of 350 to 500 min, according to the special conditions at each temperature. Carbon burn-off during the reaction increased from 25% at 500°C, to about 50% at 600 and 700°C, to 85% at 800°C. The simplest way to describe the results obtained is to explain the course of runs at two different temperatures. The main features of the interaction within the temperature range studied were the same in all the runs. Figures 1 and 2 show the concentrations of some of the different species in the exit gas for runs at 600 and

Messrs. Sappok and Walker are associated with the Materials Science Department, College of Earth and Mineral Sciences, The Pennsylvania State University, 101 Mineral Industries Building, University Park, Pennsylvania 16802.

800°C. Not all the compounds are shown. A complete picture would include also H<sub>2</sub>, H<sub>2</sub>O, and He; H<sub>2</sub> constituted about 0.5% of the exit gas at 800°C.

The first significant result is that for a certain period of time no sulfur compound was seen in the exit gas. All the sulfur was bound by the carbon bed probably forming a carbon-sulfur surface complex. After this period, H<sub>2</sub>S and COS appeared in the exit gas. Their breakthrough time increased with increasing temperature. Further, their concentration in the gas steadily increased until it either reached a maximum, as in the case of the run at 600°C, or leveled off, as at 800°C. The breakthrough profiles of H<sub>2</sub>S and COS were quite different at the two temperatures. An explanation is suggested. The reduction of the SO<sub>2</sub> occurred, especially at the higher temperatures, within a small length at the inlet of the carbon bed. The primary product of the breakdown of the SO<sub>2</sub> was probably elemental sulfur, which either formed a carbon-sulfur surface complex or, in the presence of H<sub>2</sub>, CO and H<sub>2</sub>O, was converted to H<sub>2</sub>S and COS. The latter gases interacted with free carbon sites while traveling through the bed again sulfurizing carbon. The more the surface was saturated with sulfur the less the H<sub>2</sub>S and COS were consumed, or the more was found in the exit gas. The rate of reaction of H<sub>2</sub>S and COS with the carbon increased rapidly with increasing temperature. Therefore, more of the carbon surface was saturated before any sulfur compound could leave the bed; and consequently, the break-through profile was much steeper at higher temperatures.

This is also demonstrated in a quantitative way in Table II. In column 2 of the table, the average sulfur content of the carbon bed (calculated from a sulfur balance, as will be explained later) and in column 3 the residence time of the gas in the bed at the break-

Table I. Analytical data on medium activated coconut shell charcoal.

Surface area (n-butane-BET) <sup>a</sup>	1030 m <sup>2</sup> /g
Surface area (N <sub>2</sub> -BET) <sup>a</sup>	1122 m <sup>2</sup> /g
Helium density <sup>a</sup>	2.20 g/cm <sup>3</sup>
Mercury density <sup>a</sup>	0.83 g/cm <sup>3</sup>
Open pore volume	0.75 cm <sup>3</sup> /g
Particle size	4 × 10 mesh
Ash content	1.6%
Average weight loss during degassing at 950°C in He	7.5%
Bed porosity	31%

<sup>a</sup> Ash-free basis.

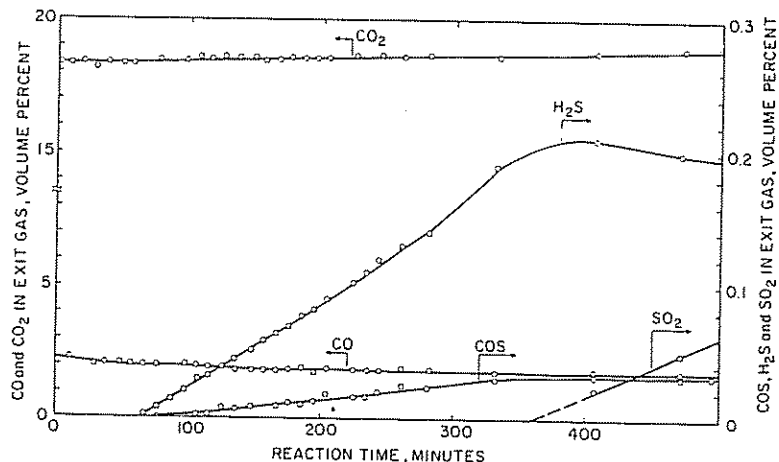


Figure 1. Interaction of flue gas with coconut shell charcoal at 600°C.

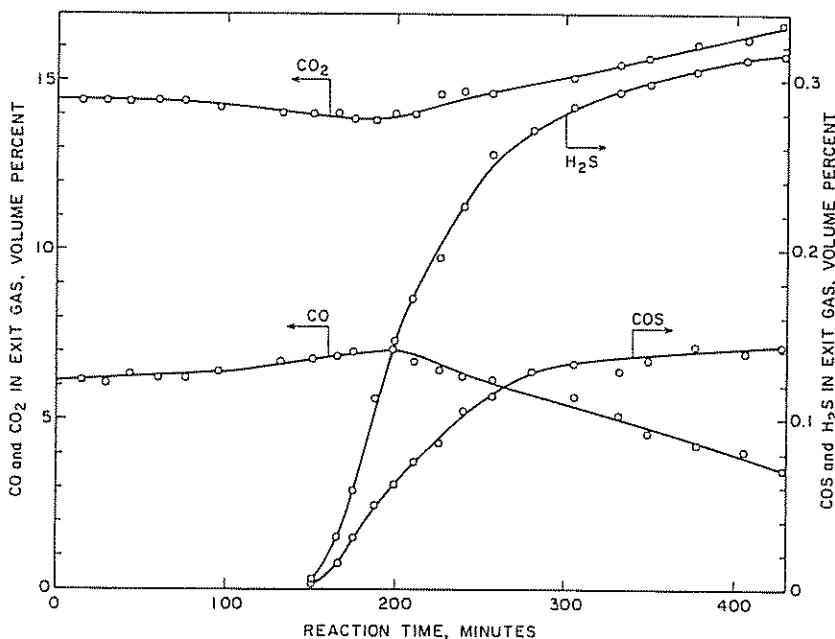


Figure 2. Interaction of flue gas with coconut shell charcoal at 800°C.

through time of the H<sub>2</sub>S and COS are listed. Even though the sulfur content of the bed at break-through increased 3.4 times from 600 to 800°C, the residence time still decreased by 40% in going from 600 to 800°C.

The H<sub>2</sub>S/COS ratio was almost constant from the very first appearance of the two gases. It was 3.3 at 500°C, increased to about 6 at 600 and 700°C, and decreased again to 2.3 at 800°C. The maximum in the experimental H<sub>2</sub>S/COS ratio at 600-700°C is consistent with what theory would predict if the two main reactions determining the ratio are H<sub>2</sub>S + CO ⇌ CSO + H<sub>2</sub>

and H<sub>2</sub>S + CO<sub>2</sub> ⇌ CSO + H<sub>2</sub>O. Taking experimental values for the product concentrations of H<sub>2</sub>S, CO, H<sub>2</sub>O, H<sub>2</sub>, and CO<sub>2</sub>, computer calculations give for the equilibrium H<sub>2</sub>S/COS ratio the following: 2.9 at 500°C, 5.4 at 700°C, and 1.9 at 800°C.

#### SO<sub>2</sub> Breakthrough and Reactivity of the Carbon Bed

Finally also SO<sub>2</sub> appeared in the exit gas. The break-through time increased from 200 min at 500°C to about 500 min at 700°C. At 800°C no SO<sub>2</sub> was seen after 450 min, at which point the run was stopped; only 15% of the

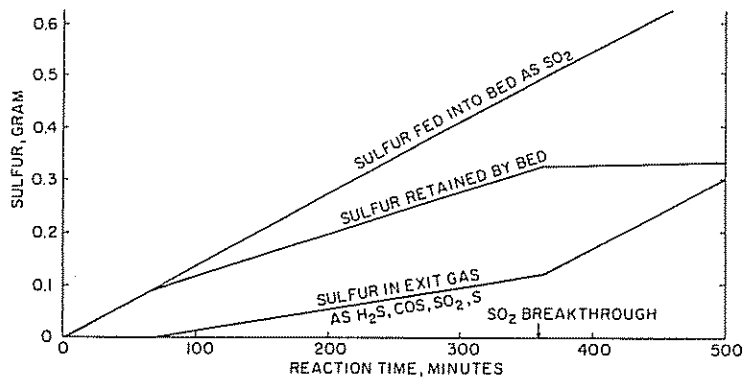


Figure 3. Sulfur balance on the run at 600°C.

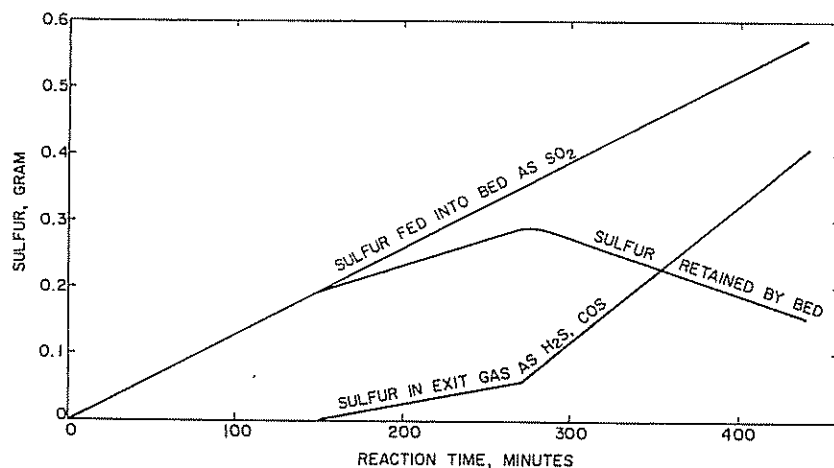


Figure 4. Sulfur balance on the run at 800°C.

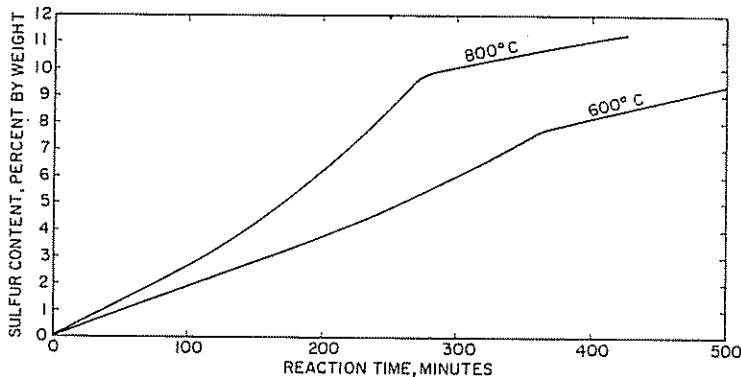


Figure 5. Sulfur retention on charcoal for the 600 and 800°C runs as a function of reaction time.

initial carbon remained. This is strong evidence that the reduction of the  $\text{SO}_2$  to  $\text{H}_2\text{S}$  and  $\text{COS}$ , at least at the higher temperatures, took place in a rather small reaction zone. In the runs at 600 and 700°C, some elemental sulfur condensed on the cooler parts of the reactor tube. It appeared at about the same time as the  $\text{SO}_2$ ; its amount was roughly one-sixth of the sulfur in the  $\text{H}_2\text{S}$  and  $\text{COS}$ .

Further conclusions on the interaction can be drawn by making a sulfur balance over the entire period of the reaction. The amount of sulfur retained by the bed is calculated as the difference between the sulfur fed into the bed as  $\text{SO}_2$  and the sulfur which appeared as  $\text{H}_2\text{S}$  and  $\text{COS}$  or in some cases as  $\text{SO}_2$  and  $\text{S}$  in the exit stream. The latter information can be derived from a quantitative analysis of the mass spectrometric data. Elemental sulfur was determined by weighing. The results of such a calculation for the 600 and 800°C runs are presented in Figures 3 and 4. All the values are expressed in grams of sulfur. In the case of the 600°C run, the sulfur content of the bed increased for the first 360 min and then remained almost constant. The explanation for this effect is thought to be straight forward. Even though carbon was continuously being consumed, the total surface area remained almost constant since the specific area of the carbon increased. At 800°C (Figure 4) the reactivity of the carbon was so great that its gasification occurred more non-uniformly. Development of additional surface area was not as efficient as at 600°C. One, therefore, finds a maximum of retained sulfur. Because some sulfur was liberated from the carbon as it was consumed, more sulfur came out than was fed into the bed for reaction times beyond 270 min. Nevertheless, the percentage of sulfur retained on the remaining carbon increased in all the runs over the period investigated. The sulfur buildup for the runs at 600 and 800°C is represented in Figure 5.

From the results of the sulfur balance, one can deduce whether a continuous conversion of the incoming  $\text{SO}_2$  to  $\text{H}_2\text{S}$  and  $\text{COS}$  at a given bed length is possible. If  $\text{SO}_2$  breaks through the bed before the bed is saturated with sulfur, then a continuous reduction at that bed length is not possible. But if, to the contrary, breakthrough occurs after saturation, the carbon bed length is sufficient. There is, of course, in the second case a minimal length or in other words a universal residence

time for the gas in the carbon bed. This value can be easily determined. Because the bed is burning down, it continuously approaches and then reaches the critical length where  $\text{SO}_2$  is breaking through. From Figures 3 and 4, it can be concluded that for the 600°C run,  $\text{SO}_2$  broke through at the same time that the bed was saturated with sulfur; for the 800°C run, the bed was saturated but no  $\text{SO}_2$  breakthrough was seen. Therefore, it can be concluded that in the runs at 600, 700 and 800°C the bed length was, for a certain time, sufficient to reduce  $\text{SO}_2$  continuously. The  $\text{SO}_2$  breakthrough occurred at the critical bed length as stated above. In the 500°C run, the situation was different as will be shown.

The residence times at the moment of breakthrough of  $\text{SO}_2$  are calculated from the experimental data. They are termed the "critical residence times" and are listed in Table II. The critical residence times can be treated like a reaction velocity constant. Because the  $\text{SO}_2$  concentration in the feed gas is kept constant, these values represent a time during which a constant amount of  $\text{SO}_2$  is reduced at a certain temperature. Plotting their reciprocal against the reciprocal of absolute temperature (an Arrhenius plot) should produce a straight line. This is indeed the case as shown in Figure 6. Since the value for the 800°C run falls on the straight line, it is suggested that the critical value was almost approached at this temperature. The value for the 500°C run is far off the line. In this experiment, the carbon bed length at the start of the run was too small; and thus the critical residence time was greater than the residence time of the flue gas in the bed at the start of the run. Saturation of the bed with sulfur was also not achieved at the time of breakthrough of  $\text{SO}_2$ .

A considerable amount of sulfur was fixed at the surface during the reaction. It should be expected that the sulfur blocked some of the active sites on the surface. Rates of the carbon-carbon dioxide and carbon-steam reactions are of concern because these reactions, in part, determine the CO and  $\text{H}_2$  concentrations in the exit gas. The effect was studied briefly. The system was simplified and instead of the flue gas,  $\text{He-SO}_2(0.447\%)\text{-H}_2\text{O}(2.7\%)$  and  $\text{He-H}_2\text{S}(0.805\%)\text{-H}_2\text{O}(2.7\%)$  mixtures were reacted with the coconut shell charcoal in the temperature range 600 to 800°C. Though the results are preliminary, they showed the expected retardation of carbon gasification but the

effects were rather small. It is interesting to note that the  $\text{CO}/\text{CO}_2$  product ratio progressively decreased as gasification proceeded in the presence of the mixtures containing either  $\text{H}_2\text{S}$  or  $\text{SO}_2$ .

#### Thermal Stability of the Carbon-Sulfur Surface Compound

For a possible application to flue gas desulfurization, the thermal decomposition of the carbon-sulfur surface compound should be considered. Therefore, the influence of heat treatment on the sulfur content of coconut shell charcoal samples sulfurized with a  $\text{He-SO}_2\text{-H}_2\text{O}$  mixture at 600 to 800°C was studied. Small samples, placed in a platinum boat, were degassed at various temperatures in a double wall reactor tube for 2 hr. The results of the experiments are shown in Table III. The decrease in sulfur content up to 1000°C is small. It is a well established fact that the carbon-sulfur complex has a high thermal stability.<sup>10,11</sup>

#### Reaction of Flue Gas with Other Carbons

The use of several other carbonaceous materials, such as chars from coal gasification processes or anthracite, has been studied briefly. Experiments were performed in the same manner and with the same equipment as described above. The weight of starting material used was about 5 to 6 g. The main features of the interaction with flue gas were similar to those with coconut shell charcoal, though in detail it is more complex. Therefore, only one run with one of the chars will be discussed briefly.

A bituminous char, resulting from partial hydrogasification of coal at about 800°C, was used. Table IV gives some of the characteristics for this particular material. The char had a relatively low  $\text{N}_2$  BET surface area, while the  $\text{CO}_2$  area was rather large, indicating that most of the open pore area was in the micropore range. Another important difference between the char and the coconut shell charcoal was the smaller particle size of the char. Under the experimental conditions of gas flow and temperature used, this and all the other chars were, contrary to the coconut shell charcoal, in a fluidized state.

Figure 7 presents results of the interaction of the char with flue gas at 800°C.  $\text{H}_2\text{S}$  and COS appeared immediately. With all coal chars studied, the break-through time for these gases was much smaller than found when coconut shell charcoal was used and the break-through profile was not as steep. Furthermore, activation of the

gas in the carbon bed during the reaction.

Re-action Temp., °C	Sulfur Content of Carbon at Breakthrough of $\text{H}_2\text{S}/\text{COS}$ , % by Weight	Residence Times for Gas at Break-through, Sec	
		$\text{H}_2\text{S}/\text{COS}$	$\text{S}_2\text{O}$
500	0.35	0.34	0.29
600	1.3	0.28	0.20
700	2.2	0.23	0.096
800	4.4	0.18	<0.05

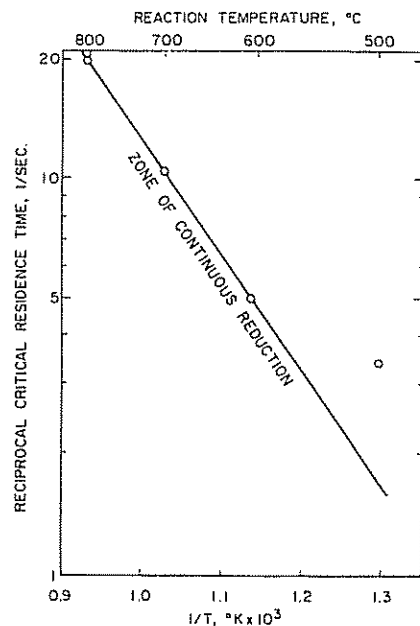


Figure 6. Temperature dependence of the "critical residence time."

Table III. Removal of sulfur from previously sulfurized charcoal by thermal treatment.

Previous Treatment Temp., °C <sup>a</sup>	De-gassing Temp., °C	Sulfur Content % by Weight
600	Original	4.84
600	700	4.88
600	800	4.76
600	900	4.54
600	1000	3.96
800	Original	5.04
800	800	5.00
800	900	4.68
800	1000	4.76

<sup>a</sup> Sulfurized with  $\text{He-SO}_2(0.447\%)\text{-H}_2\text{O}(2.7\%)$  mixture.

Table IV. Some physical properties on a bituminous char.

Property	Value
Surface area ( $\text{N}_2$ -BET) <sup>a</sup>	112 $\text{m}^2/\text{g}$
Surface area ( $\text{CO}_2$ -BET) <sup>a</sup>	479 $\text{m}^2/\text{g}$
Helium density <sup>a</sup>	1.83 $\text{g}/\text{cm}^3$
Mercury density <sup>a</sup>	0.90 $\text{g}/\text{cm}^3$
Open pore volume	0.56 $\text{cm}^3/\text{g}$
Ash content	9.1%
Particle size for screen analysis	63% 20 × 48 mesh

<sup>a</sup> Ash-free basis.

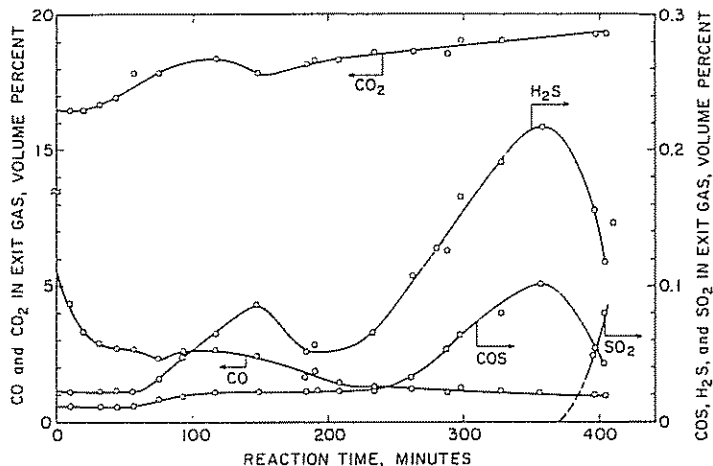


Figure 7. Interaction of flue gas with a bituminous char at 800°C.

char by the flue gas was rather pronounced. This perhaps is the reason for the increase in CO, CO<sub>2</sub>, and H<sub>2</sub> (the concentration of H<sub>2</sub> at the end of the run was about 0.2%) at times between 80 and 130 min. Also the decrease in H<sub>2</sub>S at about 150 min could be explained by this effect. More of the H<sub>2</sub>S is consumed by the freshly developed surface. The BET N<sub>2</sub> area increased from an original value of 112 m<sup>2</sup>/g to a final value of 700 m<sup>2</sup>/g. Sulfur dioxide broke through the bed after 370 min. At that time, 48% of the original char was left. The abrupt break-through of SO<sub>2</sub> and the simultaneous decrease of H<sub>2</sub>S and COS suggest that the reactivity of the bed was not decreased but rather that a good fluidized state was no longer maintained. The gas was channelling through the bed, only partly reacted. As in the case of the coconut shell charcoal, it is concluded from the sulfur balance that a continuous production of H<sub>2</sub>S and COS from SO<sub>2</sub> is possible at 800°C. The "critical residence time" is not as easily determined as with the coconut shell charcoal. A rough estimate gave a value of about 1 sec for all the char samples. This value might be somewhat too high since, as just discussed, it is suspected that ideal fluidization conditions were not achieved. The sulfur uptake of the chars was about 10% by weight.

#### Conclusions from the Results Obtained on the Removal of SO<sub>2</sub> from Flue Gases

Two possibilities for removing SO<sub>2</sub> from stack gases can be envisaged as a result of these studies:

1. Some sulfur is fixed at the surface of the carbon even in the presence of H<sub>2</sub>O, CO, and CO<sub>2</sub> before any

sulfur breaks through the bed (the bituminous char mentioned above being an exception). A process with a cycling bed could be imagined during which the SO<sub>2</sub> is bound as sulfur to the carbon surface between 600 and 800°C. The carbon bed is regenerated by heating to a temperature where the sulfur is released from the carbon.

2. Sulfur dioxide is reduced in a continuous reaction to H<sub>2</sub>S and COS. These products could be either removed by adsorption at temperatures between 25–100°C and after desorption converted by the Claus process ( $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 2\text{H}_2\text{O} + 3\text{S}$ ) to elemental sulfur or could be oxidized directly on an activated carbon. Active carbon is a good catalyst for the reaction  $\text{H}_2\text{S} + 1/2\text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O}$ . Also COS is oxidized under these conditions to sulfur, as will be demonstrated later. The final product would be elemental sulfur in both processes.

The first possibility can be ruled out for several reasons. The breakthrough time for any sulfur species is reasonable at 700 and 800°C in the case of the activated coconut shell charcoal. But it drops considerably when a char is used. In the case of the bituminous char described above, H<sub>2</sub>S and COS appeared immediately. Therefore, only a very small amount of sulfur could be fixed on the carbon. Furthermore, the regeneration of the carbon would be a serious problem. High temperatures are required to decompose the carbon-sulfur-surface complex, as was seen earlier.

More promising is the second possibility. Experiments have proved that

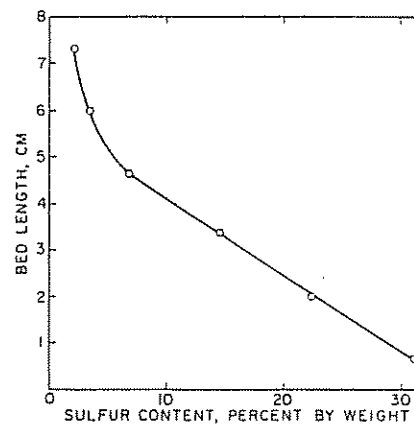


Figure 8. Concentration profile of sulfur in an active carbon bed after an H<sub>2</sub>S-oxidation experiment at 142°C.

a continuous reduction of SO<sub>2</sub> to H<sub>2</sub>S and COS within the temperature and concentration range studied is quite feasible. The adsorptive removal of H<sub>2</sub>S and COS under the actual conditions in a power plant and their conversion into elemental sulfur in a separate unit has no advantage over the direct removal of the SO<sub>2</sub> itself. The adsorption has to occur at around 100°C. At this temperature and at the concentrations involved, a large amount of adsorbent would be required. A very convenient method to remove H<sub>2</sub>S from gases is its catalytic oxidation over active carbon with elemental oxygen. This reaction has been applied on a large scale to purify gases.<sup>12</sup> It is especially applicable for gases with a very low H<sub>2</sub>S concentration. Because the temperature of the carbon catalyst is mostly kept below the dew point of sulfur, the activity decreases with the deposition of sulfur. The carbon has to be regenerated. The uptake of sulfur is considerable; up to 70% by weight of the carbon bed is reported.<sup>12</sup> Water plays an important role in the reaction. The sulfur content of the bed at the time when the first traces of H<sub>2</sub>S appear in the exit gas is, in the case of a dry H<sub>2</sub>S–O<sub>2</sub> mixture, only 7% of that when a wet stream is used. Another compound that enhances the oxidation is NH<sub>3</sub>. An important advantage of the reaction is its high velocity. The gases can be passed through the bed at very fast flow rates. Various methods have been described for the regeneration of the carbon. The sulfur can be extracted with organic solvents or ammonium sulfide or blown out with super-heated water vapor at about 160°C (the liquid sulfur is at a low viscosity).<sup>12</sup> The mechanism of the

reaction has been investigated in great detail by Siedlewski.<sup>13,14</sup>

#### H<sub>2</sub>S and COS Oxidation by O<sub>2</sub> over Coconut Shell Charcoal

COS was formed in a considerable amount during the reaction of flue gas with carbon. It was of interest to learn if COS could also be oxidized by oxygen over active carbon, as is H<sub>2</sub>S, according to the equation  $\text{COS} + 1/2 \text{O}_2 \rightarrow \text{S} + \text{CO}_2$ . The reaction was studied briefly and a comparison with H<sub>2</sub>S oxidation under similar conditions was made. Experiments were run at 143°C. A He-H<sub>2</sub>S(0.71%)-O<sub>2</sub>(0.38%)-H<sub>2</sub>O-(2.5%) or a He-COS(0.56%)-O<sub>2</sub>(0.30%)-H<sub>2</sub>O(2.5%) mixture was passed through the carbon bed. The residence time was 1.4 sec. Analysis of the product gases was performed with the mass spectrometer as described above. For the H<sub>2</sub>S mixture, breakthrough occurred when the average sulfur content of the bed was 18.6%, or after  $63 \times 10^{-3}$  moles of H<sub>2</sub>S had been oxidized. For the COS mixture, breakthrough occurred after the bed had retained only 1.6% sulfur or  $5 \times 10^{-3}$  moles of COS had been oxidized. Thus, carbon is a poorer catalyst for COS oxidation than it is for H<sub>2</sub>S oxidation. Further experiments are desirable to obtain additional information on this subject.

The sulfur in the carbon bed was not distributed homogeneously. Figure 8 shows the concentration profile of sulfur as a function of the carbon bed length after one of the H<sub>2</sub>S oxidation experiments. The sulfur content was rather high at the inlet of the bed, which is of importance in any practical application (moving bed).

A final test established the feasibility of removal of SO<sub>2</sub> from flue gas as just described. A second reactor tube containing 11 g of coconut shell charcoal was connected to the outlet of the reduction reactor tube. The flue gas was reacted at 790°C. A slight excess of oxygen, required for the oxidation of H<sub>2</sub>S and COS, was added to the converted flue gas. Then the mixture was passed through the second carbon bed, which was held at 100°C (residence time in the catalyst bed 1.6 sec). The experiment was run for 4 hr. No sulfur compound was seen in the exit gas during this period. At intervals, the gas coming from the reduction tube bypassed the oxidation tube and the H<sub>2</sub>S and COS concentrations were measured. The ratio H<sub>2</sub>S/COS was 2.5. Over the run, 0.252 g of elemental sulfur was formed, bringing the sulfur content of the catalyst bed to 2.2%.

#### Proposal of a New Flue Gas Desulfurization Process

The results of this investigation en-

courage us to outline a process for the removal of SO<sub>2</sub> from stack gases. Basically two units are required:

1. The SO<sub>2</sub> of the flue gas is converted in the first reactor to H<sub>2</sub>S and COS by reduction with carbonaceous materials.
2. The gas coming from this unit is cooled down, oxygen (air) is added, and H<sub>2</sub>S and COS are oxidized in a second reactor to elemental sulfur. Active carbon could be used as a catalyst.

From the temperature at which the two units have to be operated, their place in a power plant is determined automatically. The reduction reactor, working at high temperatures, should be located in front of the air preheater. It could be a fixed or fluidized bed reactor. Its operating temperature is a question of optimization. According to the results of this work, it should be between 600 to 800°C. A low temperature has the advantage of low CO and H<sub>2</sub> concentrations. On the other hand, the carbon bed length must be greater, resulting in a larger pressure drop. The heat required to bring the flue gas from around 300°C when leaving the steam superheaters to 600-800°C could be supplied by the combustion of a portion of the carbon in the reactor. A heat balance reveals that a minimum of 4% O<sub>2</sub> in the feed gas is necessary to heat up the gas by 500°C. If some type of heat exchange would be used, the amount of oxygen could be decreased to a level which is usual in flue gases (~2%). By these means also the amount of carbon burned in the reactor would be within reasonable limits. The heat evolved by the combustion is not wasted because it is fed back in the air preheater.

Carbon monoxide and H<sub>2</sub> are not desirable products. Their concentration could be reduced by reacting part of the flue gas, which could by-pass the carbon bed, with the converted gas. SO<sub>2</sub> and O<sub>2</sub> would reoxidize the gas, consuming the CO and H<sub>2</sub>. The fly ash could act as a catalyst. Small amounts of CO could be tolerated. The threshold limits for CO are a hundred times higher than those for SO<sub>2</sub>; thus CO is the less serious pollutant.

The second step in the process is the oxidation of H<sub>2</sub>S and COS. This unit should follow the dust collector. It could be operated at the gas temperature at that part of the system (150°C). Because no cooling is necessary, the gas does not lose its buoyancy. The catalyst bed could be a suitable type of active carbon. It is cycled and regenerated in a separate unit, where the sulfur is removed by some process as described earlier.

Whether this proposed method of desulfurization of flue gas is commercially

feasible cannot be answered at present. The results of this investigation have clearly demonstrated, however, that the method is technically possible. The authors feel it should receive further attention.

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