REMOVAL OF SO₂ FROM FLUE GASES USING CALCINED ANTHRACITE AT ELEVATED TEMPERATURES

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Interaction of a typical coal-fired power plant flue gas with calcined anthracite in a fluidized bed reactor has been studied between 700 to 900°C. Anthracite reacts with SO_2 in the flue gas at 800°C. forming elemental sulfur, a C-S surface complex, H_2S, and COS. The amount of H_2S formed is greater than the amount of COS for interaction with wet flue gas. Oxygen containing gases, in addition to SO_2, present in the flue gas also react with the anthracite resulting in its surface area development and activation. The period over which complete removal of SO_2 from the flue gas is achieved is a function of temperature, the residence time of the gases in the bed, and the extent of saturation of the anthracite surface with sulfur complexes. Complete removal of SO_2 can be continued indefinitely, at least in theory, by charging fresh anthracite into the reactor bed at a rate at which it is removed from the bed by gasification. The partially reacted anthracite is catalytically active at about 150°C. for the oxidation of H_2S, formed as a reaction product, to elemental sulfur. This sulfur is deposited on the catalyst and can be recovered by solvent extraction.

It has been shown in this laboratory (10) that SO_2 in helium, at concentrations comparable to that found in flue gases, reacts above 500°C. with medium activated charcoals yielding a carbon-sulfur complex, elemental sulfur, and CO and CO_2. A follow-up (9) of this work indicated that a process for desulfurizing flue gases, using activated charcoal or bituminous char at temperatures between 600° and 800°C. with the ultimate conversion of SO_2 to elemental sulfur, is possible. The above idea has been extended to using calcined anthracite in the present study. Interactions were studied with both dry and wet streams of flue gas at temperatures between 700° and 900°C.

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EXPERIMENT

The coal used was a medium volatile (5.8%) Pennsylvania anthracite of 60 × 100 U.S. sieve size. It contained 6.8% ash, 2.35% H, and 0.48% S. The anthracite was calcined at 650°C. for 2 hr. prior to interaction with the flue gas. Calcination was performed to prevent the exposure of the mass spectrometer filament to high concentrations of hydrocarbon gases resulting from devolatilization of the anthracite at interaction temperatures.

The interaction of a simulated (both dry and wet) flue gas with calcined anthracite was studied in a fluidized bed reactor of about 2-in. I.D. A volumetric flow rate of 1,200 to 1,250 cu. cm./min. (NTP) of flue gas was used for all runs. The height of the fluidized bed, upon which the residence time of the flue gas in the bed depends, was varied by using different starting weights of anthracite in order to observe its effect on SO_2 removal. The apparatus was equipped with rotameters to measure gas flow before and after the reactor tube. The simulated wet stream of flue gas was prepared by passing the dry gas through wash bottles, maintained at a temperature about 5°C. higher than room temperature. The gas mixture, leaving the wash bottles, cooled to room temperature and, hence, was saturated with water vapor. The reactor

was heated by a tubular furnace containing three independently pe   1 elements designed to provide a uniform zone of controlled ten.,   ature 7 in. long.

A continuous analyzer-type mass spectrometer (CEC 21-610) was used for analysis of the different constituents in the inlet and effluent gas. The simulated dry flue gas had the following composition by volume: 0.37% SO_2, 3.3% O_2, and 16.8% CO_2 in helium. The wet mixture contained about 2.7% water vapor by volume. Helium was used instead of N_2 as the carrier gas to simplify analysis of CO in the mass spectrometer. Both N_2 and He are inert gases in the process.

RESULTS AND DISCUSSION

INTERACTION WITH DRY FLUE GAS

Basic features of the interaction were ascertained by reacting the anthracite with dry flue gas at 700°, 800°, and 900°C. Initially, about 200 g. of anthracite (giving a residence time of about 2.1 sec. for the flue gas in the bed) were charged into the reactor. The starting height of the fluidized bed was about 17 cm. SO_2 broke through the bed almost immediately at 700°C. but not at 800° and 900°C. for the periods investigated. SO_2 reacted with the carbon of the anthracite at these temperatures and formed a stable carbon-sulfur complex and elemental sulfur. In addition, H_2S and COS were produced at 800° and 900°C. The O_2 in the flue gas was completely consumed by the anthracite bed at all temperatures. The rate of carbon loss, due to gasification from the bed, in   sed with increasing temperature. The major products of gasification were CO_2 and CO, with the amount of CO in the effluent decreasing progressively

with increasing reaction time at 700 and 800°C. At 900°C., however, the amount of CO in the effluent reached a maximum after about 4 hr. of reaction and then slowly decreased. The rates of development of BET surface area and of sulfur buildup on the reacted anthracite increased with increasing interaction temperature. Some important features of the reactions at 800° and 900°C. are summarized in Table 1.

It is apparent that this anthracite does not possess sufficient reactivity for a satisfactory removal of SO_2 from flue gases at 700°C. A carbon balance indicates that the loss of carbon from the bed at 700°C. is accounted for solely by gasification due to the presence of O_2 in the flue gas. Gasification of anthracite by O_2 at temperatures above 600°C. is not expected to produce significant internal porosity because of its high reaction rate (1). Insignificant development of BET area in the anthracite reacted at 700°C. was found and is attributed to lack of internal burning and gasification. The rate of gasification of anthracite at 800°C. is slightly higher than that accounted for by reaction solely with O_2. Some gasification of anthracite by CO_2 at 800°C. occurs, and the reaction is sufficiently slow to achieve internal burning (2). Consequently, the development of BET area upon gasification at 800°C. is more efficient than at 700°C. Interaction of carbon with carbon dioxide is quite significant at 900°C.; therefore, a high concentration of CO was detected in the effluent. Further, a large contribution to the overall gasification of carbon by the carbon-carbon dioxide reaction at 900°C. assures

TABLE 1. REACTION OF DRY FLUE GAS WITH ANTHRACITE AT 800° AND 900°C.

Reaction time, hr.	Cumulative burn-off, %	Surface area, sq. m./g. (m.m.c.b.) N_2	CO_2	Cumulative sulfur (m.m.c.b.), %	Products H_2S as % Feed SO_2	COS as % feed SO_2	CO_2 as % feed CO_2	CO/CO_2
				800°C.				
1	0.0	<1	420	0.46	—	—	101	0.302
2	1.7	10	420	0.64	5.2	3.6	112	0.201
4	3.1	19	360	0.93	9.7	9.2	115	0.143
6	4.5	22	354	1.12	12.2	21.2	118	0.125
8	3.9	28	415	1.22	16.0	28.0	119	0.119
10	7.5	37	380	1.45	16.0	32.4	120	0.119
12	9.0	43	384	1.65	16.0	35.4	121	0.114
14	10.6	64	394	1.98	16.0	38.0	122	0.115
16	12.2	106	415	2.25	16.0	40.5	122	0.114
				900°C.				
0	0.0	<1	214	0.46	—	—	—	—
2	3.8	54	230	0.70	6.0	4.2	68.0	1.24
4	6.0	90	292	0.98	4.7	6.0	67.3	1.33
6	9.5	140	300	1.37	5.2	8.0	68.0	1.32
8	12.8	175	340	1.85	6.1	10.4	68.6	1.30
10	16.5	213	364	2.00	7.5	12.6	70.4	1.24
12	19.5	231	408	2.35	9.0	15.2	71.6	1.15
14	23.0	268	415	3.02	11.2	17.6	73.4	1.08
16	26.0	304	415	3.25	13.7	20.0	74.7	1.07
18	29.0	327	400	3.82	16.0	22.4	74.7	1.07

substantial area development, as is seen in Table I. Anthracite is known to be a molecular sieve material (Metcalfe et al., 1963), which explains why the surface area calculated from N_2 adsorption at $-196°C$. is less than the CO_2 area calculated at 25°C.

Formation of H_2S at 800° and 900°C is attributed to the interaction of SO_2 with H_2 present in the calcined anthracite. COS, in the effluent, was produced at a slower rate at 900°C. than 800°C. (see Table I). COS is thermally unstable at high temperatures; and, moreover, the dissociation is catalyzed by anthracite at temperatures above 800°C. (6). Significant dissociation of COS at 900°C. explains its slow rate of buildup in the effluent at this temperature.

The interaction of dry flue gas with anthracite at 800°C. is visualized as optimum from two standpoints: (1) complete removal of SO_2 from the inlet stream for a reasonably long duration and (2) intermediate amounts of CO formed. The interaction at 800°C. was therefore continued for additional periods of time with a view to ascertain the profile of sulfurous gases in the effluent with reaction time, the sulfur buildup on the anthracite, and the SO_2 breakthrough point. Interaction was continued for a cumulative period of 62 hr. at which time about 45% of the feed SO_2 was breaking through the bed. The anthracite underwent a cumulative weight loss, due to gasification over the run, of about 83%. Elemental sulfur condensed on cooler parts of the reactor after about 52 hr. of interaction, which coincided closely with the time at which SO_2 broke through the bed. SO_2 breakthrough occurred after the bed underwent a cumulative weight loss of about 64%. The weight of carbon left in the bed at this weight loss was only about 45 g. At the point of breakthrough, sulfur concentration on the bed had built up to 7.0%, and the BET surface area, as measured by N_2 and CO_2, had increased to 465 and 449 sq. m./g., respectively.

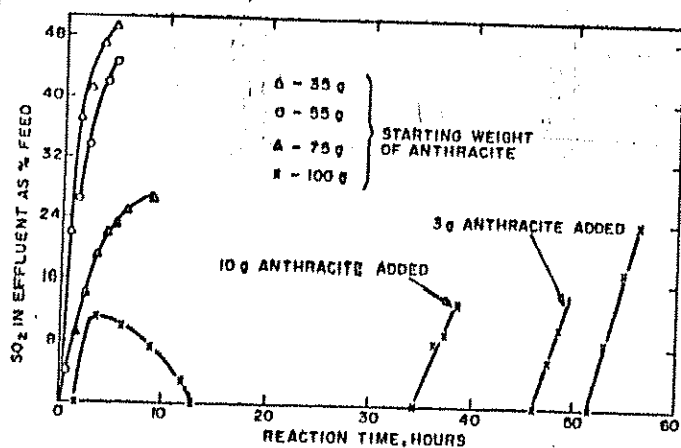The effect of residence time on the breakthrough profile of SO_2 was studied by varying the bed height by

Fig. 1. Breakthrough curves for SO_2 as a result of interaction of dry flue gas with varying starting weights of calcined anthracite at 800°C.

charging different amounts of anthracite into the above reactor. The profiles are shown in Figure 1. The results show that the overall reactivity of calcined anthracite is not very high at 800°C. But it is evident that the capacity of the bed, for any given initial bed height, increases with progress of the reaction. This is as expected, since the surface area of reacted anthracite increases with increasing reaction time. For the run with 100 g. of anthracite, complete removal of SO_2 from the inlet stream became effective after the reaction proceeded for about 12 hr. SO_2 broke through this bed only after an additional 25 hr. of reaction. Fresh charges of calcined anthracite were introduced into the reactor for this run at reaction times of 39 and 50 hr. It is noted that the capacity of the bed towards complete removal of SO_2 was restored following each addition. SO_2 broke through the bed following the additions only after the bed lost an amount of carbon essentially equal to the weight of charge. It is also interesting to note from Figure 1 that the rates of SO_2 buildup in the effluent were approximately the same following each addition of fresh charge.

INTERACTION WITH WET FLUE GAS

Studies on the interaction of dry flue gas with anthracite were conducted first in order to obtain a reasonably simple picture. Stack gases, however, are never dry. A typical flue gas contains about 2 to 3% moisture by volume. Thus, interactions of a simulated wet flue gas containing about 2.7% moisture were also studied. Experimental procedures, except for the humidification of the flue gas, were the same as used for the interaction studied with dry flue gas.

Interaction was first studied at 700°C. with about 200 g. of anthracite. SO_2 broke through the bed almost immediately at this temperature. The rate of decrease in CO concentration in the effluent, with progress of the reaction, was much slower than that observed for interaction with dry flue gas at the same temperature. Breakthrough profiles of SO_2 for reaction with wet and dry flue gas are compared in Figure 2. Difference in behavior of the bed towards SO_2 retention from the two streams is apparent; overall capacity of the bed for SO_2 retention from the wet stream is larger than from the dry stream. However, a reaction temperature of 700°C. is not sufficiently high to achieve complete removal of SO_2 for reasonable periods of time even from the wet stream.

A run was made at 800°C., using a starting weight of 100 g. of anthracite. No SO_2 was detected in the effluent until after the reaction proceeded for about 38 hr. H_2S and COS were produced immediately. Sulfur in the effluent gases appeared more from H_2S than from COS at any stage of the reaction, in contrast to the results with dry flue gas. A small amount of white sulfur condensed on the reactor walls. The rate of carbon loss, as a result of gasification, was about 1.8 g/hr., which is higher than for the interaction with the dry gas at the same temper-
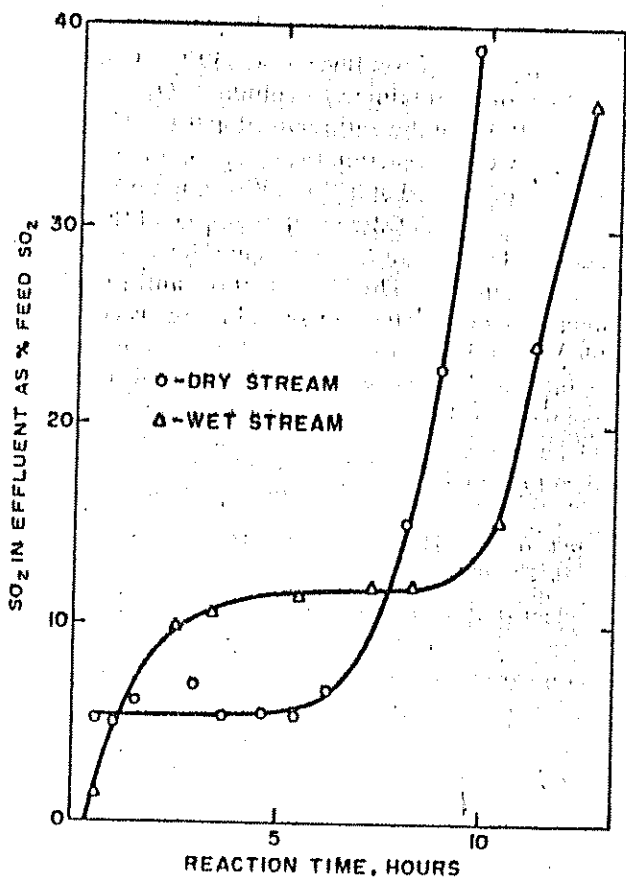
Fig. Breakthrough curves for SO₂ as a result of interaction of dry and flue gas with calcined anthracite (starting weight, 200 g.) at 700°C.

detected in the effluent. The capacity of the bed towards complete removal of SO₂ was restored for a period slightly over an hour. Breakthrough profiles for the sulfurous gases for this run are presented in Figure 3.

It is apparent from this run that the overall reactivity of the anthracite for complete removal of SO₂ from the wet stream at 800°C. is high. Bed heights of the anthracite were varied in subsequent runs in order to estimate the minimum residence time necessary for the complete removal of SO₂ at this temperature. Runs were made with three starting weights of anthracite. Figure 4 shows that the features of the breakthrough profile of SO₂ from the bed containing 35 g. of anthracite resembles those when interaction of dry flue gas with 100 g. of anthracite at 800°C. was studied (compare Figure 1). This again emphasizes that the capacity of the bed towards complete removal of SO₂ increases as reaction (or activation) of the anthracite proceeds up to some point.

ature. The development of surface areas at comparable burn-offs was also higher. The N_2 area reached a maximum of about 845 sq. m./g. (mineral matter containing basis) at a cumulative weight loss of about 77%. Total sulfur remaining in the bed reached a maximum at about 50% weight loss; however, the fraction of sulfur on the anthracite continued to increase up to about 86% anthracite weight loss. These results are summarized in Table 2.

A 2-g. sample of calcined anthracite was introduced into the bed at a time when 10% of the feed SO₂ was
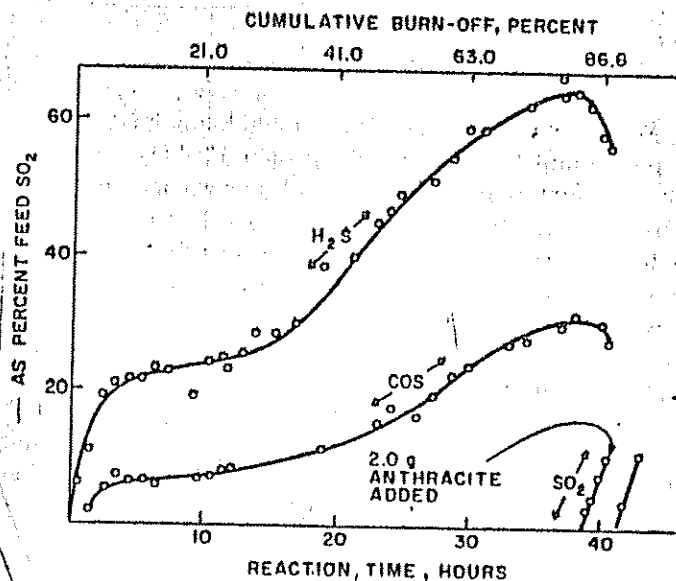

Fig. 3. Breakthrough curves for sulfur-containing gases as a result of interaction of wet flue gas with calcined anthracite (starting weight, 100 g.) at 800°C.
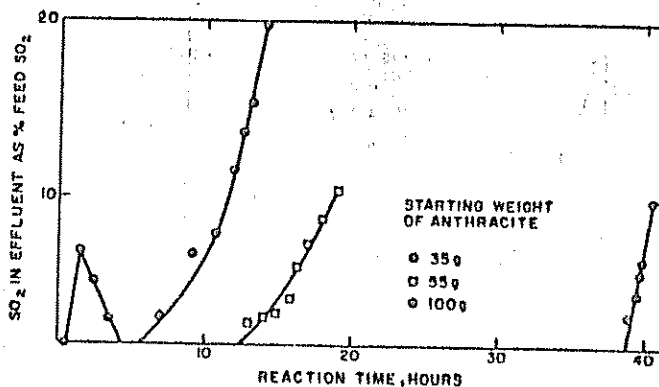

Fig. 4. Breakthrough curves for SO₂ as a result of interaction of wet flue gas with varying starting weights of calcined anthracite at 800°C.

TABLE 2. INTERACTION OF ANTHRACITE WITH WET FLUE GAS AT 800°C.

Reaction time, hr.	Cumulative weight loss, %	Surface area, sq. m./g. (m.m.c.b.) N₂	CO₂	Cumulative sulfur, % (m.m.c.b.)	Total sulfur in the bed, g.
6	12.0	121	495	2.3	2.02
12	24.6	260	567	3.5	3.66
18	37.0	368	537	5.5	3.57
24	49.8	480	525	7.3	3.94
30	63.0	660	492	8.7	3.74
	77.0	846	473	9.6	3.07
40	86.6	820	460	10.0	2.20
42	88.0	664	—	8.8	—

Unfortunately, the interaction of flue gas with anthracite at these temperatures produces CO. Figure 5 presents results for the change in CO concentration in the effluent for the reaction with wet flue gas at 800°C. There is a sharp decrease in CO concentration in the early stages of reaction and then further decrease with reaction time is slow. Reasons for the sharp drop in CO concentration is not clear. It could be due to the buildup of sulfur on some of the active carbon sites, affecting the primary CO/CO_2 ratio produced from the $C-O_2$ reaction. As expected, there is also a decrease in CO concentration with decrease in bed weight (or bed height). That is, the $C-CO_2$ and $C-H_2O$ reactions produce CO, and more of these gases will react as the height of the bed is increased.

Investigation at 750°C. with 100 g. of anthracite indicated that a complete removal of SO_2 was effective only for 1.5 hr. Buildup of SO_2 for longer times of reaction was fairly rapid. Further investigation at 750°C. was, therefore, not pursued.

INTERACTION WITH OXYGEN-ENRICHED WET FLUE GAS AT 530° C

Walker et al. (1968) and Walker and Sappok (1969) report complete removal of SO_2 from a $He-SO_2$ or a wet flue gas mixture for long periods of time when either mixture interacts with coconut shell charcoal at about 600°C. The charcoal is reported to have a BET area of about 1100 sq. m./g. It was noted earlier, when discussing the results of interaction of anthracite with dry flue gas at 800°C., that SO_2 was not completely removed at the start of the run if the initial weight of anthracite was 100 g. or less. However, it was found (7) that if the anthracite was activated with CO_2 to 12% weight loss, 40 g. of the activated material were sufficient for complete removal of SO_2 from the dry stream at 800°C.

If the development of substantial surface area during the reaction is a criterion for increased reactivity of anthracite, then a suitable and simultaneous activation at a lower temperature should effect a substantial removal of SO_2. Anthracites can be substantially activated by
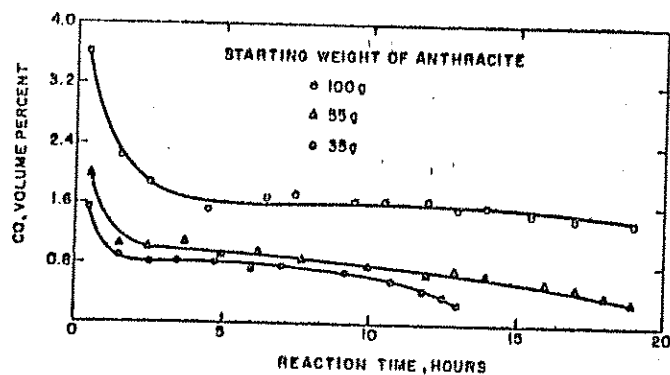

Fig. 5. Change in CO concentration in effluent with time as a result of interaction of wet flue gas with varying starting weights of calcined anthracite at 800°C.

air (1) at about 500°C. Interaction was therefore studied with oxygen-enriched wet flue gas at 530°C. The enriched mixture containing 13 volume % O_2 was contacted with 100 g. of the anthracite at 480°C. The exothermicity of the reaction raised and maintained the temperature of the bed at 530°C. Virtually no SO_2 was removed from the inlet stream at any stage of the interaction. The bed underwent a cumulative weight loss of about 27% in 5 hr. The N_2 area of the anthracite at this weight loss was 260 sq. m./g. This area is comparable to that developed by the wet flue gas at 800°C. at approximately the same weight loss. Thus, even though the area was developed through reaction of the anthracite with O_2, a temperature of 530°C. is too low to realize a significant reactivity.

RESIDENCE TIME OF FLUE GAS IN BED FOR COMPLETE SO_2 REMOVAL

It is clear that the minimum residence time required for complete SO_2 removal from the flue gas is a function of two main variables: the specific surface area of the anthracite and the specific reactivity of SO_2 with the anthracite surface. Obviously, the greater the specific area and the specific reactivity, the smaller the residence time required. The specific reactivity is expected to increase monotonically with increasing temperature; however, the efficiency of area development upon anthracite gasification is known to go through a maximum with increasing temperature (2). Thus the minimum residence time required need not necessarily decrease monotonically with increasing reaction temperature.

We have attempted to bracket the minimum residence time required when using our calcined anthracite (60 × 100 mesh size) at 800°C. Assuming a bed voidage of 50%, the minimum residence time required is about 0.7 sec. As has been discussed, this minimum time required will be reduced as activation of the anthracite proceeds. For example, after gasification to 50% weight loss, a residence time of 0.5 sec is sufficient.

THE SULFUR-CONTAINING GASES IN THE EFFLUENT

The sulfur from the SO_2 broke through the bed as H_2S, COS, and elemental sulfur when either dry or wet flue gas interacted with anthracite at 800°C. For the interaction with the dry gas the evolution of sulfur was negligible until SO_2 breakthrough occurred. On the other hand, for the wet flue gas, sulfur broke through the bed considerably prior to SO_2. The reason for this difference is not clear, but it may be related to the increased competition between hydrogen and sulfur for active carbon sites in the case of the wet flue gas. Fewer carbon sites available for sulfur chemisorption could mean an earlier breakthrough of sulfur.

H_2S and COS are the gaseous products of the interactions, with H_2S more predominant for the wet flue gas

and COS more predominant for the dry flue gas. For
; at 800°C. with the wet flue gas, the H_2S/COS ratio
gradually decreased with increasing reaction time from
about 3.4 to 2.2. This decrease was not found by Walker
and Sappok (9) who studied the interaction of wet flue
gas with coconut shell charcoal. They report a constant
ratio throughout their runs at temperatures between 600
and 800°C. Reasons for this decreasing ratio are pre-
sented elsewhere (7).

THE DEVELOPMENT OF SURFACE AREA

The cumulative fractional weight loss of anthracite in a
given reaction time depended upon the initial weight of
the anthracite used. That is, a bed of 55 g. underwent a
larger fractional weight loss in one hour than did a bed of
100 g., since the rate of gasification of anthracite followed
closely a zero order reaction with respect to the carbon
phase. The development of area in the anthracite upon
reaction with dry and wet flue gas at 800°C. has been
summarized in Tables 1 and 2. The exact increase in sur-
face area of the anthracite with gasification is dependent
in a complicated way on such factors as the relative rates
of gasification in O_2, CO_2, and H_2O; balance between
chemical and internal diffusion control of the reaction;
and activated diffusion of the N_2 adsorbate into the pore
system at 77°K. These factors are considered in more de-
tai' ewhere (7). Suffice to say, the important point is
that there is a very significant activation of the calcined
anthracite when it is exposed to a flue gas at 800°C. This
activation obviously accounts for much of the increase in
efficiency of the anthracite to remove SO_2 from the flue
gas as its consumption proceeds over a wide burn-off
range.

EFFECT OF ANTHRACITE PARTICLE SIZE ON
EFFICIENCY OF SO_2 REMOVAL

So far we have considered results when using the 60 ×
100 mesh fraction anthracite. It is expected that the
efficiency of SO_2 removal will be enhanced by using
smaller sizes; since the efficiency of activation should be
enhanced. Anthracites of particle size 100 × 140 and
140 × 200 mesh were used. At 800°C. and for starting
weights of 55 g., the period of complete removal of SO_2
from the wet flue gas was increased from 12.5 to 19 hr. in
going from the 60 × 100 to 100 × 140 mesh size. On
further reduction in particle size to 140 × 200 mesh, the
removal period decreased to 17 hr., but this result may
not be significant since excessive carry-over of anthracite
out of the reactor was noted. As expected, reduction in
particle size enhanced anthracite activation. Following
9.5 hr of exposure of the 100 × 140 mesh sample to the
wet gas, the area had increased to 475 sq. m./g. for
the 60 × 100 mesh fraction. A 16 hr. exposure resulted
in a surface area of 610 sq. m./g. Obviously, the use of
as small a particle size of anthracite as possible is desir-

able. The loss of the smaller particles by carry-over can
be minimized by known technology.

OXIDATION OF H_2S AND COS ON
PARTIALLY REACTED ANTHRACITE

H_2S and COS produced as a result of interaction of
anthracite with flue gas cannot be discharged into the
atmosphere. Commercially available active carbons are
good catalysts for the oxidation of H_2S at about 150°C.
(3). Walker and Sappok (9) report that COS can also be
catalytically oxidized on active carbons. It was, there-
fore, thought to be worthwhile to explore the possibility
of using our partially reacted anthracite as a catalyst for
the oxidation of H_2S and COS. A temperature of 150°C.
was initially selected for the oxidation studies.

The catalyst was prepared by interacting 175 g. of
anthracite with wet flue gas to about 65% weight loss at
800°C. The BET area of the activated anthracite was
820 sq. m./g. (*mmch*) and contained about 9.8% sulfur by
weight. A 15-g. sample of the catalyst was charged into a
different reactor of 1 in I.D. and brought to 150°C. It
was visually observed that a volumetric flow rate of
effluent gases from the anthracite-wet flue gas interaction
of about 1200 to 1250 cu. cm./min. (NTP) kept the cata-
lyst bed, more or less, in a fluidized state. The residence
time of the effluent gas in the catalyst bed was about 1
sec. The effluent, after 4 hr. of anthracite-wet flue gas
interaction at 800°C., contained about 0.1% H_2S, 0.028%
COS, 19% CO_2, and 1.8% CO by volume. This effluent
was enriched with O_2 such that its concentration in the
mixture was 2% by volume. The enriched mixture then
contacted the catalyst bed. The composition of the ef-
fluent from the anthracite-wet flue gas interaction and
that following the catalyst bed were monitored with the
mass spectrometer. These effluents will be referred to as
primary and secondary effluents, respectively.

The interaction of the oxygen-enriched primary ef-
fluent with the catalyst bed was continued till the con-
centrations of H_2S and COS in the primary effluent in-
creased to about 0.13 and 0.04 volume % respectively. No
H_2S was detected in the secondary effluent during this
period. However, the COS concentration in both ef-
fluents remained the same. The flow of the oxygen-en-
riched primary effluent was switched, at this point, to a
stream richer in H_2S in order to expedite the saturation
of the catalyst bed. The rich stream, containing about
0.47% H_2S and 2% O_2 by volume in helium, also con-
tacted the catalyst bed at a flow rate of 1,200 to 1,250 cu.
cm./min. Interaction was discontinued when about 10%
of the feed H_2S was detected in the secondary effluent.
Results are presented in Figure 6 and Table 3.

The following important features emerge from the
above study. The efficiency of H_2S oxidation is not
affected by the presence of large amounts of CO and CO_2.
The reactivity of the catalyst decreases only after 34%
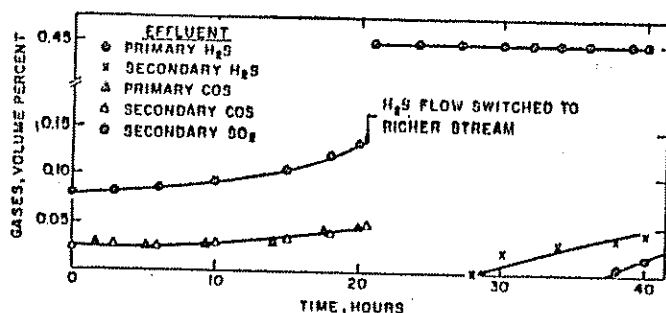
Fig. 6. Inlet and outlet concentrations of sulfur-containing gases for reaction of primary effluent and O_2 over partially activated anthracite at 150°C. After reaction for 20 hr, primary effluent stream was discontinued and new stream richer in H_2S used.

TABLE 3. N_2-AREA AND THE SULFUR CONTENT OF THE ACTIVATED ANTHRACITE AT DIFFERENT STAGES OF TREATMENTS

Sample Treatment	% S (m.m.c.b.)	Surface area, sq. m./g. (m.m.c.b.)	
		N_2	CO_2
Wet flue gas activated anthracite, wt. loss—65%	9.8	820	480
Sulfur loaded sample	36.0	93	—
Sample treated with H_2 at 800°C.	1.4	900	500
Sample extracted with carbon disulfide	10.6	680	—

sulfur by weight is accumulated on it. Water which is one of the oxidation products of H_2S does not accumulate on the catalyst at this temperature. The loss in catalyst activity after having picked up 34% sulfur is attributed to blocking of the catalyst pores by the sulfur. This effect is demonstrated by the considerable decrease in BET area of the catalyst (Table 3) with sulfur loading.

Siedlewski (5) reported the formation of SO_2 and SO_3 as a result of H_2S oxidation on carbons. We also noticed a little SO_2, less than 5% of the inlet H_2S, breaking through the catalyst bed towards the end of this study (Figure 6). No SO_3 was, however, detected at any stage of the oxidation reaction.

The sulfur picked up by the anthracite at high temperatures is not extractable by organic solvents. Failure of such recovery from carbons sulfurized at high temperatures has been reported by many workers. Desulfurization can be achieved by H_2 or CO at high temperatures. We have shown (7) that H_2 is a better desulfurizing gas than CO at 800°C. The sulfur from the loaded catalyst, however, can be recovered by solvent extraction. A 2-g. sample of the loaded catalyst was extracted with CS_2 in a Soxhlet extractor for 8 hr. Table 3 shows that the sulfur content of the extracted catalyst decreased from 36 to 10.6% by weight. The original catalyst contained about 9.8% nonextractable sulfur. Thus, about 97% of the sul-

fur derived from the oxidation of H_2S at 150°C. can be extracted.

CONCLUSION

The possible use of anthracite in controlling SO_2 emission from fossil fuel fired power plant stacks has been established in this study. The method of control is visualized as a two stage process. The flue gas containing SO_2 is contacted with anthracite at 800°C. in the first stage of the process. The effluent from this stage is mixed with air and passed, in the second stage of the process, through a bed of partially reacted anthracite obtained from the first stage. The second stage of the process is conducted at 130 to 150°C. The useful byproducts of the overall process are elemental sulfur and active carbon.

Roughly 80% of the anthracite consumed in the first stage of the process can be attributed to its reaction with O_2 in the flue gas. For a flue gas containing 3.5% O_2 by volume coming from a 1,000 MW coal fired power plant, the anthracite required per day would be about 1,600 tons. This is roughly 20% of the total fuel requirement. Estimates show that the first part of the process can be made autogenous if the level of oxygen in the stack gas is raised to about 5% by volume. This will push the anthracite requirement to about 2,300 tons/day. Since the second stage of the process is carried out at 150°C., the total fuel requirement can be substantially reduced by proper utilization of heat in going from stage 1 to stage 2. Although the technical and economical feasibility of such a process has to be worked out in greater details the process as such can be applied even to existing fossil fuel fired power plants.

Unless modified, some CO and COS will leave the stack. The amount of CO in the stack will vary from 0.4 to 2.0 volume % and that of COS from 200 to 800 ppm. The amount of COS leaving the stack can probably be reduced by blowing additional steam through the anthracite bed in the first stage of the process to form H_2S preferentially to COS. It might as well be possible to oxidize these gases in the second stage of the process by impregnating the partially reacted anthracite with a suitable catalyst.

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