

# Removal of H<sub>2</sub>S On Oxidized Iron

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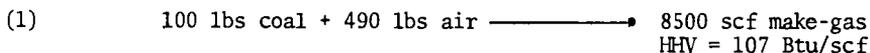
## 1.0 INTRODUCTION

This paper summarizes tests made by the Babcock and Wilcox Company to remove H<sub>2</sub>S from a fuel gas generated from the gasification of coal with air. Reported specifically are:

- (a) Results from bench top tests aimed at yielding information necessary for design purposes.
- (b) A descriptive mechanism that explains H<sub>2</sub>S removal and regeneration.
- (c) A hardware design based on these results.

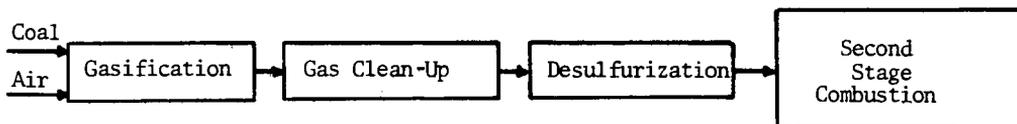
## 2.0 BACKGROUND

Air-blown gasification of coal in an entrainment or suspension type gasifier represents combustion with substoichiometric air to generate a product gas that contains chemical heat in the form of CO and H<sub>2</sub> diluted with N<sub>2</sub>. This so-called 'make-gas', after gas clean-up, is burned in a second stage combustion device to generate electric power. For example, gasification of a typical bituminous coal with 50 percent stoichiometric air is represented by



Sulfur present in the coal winds up largely as reactive H<sub>2</sub>S in the make-gas. The concentration depends on the sulfur concentration in the parent coal. Figure 2.1 illustrates the approximate H<sub>2</sub>S concentration that would be obtained in air-blown gasification of a typical bituminous coal as a function of heating value of the gas produced and the percent sulfur in the coal being gasified. The H<sub>2</sub>S levels illustrated in Figure 2.1 assume complete gasification of coal and no char product.

For electric power production the process concept is:



Justification for air-blown gasification of coal in terms of electric power production stems from the facts that:

- (a) Sulfur is concentrated in the make-gas as H<sub>2</sub>S.
- (b) H<sub>2</sub>S is more reactive than SO<sub>2</sub>.
- (c) After gas clean-up and desulfurization, the make-gas represents a high quality fuel gas that could have application as a gas turbine fuel.

### 3.0 APPROACH - BABCOCK AND WILCOX

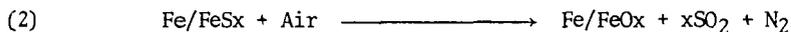
The approach taken by Babcock and Wilcox is to remove H<sub>2</sub>S from the make-gas by reaction with iron oxide at a comparatively high temperature. The objective is to minimize the amount of cooling needed between the gasifier and the second stage combustion device.

The use of iron oxide to remove H<sub>2</sub>S is not a new or unique approach. Historically hydrated iron oxide has been used for decades in oxide boxes to remove H<sub>2</sub>S from coke oven gas. At the present time, work is being done by the Bureau of Mines on a concept that removes H<sub>2</sub>S with a sintered material made from iron oxide and fly ash. Our concept is different in as much that we start out with carbon steel and generate, on the surface of the carbon steel, an FeOx scale that is used as the desulfurization agent. In terms of the mechanism of sulfur removal, it is likely that both the Bureau of Mines' and our concepts are alike.

Briefly, the concept removes H<sub>2</sub>S by:



At some point in time all of the available iron oxide scale is converted to the sulfide scale, At that point the system is regenerated with air, as follows:



The overall process accomplishes two things:

- (1) It concentrates sulfur at 0.4% volume percent in the make-gas to 10-13 volume percent SO<sub>2</sub> in the regenerant gas.
- (2) It provides SO<sub>2</sub> in the rich regenerant gas that is either (a) oxidized and recovered as H<sub>2</sub>SO<sub>4</sub> or (b) reduced to elemental sulfur.

### 4.0 OBJECTIVES

In our earlier work reported previously, a one-foot diameter gasifier was coupled to an iron grid desulfurization system. The desulfurization system was operated at temperatures in excess of 1200F. Because material problems exist at these temperatures, our experiments emphasized desulfurization at temperatures from 1200 down to 675F.

A second objective was aimed at understanding, in a descriptive sense, the reactions that occur during desulfurization and regeneration on the iron surface.

Our final objective was to design a sulfur removal system that could be coupled to a large scale gasifier.

### 5.0 EQUIPMENT AND PROCEDURE

Figure 5.1 shows a sketch of the test system. The reaction vessel was a 1-inch ID aluminum tube filled on the bottom side of the bed with inert mullite chips. The chips served to support the test bed and to preheat the make-gas to the desired temperature.

The modified Reich idiometric technique was used to measure H<sub>2</sub>S. This technique does not differentiate between H<sub>2</sub>S or SO<sub>2</sub>; total sulfur is measured. The SO<sub>2</sub> produced in the air regeneration was measured by an ultraviolet detector developed by the Babcock and Wilcox Company.

The synthetic make-gas composition was:

<u>Constituent</u>	<u>Percent (Volume)</u>	
CH <sub>4</sub>	1.0	
CO	12.0	
H <sub>2</sub>	8.0	HHV = 74 BTU
CO <sub>2</sub>	8.0	SCF
H <sub>2</sub> O	6.0	
H <sub>2</sub> S	1.0	
N <sub>2</sub>	Bal.	

Each test was started by heating the reactor to the desired temperature with a nitrogen purge. On attaining test temperature, make-gas was started through the unit; this defined zero time. The H<sub>2</sub>S concentration of the desulfurized gas was continuously monitored and the absorption bed was considered saturated when the desulfurized make gas reached 0.10 percent H<sub>2</sub>S. At that point the bed was regenerated with air at the same conditions of temperature and flow rate as the sulfur absorption.

The sulfur absorbent was designated as low hardness, perma-abrasive, plain carbon-steel shot with the following analysis:

Total carbon	2.5	-	2.8 wt. %	Phosphorous	0.02 - 0.04 wt. %
Graphite carbon	0.5	-	1.25 wt. %	Hardness	32 - 40 (Rockwell C)
Silicon	1.0	-	1.4 wt. %		

## 6.0 RESULTS

### 6.1 Desulfurization Results

Figure 6.1 is a plot of the sulfur concentration of the desulfurized make-gas versus time or volume of make-gas passed through the bed. The shape of the curve is typical of all results obtained at temperatures less than 1000F down to the minimum temperature considered, or 675F. In these tests, initially, a sharp sulfur concentration spike occurred. After the sulfur concentration spike the sulfur level dropped to a very low value, then increased with time or volume of make-gas treated. The increasing sulfur concentration was due to the depletion of available iron oxide scale. Arbitrarily, a test was terminated after the sulfur level increased to 0.1 percent, or when the make-gas at that point was 90 percent desulfurized.

The average sulfur concentration of the make-gas was determined by integrating the area under the curve to the 0.1 percent end point. For the case illustrated in Figure 6.1 the average sulfur concentration was 0.05 percent. Although the average sulfur concentration is relatively low (0.05 percent), because of the concentration spike, the instantaneous level at the top of the spike is higher 0.14 percent. What this means is that in the design of a workable desulfurization device, a number of beds staggered with respect to the regeneration cycle should give a product gas that approaches the average sulfur value, or for 675F operation a gas of 0.05 percent sulfur.

In general the magnitude of the concentration spike decreased as the temperature was raised to 1000F. Operation at 1000F and higher eliminated the concentration spike. Figure 6.2 illustrates the sulfur level of make-gas as a function of operating temperature. These results represent:

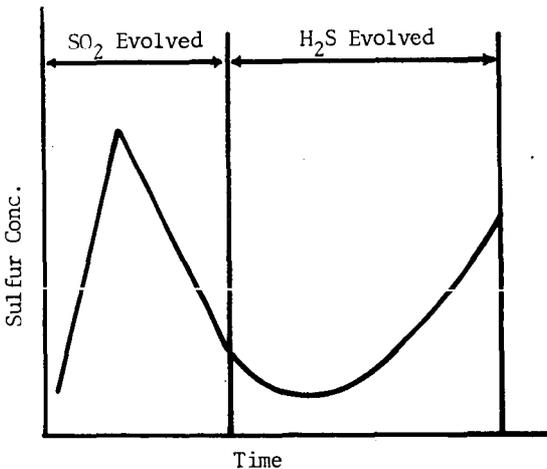
- (a) Operation at space velocities from 2000 to 2500 volumes of gas per volume of bed per hour.
- (b) An end point of 0.1 percent sulfur.

At the same conditions, Figure 6.3 illustrates the sulfur pick-up on a well conditioned surface, namely, the volume of H<sub>2</sub>S removed or reacted with the iron oxide scale at 60F and 14.7 psig, based on 100Ft<sup>2</sup> of iron surface initially charged to the desulfurization unit. The results represented in Figure 6.3 were also determined using an end point of 0.1 percent sulfur for the treated make-gas and space velocities of 2000-2500 vol. gas per vol. bed per hour.

### 6.2 Descriptive Mechanism

Because of the presence of the unwanted sulfur concentration spike observed during sulfur absorption at temperatures less than 1000F, a series of short tests were made with the objective of defining, in a descriptive sense, the important reactions that govern sulfur removal and regeneration. Some of the pertinent results were:

1. The spike results from SO<sub>2</sub> evolution and not H<sub>2</sub>S, even though only H<sub>2</sub>S is fed to the bed. This is illustrated below.



- 2 The regeneration temperature determines whether the spike will occur. For example, if regeneration is conducted at a temperature greater than 1000F and the bed is cooled to say 675F for desulfurization, no spike results.
- 3 Pretreating a regeneration bed (low temp) with CO or H<sub>2</sub> eliminates the spike. If, however, the reduced bed is subsequently purged with air SO<sub>2</sub> is evolved.
- 4 Heating and cycling a fresh surface between make-gas and air, in short tests, does not develop a thick scale necessary for desulfurization.
- 5 For short tests the surface is developed by cycling at temperatures around 1450F.
- 6 A high concentration of steam in the make-gas decreases the efficiency of sulfur removal.

The following reactions explain the observed results. In addition thermodynamic calculations suggest these reactions are feasible at temperatures of our system.

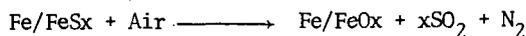
1. Heating in air at temperatures to 1400F develops a thin surface layer of FeOx. Surface not activated.



2. Activation 1450F



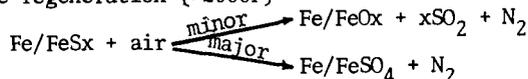
3. High temperature regeneration (>1000F)



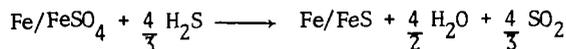
4. Equilibrium sulfur removal



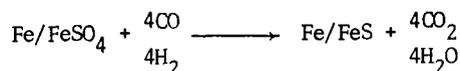
5. Low temperature regeneration (< 1000F)



6. Sulfur concentration spike



7. Prereduction (800F)



## 7.0 HARDWARE CONCEPT

The hardware concept for sulfur removal and regeneration should:

- (a) Have a large number of compartments at various stages of regeneration to give an average  $H_2S$  concentration relatively independent of the regeneration cycle.
- (b) Give a maximum concentration of  $SO_2$  in the regenerant gas.

The hardware that has been designed uses a number of compartments for sulfur removal and the so-called counter-current principle for air regeneration. The desulfurizer uses a modified regenerative type air heater and is referred to as the "regenerative desulfurizer." Figure 7.1 illustrates this concept. The cylindrical unit is segmented into 16 compartments. Each compartment is filled with carbon-steel plates oriented longitudinally with the gas flow. Within each compartment the longitudinally oriented carbon-steel plates will contain about 100 square feet of surface of the carbon-steel plates. The vessel itself will be constructed from high alloy steel.

### 7.1 Sulfur Removal

Sour  $H_2S$  containing make-gas from the gasifier passes downward through 13 of the 16 compartments where desulfurization occurs on the surface of the carbon-steel plates that fill each compartment. The sweet make-gas issues from the base of the unit and is routed to a second stage combustion device.

### 7.2 Regeneration

The sulfided iron surface is converted back to the oxide in 3 of the 16 compartments shaded in the sketch. The regeneration air passes in and upward in the first compartment to a cross-over, then downward for a second pass, and upward for a third and final pass. At two revolutions per hour each of the 16 compartments is regenerated twice per hour.

Air at 21 percent  $O_2$  enters the first regeneration compartment where it contacts a partially regenerated surface accomplished in the second and third pass down stream. At the end of the first pass the  $O_2$  concentration is well below 21 percent. During the second pass, the  $O_2$  concentration is further reduced while  $SO_2$  increases. Purging the third (most  $FeS$  fouled) compartment with a gas containing a minimum concentration of  $O_2$  and a maximum concentration of  $SO_2$  insures a maximum  $SO_2$  concentration of the final regenerant gas. The regenerant gas should contain from 10 to 13 percent  $SO_2$  and up to 4 percent  $O_2$  and nitrogen.

In practice  $SO_2$  in the rich regenerant gas can be:

- (a) oxidized and recovered as sulfuric acid
- (b) reduced to elemental sulfur.

We believe the better approach is reduction and recovery as elemental sulfur. In coal gasification systems, two reductants are available, i.e., make-gas itself ( $CO + H_2$ ) or char. Currently, B&W is actively studying  $SO_2$  reduction using char that will be available from gasification of coal.

## 8.0 CONCLUSIONS

After a thick layer of iron oxide or sulfide scale is generated on the surface of plain carbon steel, the scale effectively removes more than 95 percent of the sulfur in a make-gas generated from air gasification of coal. The process works at temperatures as low as 675F; however, because of regeneration, operation at temperatures in excess of 1000F is desirable.

Conservative operation of the process should yield SO<sub>2</sub> values of 0.5 - 0.6 lbs per million Btu input, or a value well within the EPA guidelines.

The concept has been demonstrated in bench scale equipment and a hardware design has been developed. The workability of the concept on a large scale, however, has yet to be demonstrated.

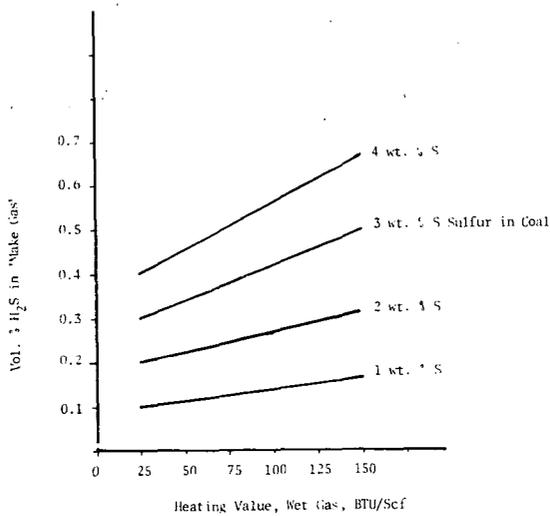


FIGURE 2.1 H<sub>2</sub>S CONC. VS. HEATING VALUE COMPLETE GASIFICATION

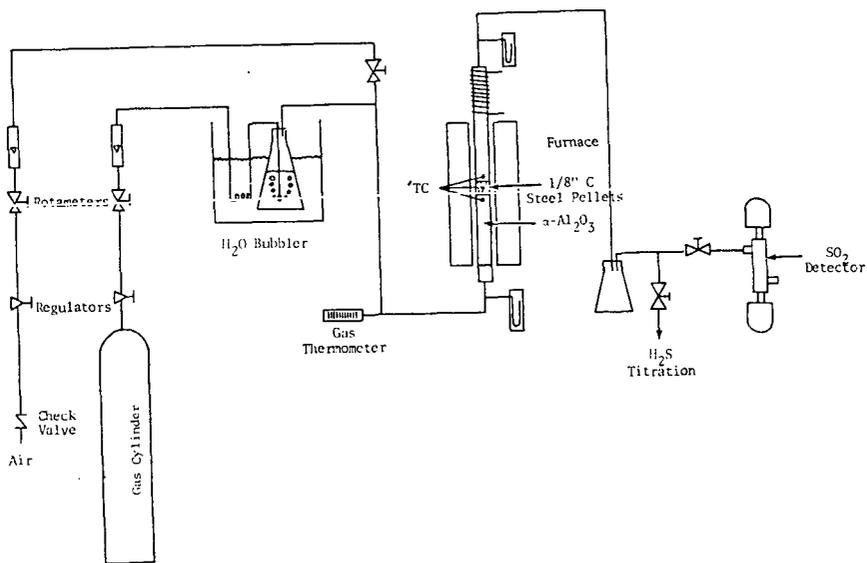


FIGURE 5.1 TEST EQUIPMENT

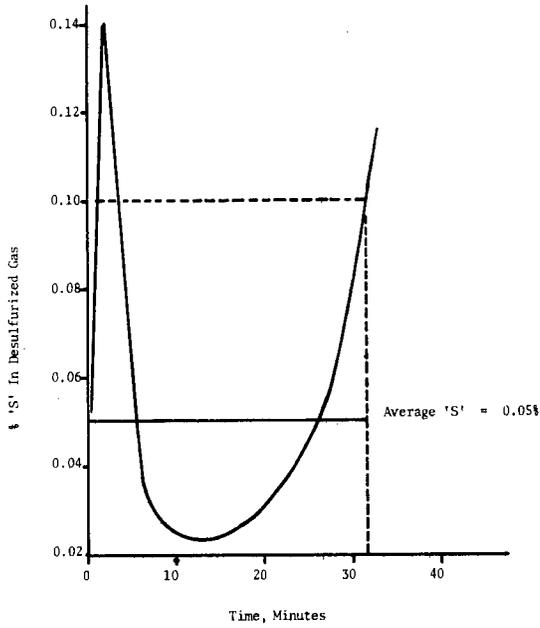
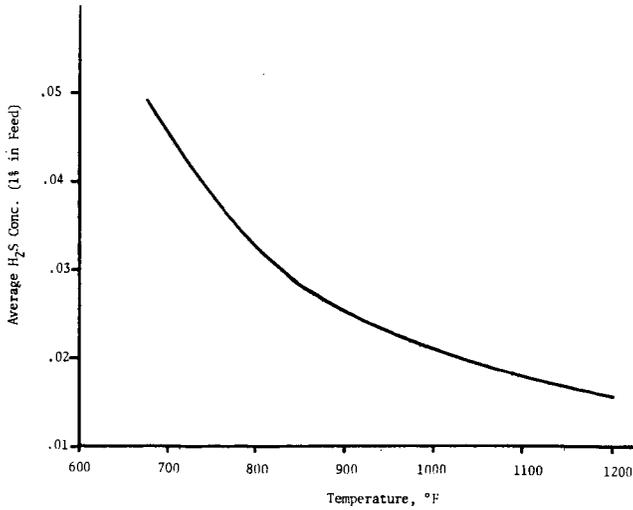


FIGURE 6.1 SULFUR CONC. DESULFURIZED GAS



Space Vel. = 2000-2500 v/v-Hr.  
 End Point = 0.10 percent sulfur

FIGURE 6.2 SULFUR CONC. VS. TEMPERATURE

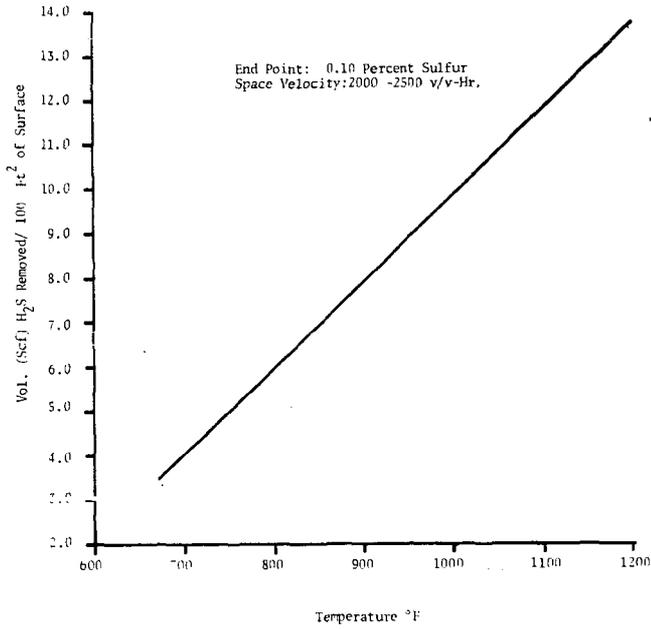


FIGURE 6.3 SULFUR PICK-UP

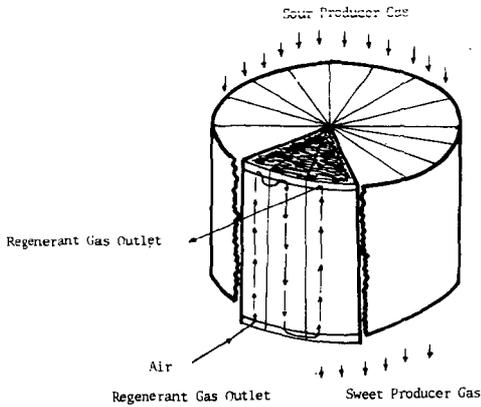


FIGURE 7.1 REGENERATIVE DESULFURIZER