

HOT GAS CLEANUP PROCESS FOR REMOVING H₂S
FROM LOW-BTU GASES USING IRON OXIDE ABSORBENTS

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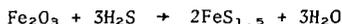
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INTRODUCTION

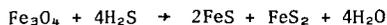
Research is continuing at the Morgantown (West Virginia) Energy Research Center, Energy Research and Development Administration, to develop a hot gas cleanup process using solid regenerable sorbents to remove hydrogen sulfide from hot (1000^o-1500^oF) low-Btu fuel gas made from coal. A suitable process is needed whereby sulfur can be removed from low-Btu gases so that high sulfur coals can be utilized to provide clean energy and meet the environmental standards regulating the amount of sulfur released to the atmosphere. Removal of hydrogen sulfide without cooling the gas would conserve the heat lost in conventional gas purification methods, thus increasing the thermal efficiency by 15 percent.

The use of iron oxide to remove H₂S from industrial gases has been practiced for many years. Indeed, research by the Appleby-Frodingham Steel Company during the late fifties led to the construction and operation of a plant desulfurizing about 2½ million cubic feet of coke oven gas per day followed by construction of a 32 million cubic feet per day plant before operational problems and economic costs shut down the operations. The crude coke oven gas was passed through a fluidized-bed of sintered iron oxide powder (-16 mesh + 100 mesh) where reaction with H₂S and Fe₂O₃ took place at temperatures approaching 400^oC. This process, as reported by Reeves et al (1), removed 95-98 percent of the H₂S from the coke oven gas. The principal problems encountered, as far as the use of iron oxide was concerned, were massive attrition and replacement of the fines, plugging and erosion of pipes transporting the iron oxide. These difficulties encountered by the Appleby-Frodingham process have been overcome by placing the iron oxide particles on a supporting matrix composed of fly ash, or silica, by thoroughly mixing the two components, extruding the paste-like mixture into 1/4-inch diameter by 3/4-inch long cylinders and sintering at 1800^oF.

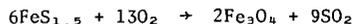
The chemistry involved in absorption and regeneration using iron oxide shows that iron sulfides are produced when H₂S reacts with Fe₂O₃ with the empirical composition approaching FeS_{1.5}



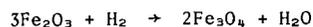
However, according to Imperial Chemical Industries Catalyst Handbook (2), fresh iron oxide is converted to Fe₃O₄ in the presence of hydrogen and at temperatures above 650^oF. Therefore, the reaction would be written as



During regeneration, air oxidizes the FeS and FeS₂ to Fe₃O₄ and SO₂:



However, in the presence of excess oxygen, the Fe₃O₄ is converted to Fe₂O₃. If this condition exists, then upon the start of another absorption cycle, some hydrogen is consumed from the raw producer gas while conversion to Fe₃O₄ is taking place



A review of the literature reveals that coke oven gases have been desulfurized in both fixed and fluid beds of iron oxide at temperatures up to 752°F (1). Abel et al (3) and Shultz (4) reported the results of laboratory-scale investigations of solid sorbents to remove hydrogen sulfide from hot (1000°-1500°F), clean, simulated low-Btu fuel gas. Clay and Lynn (5) reported the use of iron oxide supported on alumina to remove NO_x and SO_x from powerplant stack gases at temperatures approaching 1000°F, using an injected stream of synthesis gas (CO + H₂) to reduce the SO₂ to H₂S and NO to N₂ before passing the flue gases over the catalyst. Oldaker et al (6,7,8,9) reported the results of tests involving fly ash-iron oxide and silica-iron oxide sorbents to remove H₂S from hot (1000°-1500°F) low-Btu gases.

EXPERIMENTAL WORK

The Research conducted thus far has been two-pronged; lab scale investigations for the development of an efficient sorbent for removing H₂S from hot low-Btu gases made from coal, and process development to identify the major parameters required for scale-up design criteria utilizing data from bench scale operations up to 9000 scfh gas flows.

The absorbent research has been directed toward the development of sorbents with the following criteria:

- a. Efficient removal of H₂S at temperatures above 1000°F;
- b. Physical strength required to withstand handling;
- c. Economic feasibility; and
- d. Process feasibility--regenerability, form and composition and acceptable life.

Attrition of the iron oxide sorbent resulting in unacceptable carry over and absorbent replacement, plugging or fouling of system components, led to development of a more suitable matrix support for the iron oxide. Fly ash and silica satisfied this requirement and permitted adequate gas contact for removal of H₂S, while withstanding process temperatures.

The next step toward the development of the sorbent hinged on the necessary preparation techniques required to strengthen these sorbents in the categories of H₂S absorption capacity and efficiency, physical strength, and economic costs.

Several tests were carried out to determine the effects of additives on the physical strength and absorption capacities. It was found that one percent bentonite added to the fly ash-iron oxide mixture produced a superior sorbent having good physical strength and absorption capacity. This was not true when using silica-iron oxide mixtures as both the physical strength and absorption capacity were reduced. On the other hand, using sodium silicate as the additive produced an excellent sorbent when using either fly ash or silica as the support material. Data are shown in table 1.

Another major difference between the support materials is the amount of iron oxide that can be admixed. It was found that 25 percent iron oxide added to the fly ash was the maximum amount that could be tolerated without reducing both the physical strength and the absorption capacity, whereas 45 percent iron oxide could be added to the silica without any detrimental effects on the physical strength or absorption capacity of the sintered sorbent. This increased amount of iron oxide accounts for the much higher H₂S absorption capacities shown in table 1 for the silica sorbents.

The temperature limitations imposed on each type of sorbent is significant because of the highly exothermic reaction taking place during the regeneration of the sorbents. Using fly ash as the support material imposes a temperature limitation

of 1500°F for the sorbent to have a good level of absorption capacity and life expectancy. This is because fly ash acts as a glass-fusing at around 1500°F. The fusing characteristic would cause loss of pores thus cutting down on surface area available for good gas contact and eventually rendering the sorbent useless for removing H₂S from hot producer gas.

Silica, on the other hand, has a much higher fusion temperature permitting higher temperature operation without affecting the ability of the sorbent to perform. The recommended operating temperature indicated by limited data is believed to be in the range of 1700°-1800°F. This range is well above most if not all coal gasification processes being developed at this time. Provided that the present work being carried out on other than low-Btu gases does not contain constituents detrimental to the sorbent material or reactions, the two sorbents could be used on most coal gasification processes efficiently and economically. Particulate matter carried over from the gasification process may cause detrimental effects especially if the fixed bed concept is utilized, although the lab scale investigations indicate the carbonaceous material is burned off during the regeneration cycle. There is much research work going on at the present time on hot particulate removal from coal-derived gases, which is essential to projected combined cycle and turbine applications.

Figure 1 is a flow diagram of the laboratory apparatus used to test and evaluate the various sorbents. Generally, the gases were metered into the system to simulate the actual composition of producer gas. Coal was fed into the system at rates up to 500 grams/hr through the carbonizer to provide the actual tars and particulates found in producer gas. After being preheated, the producer gas flows into the absorber containing approximately 700 grams of prepared sorbents. The H₂S is monitored at the input and output of the absorber by means of the Tutwiler technique (10) to determine the absorption capacity and efficiency of the particular sorbent being tested. The temperature of the absorbent bed is maintained at operating temperature by means of electric heaters, usually at 1100°F. The gas output is also monitored by analyzers for CO and H₂.

Life expectancy is another major parameter used to evaluate the worth of a high temperature solid absorbent for H₂S removal. Therefore, an iron oxide-fly ash absorbent was tested on the lab scale unit using simulated producer gas containing tars and particulates to determine some degree of life expectancy. Thirty complete absorption-regeneration cycles were completed on the same absorbent. It was found that the recycling of the sorbent did not affect the ability of the sorbent to remove H₂S from the hot producer gas maintaining an average absorption capacity of 10 wt.-% during the tests. Upon completion of these tests, the sorbents were in excellent condition without any signs of physical deterioration or caking between the individual sorbents. Figure 2 indicates the sorption capacities achieved during the thirty runs. These tests were conducted at 1100°F. Regeneration was accomplished by using 12 scfh air flow rate through the absorber for approximately two hours. During regeneration, the bed temperature increased to 1700°F momentarily in the actual wave front or zone of reaction. Although this temperature reached 1700°F momentarily, without apparent harm, it is believed that 1500°F would be the highest temperature fly ash-iron oxide sorbents should be exposed for optimum life expectancy. Further life tests are now being conducted where an optimum sorbent is recycled until the H₂S absorption capacity decreases significantly so that better defined limits can be predicted. Table 2 shows the typical data from six of the thirty sorption capacity tests using the fly ash-iron oxide sorbent. Note that the H₂S absorption efficiency is given using 400 grains/100 scf as the break through limit. These percentages would be much higher using 150 grains/100 scf as the stopping point for absorption.

Further testing, using much higher gas flows and increased amounts of sorbent material was believed necessary to generate data that are required for scale-up criteria. A 9000 scfh atmospheric producer and hot gas cleanup facility has been designed, built and installed at MERC for this purpose.

The general overall range of operating conditions include:

| | |
|------------------|---|
| Space velocities | 500-3500 vol/vol/hr |
| Coal feed rates | 60-200 lb/hr |
| Pressures | 3-15 psig |
| Temperatures | 600 ^o -1500 ^o F |
| Make gas flows | 5000-9000 scfh |
| Gas analyses | CO-H ₂ -CO ₂ -H ₂ S-N ₂ -CH ₄ -COS-CS ₂ -C ₂ H ₆ -O ₂ -SO ₂ |

The overall flowsheet is shown in figure 3. The detailed instrumentation has been removed to permit better understanding of the process. Also, it is well to remember that particular designs or instrumentation shown here are only tools needed to procure design criteria and not necessarily the approach that would be used for commercial application.

Air and steam are fed into the 16-inch diameter producer through the revolving, eccentric grate into the combustion zone to gasify the coal. The depth of the coal bed can be varied depending on operating conditions required. Normally, the bed depth averages about 32-36 inches. An agitator-stirrer mechanism providing continuous vertical and circular movement permits stirring in various levels of the coal to minimize agglomeration or break up voids while running on bituminous coal. The coal is choke-fed downward through the coal feed tube, the length of which establishes the bed height. From shakedown operations, it has been necessary to revise the coal feed system. The extremely slow movement of the coal through the coal feed tube permitted the coal particles to become somewhat plastic or sticky and adhere to tube walls eventually blocking coal feed to the producer. This system is now being revised by feeding the coal through a pocket feeder and metering screw. The bed level will be established by the speed of the screw and monitored by nuclear gauges similar to those on the MERC 42-inch diameter pilot scale producer (11).

The make gas exits from the producer into a standard-design refractory cyclone to remove the larger dust particles--above 10 micron--and is then piped into either of the two absorbers, which are loaded with fly ash or silica supported iron oxide absorbents. For testing at 2500 space velocity using 7500 scfh gas flow, around 225 pounds of sorbent would be used. The absorbent bed temperature is held above 900^oF by maintaining the sensible heat of the exit gas through insulation, refractory, and the circulation of hot gases from a gas-fired POC heater. During regeneration, which is accomplished with air, the heat from the highly exothermic reaction is controlled by dilution gases and/or the natural heat-sink effect of the refractory lined vessel.

The off gases from the absorber are then piped through a back pressure regulator and a metering orifice to the flare stack.

Three sampling ports are located in the flow system for gas analyses. One gas sampling point is located immediately downstream from the cyclone, where the raw producer gas is continuously monitored by a gas chromatograph. Another sampling point is located downstream from the absorbers in the piping system handling the make gas. This point continuously monitors the H₂S concentration remaining in the make gas after passing through the iron oxide sorbents. The last gas sampling port is located in the exit gas piping carrying the SO₂ enriched stream to the vent stack. This port continuously monitors the SO₂ concentration in the off gas during regeneration cycle.

Figure 4 is a cross sectional view showing the interior arrangement of the producer. The most important parts are the eccentric, cone crusher-type grate, the 16-inch water cooled combustion zone, the agitator-stirrer mechanism, and the coal feed tube.

Figure 5 is a cross sectional view of the refractory lined absorber which is 12-inches inside diameter. The absorber gas flow is down flow during absorption and up flow for regeneration. This flow pattern is presently being reversed in an attempt to prevent build-up of particulates on top of the sorbent bed.

Preheated gas from a gas fired POC heater enters through the bottom of the absorber and passes through the sorbent bed to provide the heat-up necessary before the start of an absorption cycle. As shown, thermocouple ports are located 18 inches apart in order to measure temperatures and thus identify the wave front or zone reaction as it passes through the sorbent bed.

Preliminary data generated thus far on the bench scale unit fairly well parallels data taken on the lab scale apparatus. For instance, the data generated while using the lower temperature extreme of 616°F while using anthracite coal provides almost the same absorption capacity--6.43 wt.-pct., although the space velocity was increased from approximately 500 on the lab unit to 2500 vol/vol/hr on the bench scale facility. Also, a slightly higher bed temperature of 672°F increased the absorption capacity by 18 percent to 7.62 wt.-pct. This shows that increased temperatures give better absorption results. Previous tests on laboratory apparatus showed the highest absorption results were obtained around 1500°F, the limit of the fly ash-iron oxide sorbents. Table 3 shows typical data generated at these lower temperatures on the bench scale facility. The data indicate also that efficiency decreases as temperature during absorption is lowered. More data generated on the bench scale facility will be made available in the immediate future after shakedown operations and equipment design modifications are completed.

CONCLUSION

The research results thus far indicate that the hot gas cleanup process is an acceptable alternative for removing H₂S from low-Btu fuel gases derived from coal. The solid absorbents performed well at temperatures between 1000°-1500°F.

Further engineering development is needed on hot particulate removal and it is being intensely investigated at this time by several firms. Several independent studies are also being made on various regenerative techniques, using recycled SO₂, for instance, to increase the SO₂ concentration in the effluent gas stream to permit more efficient processing to elemental sulfur. Engineering studies concerning the geometry of the absorber-reactor are being made with particular emphasis on heat transfer mechanisms to handle the high temperatures during regeneration. Fluid bed and moving bed concepts along with the fixed bed are being evaluated and some testing programs are already underway.

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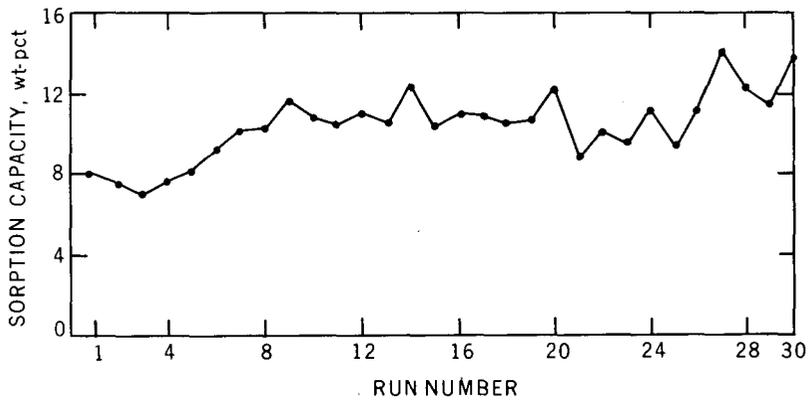


FIGURE 2. — Sorption Capacities Achieved During Thirty Absorption Regeneration Tests

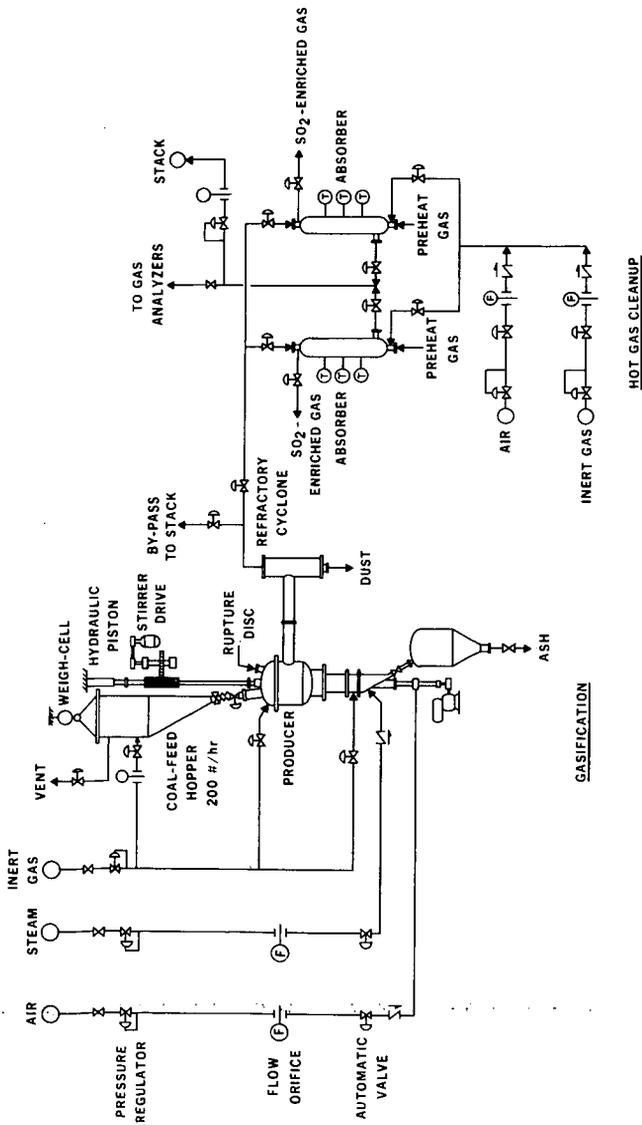


FIGURE 3. — Bench Scale Producer and Hot Gas Cleanup Facility.

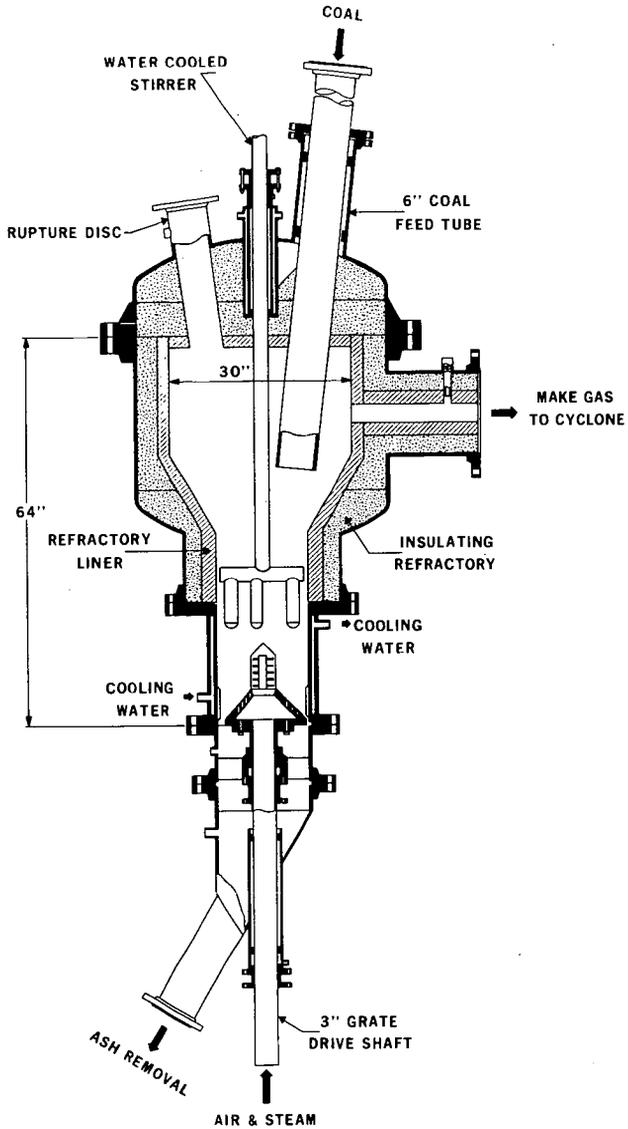


FIGURE 4. — 16-inch Gas Producer for Bench Scale Hot Gas Cleanup Facility. 88

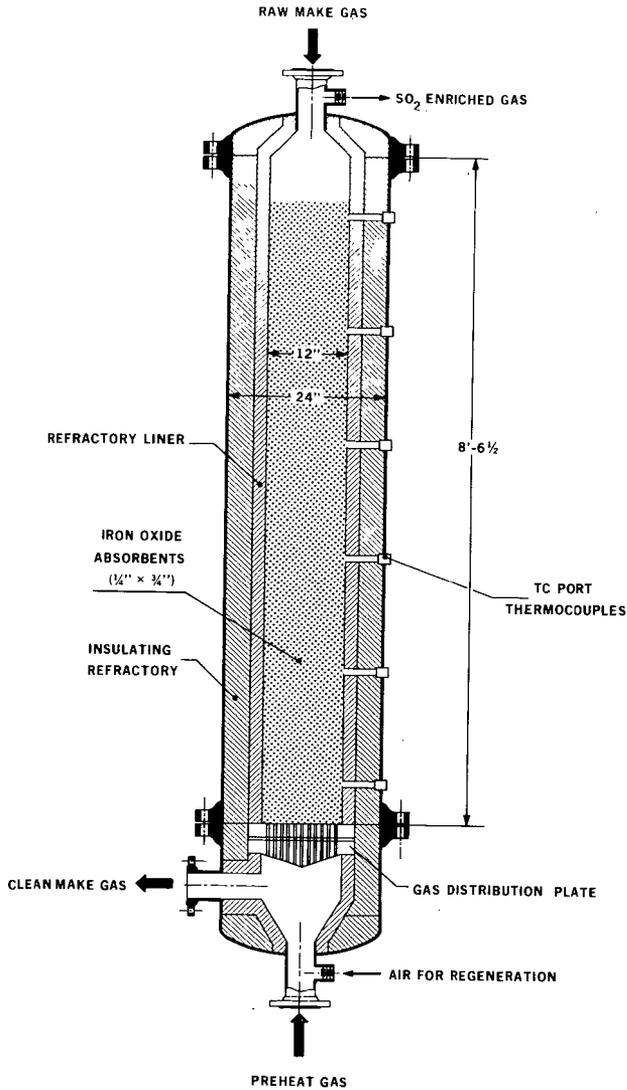


FIGURE 5. — 12-inch Absorber Vessel for Bench Scale Hot Gas Cleanup Facility.

| Sorbent Composition | Physical Strength lb/cm | Surface Area m ² /gm | H ₂ S Sorption Capacity wt.-% |
|--|----------------------------|------------------------------------|---|
| 55% silica + 45% Fe ₂ O ₃ | 75 | 2.5 | 16.1 |
| 55% silica + 45% Fe ₂ O ₃ + 1% bentonite | 31 | 4.3 | 14.5 |
| 55% silica + 45% Fe ₂ O ₃ + 6 ml sodium silicate/lb | 68 | 2.1 | 22.8 |
| 75% fly ash + 25% Fe ₂ O ₃ | 16 | 0.9 | 11.5 |
| 75% fly ash + 25% Fe ₂ O ₃ + 1% bentonite | 59 | 1.5 | 10.5 |
| 75% fly ash + 25% Fe ₂ O ₃ + 10 ml sodium silicate/lb | 69 | --- | 10.4 |

TABLE 1 — Data Indicating Effect of Additives On Sorption Capacity and Physical Strength

| Total gas flow, std. cu. ft. | Gas flow rate, std. cu.ft./hr. | Run duration, hr. | Space velocity, vol/vol/hr | H ₂ S absorption | | | Total quantities through bed | |
|---------------------------------|-----------------------------------|----------------------|-------------------------------|-----------------------------|-------|-----------------|------------------------------|-----------|
| | | | | Total grains | wt.-% | Efficiency pct. | Far. gas | Dust, gas |
| 89.62 | 14.27 | 6.28 | 501 | 1118 | 10.35 | 92.5 | 31.5 | .2 |
| 91.83 | 15.97 | 5.75 | 563 | 1193 | 11.04 | 95.0 | 30.8 | .6 |
| 94.14 | 16.37 | 5.75 | 570 | 1180 | 10.92 | 93.5 | 28.2 | .4 |
| 90.07 | 16.38 | 5.50 | 587 | 1135 | 10.51 | 93.1 | 33.5 | .5 |
| 91.40 | 15.23 | 6.00 | 529 | 1159 | 10.73 | 94.2 | 32.3 | .5 |
| 109.38 | 15.09 | 7.25 | 549 | 1332 | 12.33 | 92.2 | 33.4 | .5 |

TABLE 2 — Typical Data From Six of Thirty Sorption Capacity Tests

| Average Bed Temp. | 616°F | 672°F |
|---|---------|---------|
| Time to breakthrough, hrs | 4.66 | 5.60 |
| Producer gas flow rate, scfh | 7500.00 | 7322.94 |
| Space velocity, vol/vol/hr | 2500 | 2450 |
| Gas to breakthrough, scf | 34,975 | 40,992 |
| Total H ₂ S absorbed, grams | 6544.8 | 7711.2 |
| Weight percent | 6.43 | 7.60 |
| Percent of total (using 100 grains/100 scf as breakthrough) | 82.61 | 82.07 |

TABLE 3 — Sorption Data Obtained During Regeneration Study on Bench Scale Hot Gas Cleanup Facility