

LABORATORY EVALUATION OF PROPERTIES  
OF FLY ASH-IRON OXIDE ABSORBENTS FOR H<sub>2</sub>S  
REMOVAL FROM HOT LOW-BTU GAS

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INTRODUCTION

The Morgantown Energy Research Center is conducting research on solid, regenerable absorbents to remove H<sub>2</sub>S from hot (1,000°-1,500°F) low-Btu fuel gas made by gasifying coal with air and steam. The heating value of low-Btu gas ranges from 100 to 150 Btu per cubic foot, which makes it uneconomical for long distance transport but is suitable for "on-site" utilization to fire powerplant or industrial boilers. Removal of the sulfur (largely H<sub>2</sub>S) from the gas while still hot affords two benefits for the utilization of low-Btu gas as a fuel. First, the gas can be directly fired in boilers and meet environmental standards concerning sulfur emissions to the atmosphere. Second, the sensible heat of the gas is retained, thereby increasing the overall thermal efficiency of the fuel.

The use of iron oxide to remove H<sub>2</sub>S from industrial gases has been practiced for many years. Coke oven gases have been desulfurized by fixed or fluid beds of iron oxide at temperatures up to 752°F (1). Abel et al. (2) and Shultz (3) reported the results of laboratory studies in which solid absorbents were used to remove H<sub>2</sub>S from hot, simulated and actual producer gas. Clay and Lynn (4) described the use of iron oxide supported on alumina to remove NO<sub>x</sub> and SO<sub>x</sub> from powerplant stack gases at temperatures approaching 1,000°F. They injected a stream of synthesis gas (CO + H<sub>2</sub>) to reduce the SO<sub>2</sub> to H<sub>2</sub>S and NO to N<sub>2</sub> before passing the flue gases over the catalyst.

Laboratory investigations are being directed toward developing a solid, regenerable absorbent composed of iron oxide supported on a matrix of fly ash which has both the absorption capacity and physical strength believed to be required for a commercial application in removing H<sub>2</sub>S from low-Btu fuel gases at temperatures above 1,000°F.

Mechanical problems involving attrition of the iron oxide leading to unacceptable carry-over and absorbent replacement, and plugging or fouling of system components were some of the shortcomings of previous work using iron oxide to remove H<sub>2</sub>S from various type gases. By supporting the iron oxide upon a matrix of fly ash, these problems are overcome. The development of a solid, pellet-sized absorbent having adequate surface area or pore volume which effectively removes H<sub>2</sub>S eliminates the need for fluidization and/or the use of very small iron oxide particles. Another advantage is the lower capital and operational costs when using a fixed bed for absorbing, in which continuous recycling and replacement of iron oxide is not required.

The process described herein is designed to remove H<sub>2</sub>S from raw producer gas above 1,100°F by passing it through a fixed bed of fly ash-iron oxide absorbents. The H<sub>2</sub>S reacts with the Fe<sub>2</sub>O<sub>3</sub> to form FeS and FeS<sub>2</sub>. When the absorbents are fully sulfided, the FeS+FeS<sub>2</sub> is easily returned to Fe<sub>2</sub>O<sub>3</sub> by passing air through the bed for a short period.

MATERIAL, EQUIPMENT AND PROCEDURES

Fly ash from a coal-fired powerplant near Morgantown, West Virginia, was used exclusively as supporting material for the fly ash-iron oxide absorbents. This fly ash was similar to the fly ash from three other local sources. A typical analysis

of the fly ash was:  $\text{SiO}_2$ -51.7%,  $\text{Al}_2\text{O}_3$ -24.6%,  $\text{Fe}_2\text{O}_3$ -15.9%,  $\text{CaO}$ -3.06%,  $\text{K}_2\text{O}$ -2.38%,  $\text{MgO}$ -0.94%,  $\text{TiO}_2$ -0.84%,  $\text{Na}_2\text{O}$ -0.66%, and  $\text{P}_2\text{O}_5$ -0.34%. The BET surface area was 0.95  $\text{m}^2/\text{gm}$ . The fly ash was dried and screened to remove agglomerates but was not otherwise processed.

The iron oxides used were Fisher Certified or MCB Technical Grade with BET surface areas of 10 and 8.5  $\text{m}^2/\text{gm}$  respectively. (These iron oxides were used to maintain consistent data throughout the investigations. Commercial iron oxides will be used for later tests.)

Laboratory grade, high-swelling bentonite (2 grams to 24 milliliters) of 63%  $\text{SiO}_2$  and 19%  $\text{Al}_2\text{O}_3$  content, and technical grade 40-42° Baume (3.22  $\text{SiO}_2/\text{Na}_2\text{O}$ ) sodium silicate solution, were used as additives to improve physical strength.

The dry ingredients were thoroughly mixed using a split-sleeve mixer, then transferred to a small portable-type cement mixer. Water was added to the mixture to obtain correct consistency for extrusion. The extrusion apparatus produced 3/16-inch diameter by 3/4-inch long extrudates through a multiple die arrangement at the end of a 2-inch diameter by 6-inch long barrel and auger. The solid extrudates were dried, then sintered at temperatures and times required. The crush strength (force applied across the diameter) was measured on a Tinius-Olsen testing machine.

Figure 1 is a flowsheet of the equipment used to conduct absorption and regeneration experiments with the iron oxide-fly ash absorbents. An entrainment carbonizer, used in previous coal carbonization research (5) was adapted to simulate on a small scale the production of hot, raw producer gas (containing coal-related tars and particulates) or clean, hot producer gas. Various gases to make up the producer gas were supplied from bottled gases metered into a manifold and into the gas preheater. Water was metered and injected into the gas preheater to simulate the amount of steam in actual producer gas.

When tars and particulates were required in the experiment, coal was fed into the carbonizer by a screw-type feeder. The coal entered the top of the carbonizer, 4-inch diameter by 18-inches high which was electrically heated, and was charred as it fell through; char and ash were removed through a lock hopper at the bottom. The outlet gas contained tars, light oils, and particulates and the gas make up was similar to actual producer gas. Eighty percent of the total gas passed through the absorption bed; the other 20% provided a sample of the input for analysis. The absorption vessel was 2-inches inside diameter by 45-inches long. A stainless steel screen 31-inches down from the top supported the absorbent bed. The vessel was externally heated by high temperature heating tapes. Both the vessel and heating tapes were covered with insulation to prevent excessive heat losses. Five internal thermocouples were used to monitor bed temperatures.

The input gas sample system consisted of a heated dust filter, an electrostatic precipitator, a water-cooled condenser, a silica gel trap and a dry gas meter. The input gas was analyzed for  $\text{H}_2\text{S}$  only using the Tutwiler method (6). The gas sample system following the absorption bed was identical to the input sample system except the gas stream passed through a bank of infra-red gas analyzers and was analyzed for  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2$ .  $\text{H}_2\text{S}$  was again analyzed by the Tutwiler method.

On start-up, the preheater was heated to 950°F and the carbonizer chamber preheated to 1,300°F. The absorbent bed was heated to 1,100°F before starting the absorption period. The gas flow was allowed to proceed until a predetermined amount of  $\text{H}_2\text{S}$  was found in the gas passing through the absorption bed, usually 400 grains  $\text{H}_2\text{S}$  per 100 standard cubic feet of gas. The input  $\text{H}_2\text{S}$  concentration, as near as possible, was maintained at a level decided upon before the start of the experiment.  $\text{H}_2\text{S}$  concentrations much higher than normal producer gas were used to shorten the time required to complete an experiment. Results have been cross checked with those

made with producer gas  $H_2S$  concentrations and no major differences in results were obtained. Total gas flow through the system varied with the experiment and ranged from 25 to 35 scfh. When the predetermined  $H_2S$  concentration was reached, the input gases were turned off and a nitrogen purge started. The system was purged for 30 minutes with nitrogen to prepare the system for the regeneration cycle.

Figure 2 is a flow diagram for the absorption tests made using a 1,500 scfh side stream from the MERC stirred, fixed-bed gasifier (7). The gas was maintained at its exit temperature of  $1,100^{\circ}F$  by means of electric heaters and insulation surrounding the pipe. The hot gas was brought into contact with the iron oxide-fly ash absorbents in a 6-inch diameter, 4 foot high stainless steel absorber equipped with electric shell heaters and insulated for temperature control. The sulfided absorbents were regenerated by introducing air at  $70^{\circ}F$  into the 1-inch inlet of the absorber and piping the  $SO_2$ -rich gas to the stack through the 1-inch exit line. Inert gas was also piped into the absorber inlet for bed temperature control during regeneration. The complete system was maintained above  $1,000^{\circ}F$  to prevent condensation of the tar which would affect the absorbents or plug the lines to and from the absorber. The absorber contained 73 pounds of 3/16-inch diameter absorbents, composed of 25% iron oxide and 75% fly ash with 3%, by weight, of bentonite added as a binder. A space velocity (scfh gas/cu.ft. absorbent) of 1,900 was maintained throughout the tests.

#### EXPERIMENTAL RESULTS

Four important criteria must be met before an absorbent can be considered optimum for process consideration. The absorbent must be physically strong to withstand handling, loading and cyclic thermal degradation. The absorbent must have the necessary surface area containing iron oxide particles to effectively react with  $H_2S$  and provide enough absorptive capacity for economical operations. The absorbent should be regenerable so that material and replacement costs are at a minimum. Finally, and equally important, the absorbent should have a satisfactory life expectancy.

Absorbents containing additives such as bentonite, sodium silicate and magnesium sulfate were prepared and tested for their effect on physical strength. The addition of bentonite greatly increased both hardness and crushing strength. However, the addition of 3% bentonite caused a sharp decrease in  $H_2S$  absorption capacities. The data, as shown in Table 1, indicate that bentonite does not adversely effect absorption capacity until 1.5% is added and the lesser amounts are effective in providing strength to the absorbent. Sodium silicate also produced an extrudate having a crush strength of approximately 70 pounds per one centimeter length, as opposed to around 16 pounds for an untreated extrudate, without appreciable loss in absorption capacity. On the other hand, the addition of magnesium sulfate decreased the absorption capacity without benefiting the physical strength of the absorbent.

The variables effecting absorption capacity that were tested included porosity, amount of iron oxide contained in the absorbent and steam concentrations of the hot gas being desulfurized. Ten percent, by weight, of ordinary starch was added to and burned out from the fly ash-iron oxide absorbent mixture to determine if additional porosity could be obtained. This absorbent showed nearly twice the absorption capacity of the untreated absorbent; however, it did not develop the crush strength observed earlier with a similar absorbent containing 1% bentonite. After sintering for 2 hours, the absorbent showed a decrease in absorption capacity with very little increase in physical strength.

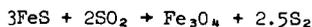
By adding varying amounts of iron oxide mixed with fly ash in preparing an absorbent mixture, it was found that 25% iron oxide with 75% fly ash showed the better absorption capacity. When 33% iron oxide was used, a significant decrease in absorption capacity was noted (2). When 13% iron oxide was used, the same significant decrease was observed. It is believed that particle size distribution of the iron

oxide and fly ash controls this phenomenon. Another disadvantage of higher amounts of iron oxide was the lesser physical strength indicated by noticeable amounts of absorbent degradation during testing while those at lesser percent were quite resistant to degradation.

Abel (2) reported that producer gas containing steam reduced the capacity of the absorbent to react with  $H_2S$ . At  $1,500^{\circ}F$  the absorption capacity was reduced about 25% in wet (8%) simulated gas. This phenomenon is not surprising since steam is a product of reaction in the absorption of  $H_2S$ . Tests performed under the present investigations using improved absorbents also showed reduced capacity. The water-gas shift reaction,  $CO + H_2O = CO_2 + H_2$ , occurred with the iron oxide-fly ash absorbent bed catalyzing the reaction to show an approximate shift of 2% for  $H_2$  and  $CO_2$ . This effect may be beneficial when the end use is feed stock for a methanation plant since the  $H_2/CO$  ratio is brought closer to the desired 3 to 1 value for the dry  $CO_2$ -free gas.

Regeneration of the sulfided absorbents was accomplished by using air or mixtures of air and nitrogen. Air regeneration at 12 scfh produced bed temperatures of  $1,700^{\circ}$  to  $1,900^{\circ}F$  in the zone of regeneration. Lower flow rates reduced temperatures  $100^{\circ}$ - $400^{\circ}F$ . Dilution of air with nitrogen had a similar effect.

At  $900^{\circ}F$  regeneration started immediately and proceeded rapidly, depending on the space velocity, to completion. The higher the rate of air introduction, that is, the greater the flow of oxygen, the higher the temperature of regeneration. The temperature increased and decreased rapidly as the zone of reaction passed through the bed and it was not known how much damage to the absorbent occurred at high temperatures for short durations. It was postulated to be around  $1,800^{\circ}F$  but a safer long-term maximum temperature for the absorbents should be  $1,500^{\circ}F$ . The dilution of the air with nitrogen was one method of controlling the maximum bed temperature without losing time in regeneration at lower flow rates. Figure 4 shows a typical temperature profile on regeneration using 12 scfh air flow rate compared with using 12 scfh air and 12 scfh nitrogen or a total of 24 scfh flow rate. Number 1 thermocouple is near the inlet while No. 5 thermocouple is located near the exit from the bed. TC-5 was consistently lower in all regenerations. This was believed to have been caused by the partial regeneration of the bed by unreacted oxygen from the main zone of regeneration with possibly some credit given to the endothermic reaction between  $FeS$  and  $SO_2$ . Elemental sulfur was found in the exit piping and valves. It would be produced according to the following reaction:



Sulfur balances calculated using the  $H_2S$  input versus  $SO_2$  in the outlet gas averaged about 95% recovery as  $SO_2$ . Several batches of regenerated absorbents were analyzed for total sulfur after several cycles of absorption and regeneration and the sulfur content was found to be less than 1%. This would indicate that very little sulfate was formed at the high regeneration temperatures used.

Regeneration was essentially completed in 120 minutes when the air flow rate was 12 scfh. At 6 scfh, regeneration required 190 minutes. A 1 to 1 mixture of air and nitrogen at 24 scfh flow rate required a regeneration time of 150 minutes. Since the normal absorption cycle required about 5 hours, enough time was available to use any of the above flow rates. Aside from critical temperature design criteria, another consideration was the  $SO_2$ -enrichment that was needed for downstream conversion or reduction. The  $SO_2$  concentration in the effluent gas approximated 11½-12% when using air for regeneration; however, when dilution gas was used, the  $SO_2$  concentration was proportionate to the amount of diluent used, being around 5½-6% at 1 to 1 dilution of air with nitrogen. Typical regeneration curves, depicted by Figure 5, showed that maximum  $SO_2$  concentration was reached in less than 5 minutes and dropped from maximum to base line in approximately 20 minutes. These time factors are noted for both air and diluted air regeneration schemes.

The life expectancy of a specific absorbent could only be determined with accuracy by continuous cycling until the absorption capacity dropped below acceptable limits or degradation and fusion caused operational problems. This was costly in terms of money and manpower. However, one absorbent bed has been through 30 absorption-regeneration cycles using simulated producer gas containing both coal-related tars and particulates to study the cyclic effect upon the absorbents. Absorbents used in this study were prepared by adding 10%, by weight, of starch to an absorbent mixture containing 25% iron oxide and 75% fly ash. The absorbent was sintered at 1,800°F for 30 minutes in an oxidizing atmosphere. The producer gas was maintained at 1,100°F throughout the absorption cycle at an average flow rate of 15 scfh. The H<sub>2</sub>S concentration in the inlet gas stream was maintained at 2% and the steam content between 7 and 11%.

Regeneration after each absorption cycle was accomplished by using a 12 scfh air flow rate for approximately 2 hours. The average absorption cycle lasted 5 hours. Figure 3 indicates the absorption capacity of each cycle. The increasing absorption capacity through the first few cycles was believed due to the result of burn-out of the residual starch during regeneration where temperatures approached 1,300°F for short periods. The continuing starch-char burnout would open more pores for better gas penetration to the iron oxide particles in the absorbent. After 30 cycles, the absorbent was in good condition without visible signs of deterioration or caking. Table 2 lists 6 of the 30 runs which were representative of the typical information computed from the raw data obtained during operations.

Abel (2) earlier reported that sintered pellets containing 25% iron oxide and 75% fly ash underwent 174 absorption-regeneration cycles using hot (1,000°-1,500°F), clean simulated producer gas without visible damage to the pellets or appreciable loss in absorptive activity. The absorption capacity averaged 8% for those tests conducted at 1,100°F. The pore volume reached a constant value of 0.12 cubic centimeters per gram after 30 absorption-regeneration cycles.

Four 15-hour absorption runs were completed using a 1,500 scfh sidestream of hot (1,100°F) raw producer gas made by gasifying high volatile bituminous coal with air and steam in a 42-inch stirred, fixed-bed gasifier (7). These runs were made primarily to demonstrate the feasibility of the process at much higher gas flow rates and at actual process conditions. The four 15-hour runs were completed successfully with an average absorption capacity of 8.25 wt.-pct. Ninety to 94% of the H<sub>2</sub>S was removed from the hot producer gas which averaged 0.5% H<sub>2</sub>S entering the absorber. Table 3 shows the data and run conditions for the 4 periods. The absorbents remained in good condition for the duration of the tests and were not adversely affected by the tars and particulates in the effluent gas. The tars could be tolerated if the absorber bed temperature remained above 1,000°F. The fine carbonaceous particulate accumulated in the absorber bed during absorption was burned off during the regeneration cycle. An insignificant amount of ash residue remained in the bed after regeneration which was determined by visual inspection of the bed after completion of the 4 cycles. Pressure drop across the bed increased to 8-9 psig at the end of the absorption periods but returned to 1.5 psig after regeneration of the absorbent bed.

#### CONCLUSION

The laboratory tests conducted thus far indicate that the fly ash-iron oxide absorbent containing bentonite is an adequate absorbent for removing H<sub>2</sub>S from raw producer gas at temperatures between 1,000°F and 1,500°F. The physical strength, expressed as the crush strength (measured across the diameter), of 50 to 100 pounds per one centimeter of length is considered adequate to withstand handling, transportation and placement of the absorbents. The absorbent is regenerable and has an average capacity of 10 wt.-pct. This amount of absorptive capacity coupled with an efficiency of 90-94% permits ample time "on line" and provides an effluent gas which meets the existing environmental air standards.

Thirty and 174 absorption-regeneration cycles were completed without visible deterioration or loss of absorptive capacity. Although not conclusive, these tests indicate that the absorbents could withstand many more cycles. Eventual pore closing by fusion due to long time thermal cycling and/or micron size particulate exposure needs to be investigated further. These two occurrences would be the most likely limiting factors on life expectancy of the absorbents.

Laboratory work is now being performed to find a suitable substitute for the fly ash so that higher temperatures and faster regeneration would be permissible. Finding cheaper sources of iron oxide and comparing results of these oxides should be investigated so that availability of iron oxide would be assured. Finally, a pilot plant hot gas cleanup facility should be operated so that its feasibility for commercial application would be demonstrated along with hardware development and scale-up design criteria established.

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TABLE 1. - Effect of Bentonite on Absorption Capacity of Fly Ash-Iron Oxide Absorbent Using Apparatus Shown in Figure 1

Bentonite, percent	Gas flow rate, std. cu.ft./hr.	Run duration, hr.	Space velocity, vol/vol/hr	H <sub>2</sub> S absorption		
				Total, grains	Capacity wt.-pct.	Total absorbed, pct.
0.5	17.19	4.11	510	1290	11.94	96.3
1.0	15.30	5.75	454	1265	11.70	96.6
1.5	14.27	4.52	423	1134	10.5	97.2
3.0	17.58	3.15	521	678	6.28	94.1

Absorption temperature -- 1,100°F  
 Saturation point -- 400 grains/100 scf  
 Weight of absorbent -- 700 grams

TABLE 2. - Typical Data from Six of Thirty Absorption Capacity Tests (Figure 1) Using Same Fly Ash-Iron Oxide Absorbent Containing 10 Percent Starch

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

Absorption temperature -- 1,100°F  
 Saturation break-through point -- 400 gr/100 scf  
 Weight of absorbent -- 700 grams

TABLE 3. - Run Data Obtained During Four Absorption Periods Using Raw Producer Gas from MERC Producer (Figure 2)

	Run 1	Run 2	Run 3	Run 4
Volume of bed, cubic feet	0.785	0.785	0.785	0.785
Weight of absorbents, pounds	73	73	73	73
Gas flow rate, scfh	1,500	1,500	1,500	1,500
Space velocity, $\frac{\text{scfh}}{\text{cu. ft. absorbent}}$	1,910	1,910	1,910	1,910
Duration of run, hours	15.87	9.78	14.50	10.75
Inlet steam concentration, percent	8.5	3.3	3.1	6.3
Bed temperature, °F	1,085	1,085	1,085	1,085
Absorption capacity, weight-percent	9.19	6.17	8.35	9.29
H <sub>2</sub> S absorbed, grains	46,950	31,532	53,624	47,450
H <sub>2</sub> S absorbed when 150 grains = point of saturation, percent	83	83	81	86
H <sub>2</sub> S absorbed if 50 grains = point of saturation, percent	92.9	91.4	90.7	94.2

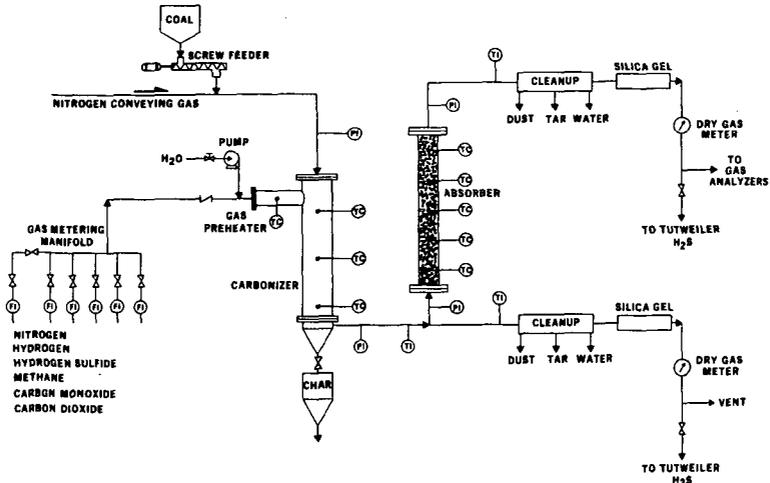


Figure 1. - Flow Diagram of Apparatus for Measuring Absorption Capacity

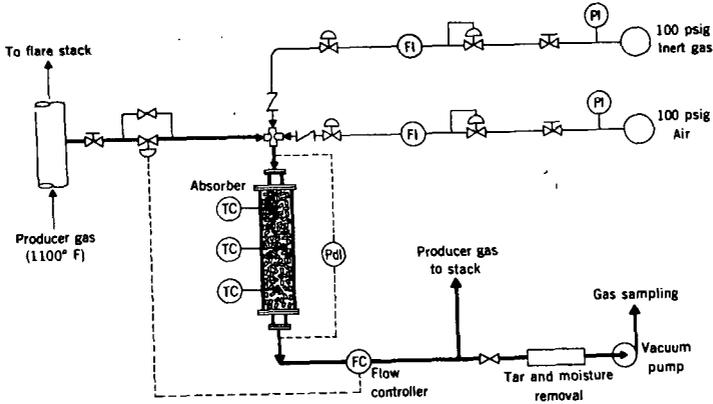


Figure 2. - Flow Diagram of Apparatus for Testing Solid Absorbents Using Hot Producer Gas

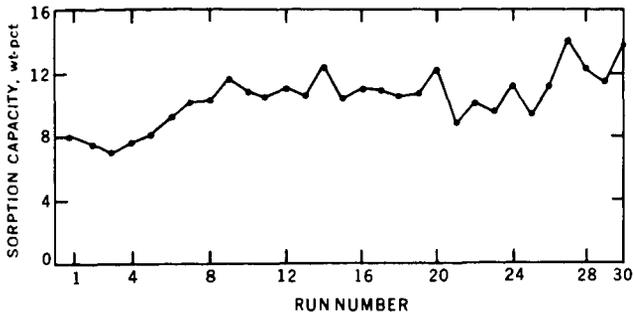


Figure 3. - Absorption Capacities Achieved During Thirty Absorption-Regeneration Test Runs Using the Same Absorbent, with Operating Conditions Listed in Table 2

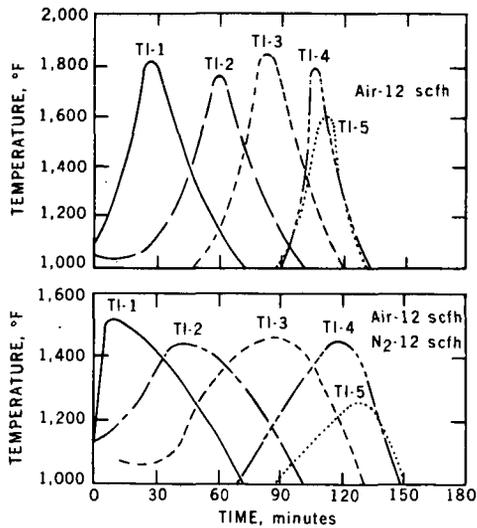


Figure 4. - Comparison of Bed Temperature Profiles With and Without Dilution Gas for Regeneration of Sulfided Absorbents

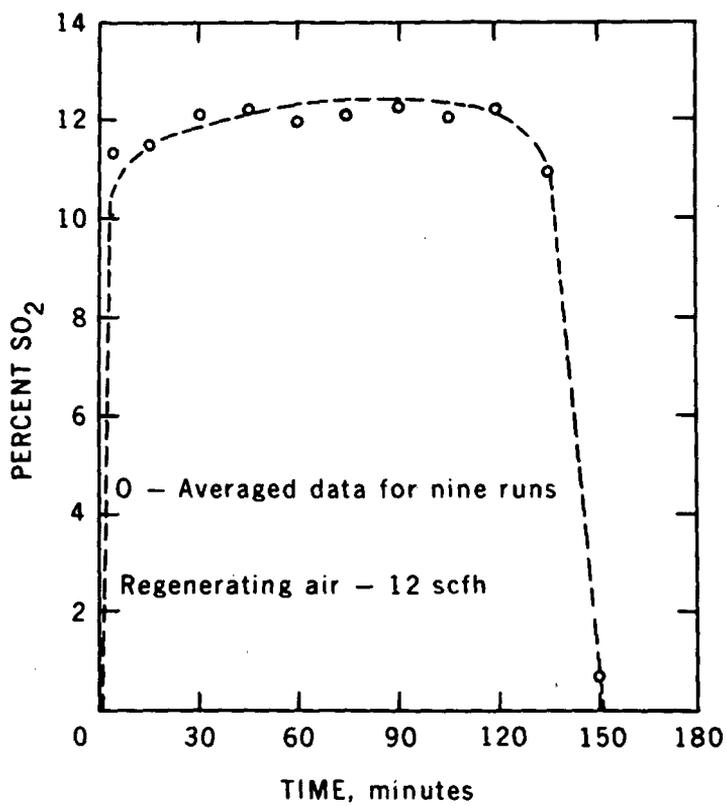


Figure 5. - Typical Curve Showing SO<sub>2</sub> Concentration in the Effluent Gas During Regeneration of the Sulfided Absorbents