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Hydrogen Sulfide Removal from Hot Producer Gas with Sintered Absorbents

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The Bureau of Mines prepared three sintered materials capable of removing H_2S from producer gas at 1000° to 1500°F. They are mixtures of ferric oxide and fly ash, ferric oxide and pumice stone, and red mud (a ferric oxide-containing residue from processing bauxite). All three absorbents were virtually completely regenerable with air. A sintered Fe_2O_3 (25%)-fly ash (75%) mixture was tested through nine H_2S absorption-air regeneration cycles without loss of absorption capacity or attrition of the pellets. The absorbent with the greatest capacity was a red mud, absorbing 16.0% by weight of sulfur at 1000° F, 24.0% at 1250° F, and 45.1% at 1500° F.

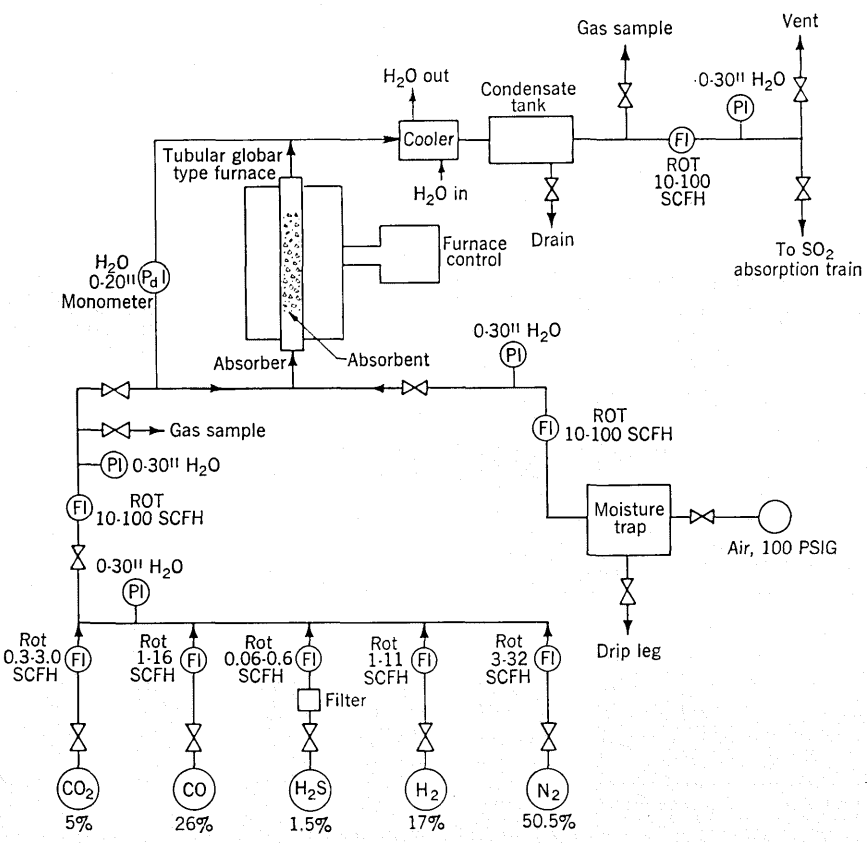

Figure 1. Flowsheet for removal of sulfur from hot producer gas.

Gas producers have been receiving attention in recent years as a potential source of clean, pressurized gas for a variety of industrial purposes. Removal of H_2S (hydrogen sulfide) from the hot producer gas is of interest because hydrogen sulfide is an air pollutant, deteriorates equipment, and removal while still hot should be less costly.

Temperature of the producer gas to be treated for H_2S removal ranges from 1000° to 1500°F. To economically utilize the sensible heat of producer gas for power generation, the H_2S must be removed near the generation temperature of the gas. This precludes the use of liquid absorbents and limits the process to the use of solid absorbents that can react with H_2S at elevated temperatures. The material should also be regenerable for re-use through several cycles of H_2S absorption followed by air regeneration.

Literature references on producer gas clean-up in the 1000° to 1500°F range are quite limited. Information is available on the desulfurization of industrial gases between 68° and 1292°F with $-16 + 100$ mesh iron oxide, including data on static and fluidized beds between 617° and 752°F.[1] Static beds were tested at a space velocity (gas volume per absorbent volume per hour) of 100 and fluidized beds at 3000 vol/vol/hr. An absorption capacity of 30% by weight of sulfur per unit weight of absorbent was obtained at higher temperatures and H_2S removal efficiency was 95 to 99.9%. A full-scale operating plant was built with a capacity for treating 32 million cubic feet of coke oven gas per day.[2] Iron oxide was the absorbent in a fluidized bed operating at 680° to 752°F. Although over-all operation of the plant was satisfactory, troublesome accumulations of fine oxide dust

reportedly were experienced in various parts of the plant.

This paper gives the results of an investigation of prepared solids for their capacity to remove H_2S from hot producer gas. Solids utilized were (1) a sintered mixture of ferric oxide (Fe_2O_3) plus fly ash; (2) pumice stone coated with fused Fe_2O_3; and (3) sintered pellets prepared from red and brown muds, aluminum refining residues that contain large amounts of Fe_2O_3.

Apparatus and Procedure

Bench-scale apparatus utilized in this study is shown in Figure 1. Gases from cylinders of nitrogen, hydrogen, hydrogen sulfide, carbon monoxide, and carbon dioxide are metered to form a stream of simulated producer gas devoid of ash and tars and containing approximately 1.5 volume percent H_2S. The percentage of other constituents is listed on the flowsheet.

Simulated producer gas was passed through a bed of the test absorbent contained in an electrically heated section of 1 inch diameter by 5 feet long schedule 40 stainless-steel pipe. Alumina spheres in the bottom 22 inches of the pipe extended 10 inches into the hot zone of the furnace. These spheres supported the absorbent bed and preheated the gas. Regeneration facilities, shown in the center right portion of the flow sheet. consisted of an air supply with pressure regulator and flow meter. Purified producer gas and the regeneration gas were vented through a common system. Fifteen inch depths of absorbent were subjected to a gas flow rate of 15 scfh (7.08 liters per minute), which is equal to a space velocity of 2000. Hydrogen sulfide concentration in the simulated producer gas is controlled to equal 20.6 to 22.9 mg/l (mg/l $\times$ 43.7 = g/100 ft^3). Experiments were conducted at 1000°, 1250°, and 1500°F. The runs were terminated when the H_2S concentration in the effluent gas stream of the test bed, originally near zero, reached 2.3 mg/l. Sulfur capacities of the absorbent were calculated from the product of H_2S concentration, flow rate, and time duration of the test.

Analytical Methods

Hydrogen sulfide concentration of the gas stream was determined by the Tutwiler method[3] and verified by chemical detection tubes and gas chromatography. Reasonable agreement was found between the different methods. Absorbent was regenerated by passing an air stream through the tube at 1000° to 1500°F. During the first several tests, SO_2 liberated during regeneration was absorbed in 2.5 N caustic soda solution, an aliquot was acidified with HCl, and titrated to a starch end point with iodine. The weight of sulfur regenerated was calculated and compared with the calculated weight of sulfur absorbed to determine the error in the sulfur balance. These balances usually checked within 20%. Part of this variance is explained by the fact that during regeneration some of the sulfur was evolved in elemental form and collected in the filter at the effluent end of the reaction tube, thus was not measurable. Later, SO_2 concentrations were measured by means of impregnated silica gel detection tubes.

Absorbents

Several commercial absorbents were tested first, but they did not give satisfactory results, all of them disintegrating in the temperature range used. Included among these were chromium-promoted iron oxide, calcined pellets of dolomite, and alkalized alumina pellets. Seeking more satisfactory absorbents, several other materials were prepared for investigation. The first material consisted of a mixture of fly ash (−4 + 6 mesh) from a bituminous coal-burning power plant (Table I) and pure Fe_2O_3. Fly ash and oxide were thoroughly mixed, water was added, and pellets were formed and sintered at about 1800°F. Tests were also made with sintered taconite and sintered (pure) Fe_2O_3.

The second absorbent that was prepared consisted of granular pumice stone (−4 + 8 mesh, Table II) impregnated with 99+% pure Fe_2O_3. Pumice stone granules were coated with the oxide as follows: moistened granules were placed in a tumbler, dry oxide was added and the mixer was operated until a fairly uniform coating of the granules was observed. These were then heated at 1500°F for 2 hours to bond the two materials. Some shrinkage occurred during the heating, but the granules remained porous and the oxide adhered well to the pumice stone. Excessive shrinkage and loss of porosity occurred when the absorbent was heated at 1900°F.

The third material consisted of red or brown mud residues from aluminum refining. They were received in powder or lump form, the latter being reduced to powder before use. The powder was moistened with enough water to form a putty-like material that was formed into ¼ inch spheres, predried at 500°F, then heated at 2000°F for 10 to 20 minutes to produce a hard pellet. Chemical analyses of the muds are given in Table III.

Absorption Tests

Results of tests with these materials are given in Table IV. The fly ash (75%) and Fe_2O_3 (25%) formed a pellet with high sulfur-absorption capacity and did not disintegrate at the test conditions. Tests 1 through 10 give the absorptive capacity of this fly ash-Fe_2O_3 mixture and contains the results of nine

Table I. Chemical composition of sintered fly ash used for H_2S absorption.

Constituent	Percent
SiO_2	47.9
Al_2O_3	23.8
Fe_2O_3	15.7
P_2O_5	0.6
TiO_2	2.8
CaO	3.6
MgO	1.5
Na_2O	1.9
K_2O	2.2

Table II. Chemical composition of the granular pumice stone.

Constituent	Percent
SiO_2	73.49
Al_2O_3	13.55
Fe_2O_3	1.51
Na_2O & K_2O	8.06
CaO & MgO	2.93

Table III. Chemical analyses of muds.

Mud No.	L.O.I.[e]	Fe_2O_3	SiO_2	TiO_2	Al_2O_3	CaO	Na_2O
1[a]	11.2	42.4	8.1	4.4	18.8	5.3	5.6
2[b]	5.6	7.5	23.3	3.7	6.9	46.4	3.5
3[c]	11.5	53.2	3.6	7.2	12.8	7.3	2.1
4[d]	11.2	34.7	13.9	9.0	19.4	5.8	6.0

[a] Red Mud from Alcoa's Point Comfort Operations.
[b] Brown Mud from Alcoa's Arkansas Operations.
[c] Field Dried Red Mud from Reynolds Metals Co. Sherwin Plant.
[d] Mobile Red Mud from Alcoa.
[e] Loss on ignition at 1100°C.

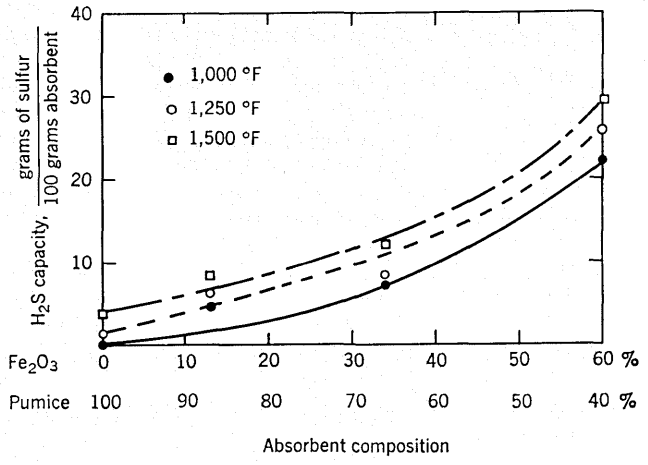

Figure 2. H_2S absorption capacity of sintered pumice stone.

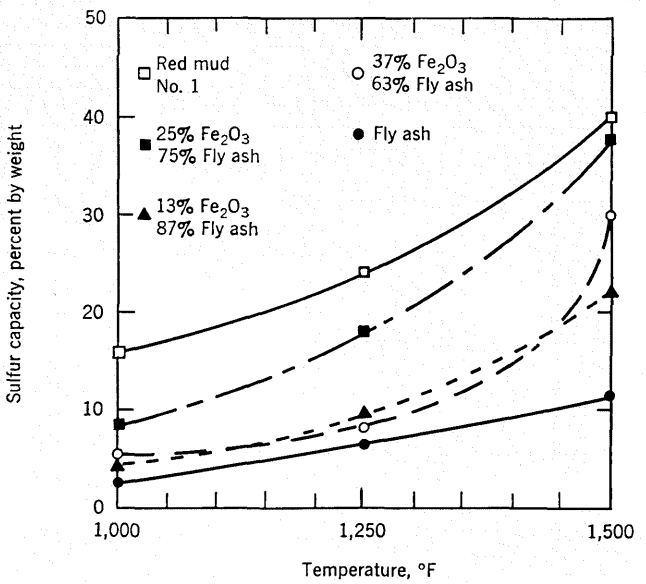

Figure 3. Sulfur capacities of absorbents at 1000° to 1500°F.

successive H_2S absorption-air regeneration cycles on one batch of absorbent. The data show that there is no loss in absorptive capacity nor any attrition of the pellets. Absorbents with more than 37% Fe_2O_3 were difficult to test because the pellets either disintegrated or the materials fused.

Compositions and results obtained with pumice stone coated with ferric oxide are listed in Table V and Figure 2. This material did not exhibit any tendency to disintegrate, and showed some tendency to fuse into larger particles.

Results obtained with the muds are listed in Table VI. Red mud No 1 formed a very durable pellet and had the highest capacity of any material tested.

Figure 3 shows sulfur capacities of the materials that did not disintegrate or fuse and appeared suitable as H_2S absorbents.

Regeneration of Absorbents

During regeneration of absorbents, all at space velocities of 2000 calculated at standard conditions (68°F and 1 atm pressure), instantaneous SO_2 concentrations were measured by chemical detection tubes. Error in the sulfur balance amounted to about 15% or less when the regeneration temperature was 1000° or 1250°F. When regeneration was attempted at 1500°F, the material fused into a mass that could not be regenerated. About 1000° appeared to be the optimum temperature for regeneration of these types of absorbents. Release of heat from the exothermic regeneration reaction is sufficient to increase the bed temperature about 400°F.

Complete regeneration of absorbents appears impractical; a few parts per million of SO_2 were measurable even after 80 hours of regeneration. Regeneration proceeds at a high rate (6 to 10 volume percent SO_2) for the first 30 to 50 minutes of regeneration, drops to about 1% by volume after 1 hour, then rapidly decreases and slowly approaches zero. Figure 4 is a plot of SO_2 concentrations versus time for tests in which the absorption temperatures were 1000°, 1250°, and 1500°F, and the regeneration temperature was 1000°F. The weight of sulfur regenerated in any of these three tests during the first hour was at least 80% of the total that was regenerated. Tests 18 and 19 (Table IV) were conducted with a regeneration temperature of 800°F. This temperature was adequate to rapidly regenerate the pellets of test 18 with a low sulfur content of 8.1 wt-pct, but did not achieve a fast regeneration in test 19 in which the pellets had a high sulfur content, 34%. Pellets with a low sulfur content (10% or less) appeared to regenerate more quickly than pellets with a sulfur content of 30% or more, indicating that regeneration should be started before the absorption capacity limit is attained.

Discussion

Mixtures of 75% fly ash-25% Fe_2O_3 gave absorption capacities ranging from 8.1% by weight of sulfur at 1000°F to 42.7% at 1500°F. Pellets containing 40% pumice and 60% Fe_2O_3 showed sulfur capacities of 23.3% at 1000°F to 30.6% at 1500°F. The most effective absorbent was a red mud having capacities ranging from 16.0% at 1000°F to 45.1% at 1500°F.

Spectrographic analysis of reaction products revealed the formation of troilite (FeS). Stoichiometric calculations indicate the formation of ferric sulfide (Fe_2S_3) and pyrite (FeS_2) as products of the reaction. No attempt was made to define precisely the stoichiometry because of the numerous forms in which iron sulfide can occur. The reaction is complicated further by the existence of other metal oxides in the absorbent that may or may not absorb H_2S under the test conditions investigated.

Possible methods of recovering the sulfur contained in the SO_2 during regeneration are the catalytic conversion to SO_3 with subsequent production of sulfuric acid, or the reaction of the SO_2 with some of the producer gas over a suitable catalyst to form elemental sulfur.

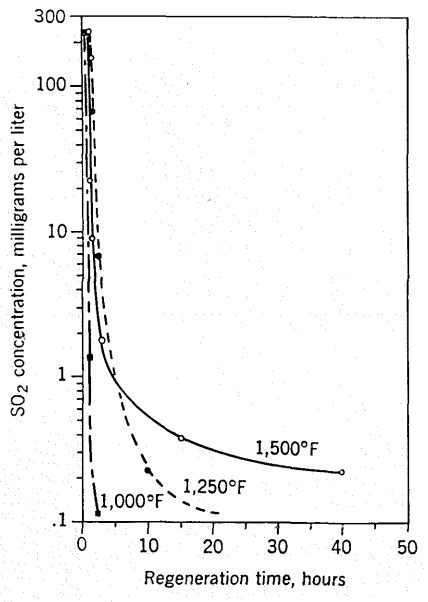

Figure 4. Typical SO_2 concentration versus regeneration time.

Table IV. H_2S absorbing capacities of sintered materials at 2000 space velocity.

Test No.	Material	Absorption Temp., °F	Capacity, g Sulfur / 100 g Material
1	75% Fly ash—25% Fe_2O_3	1000	8.7
2	do.	1000	8.2
3	do.	1000	8.1
4	do.	1250	16.4
5	do.	1250	21.1
6	do.	1250	16.5
7	do.	1250	13.3
8	do.	1250	15.8
9	do.	1500	41.1
10	do.	1500	42.7
11	Taconite	1000	3.5
12	do.	1250	4.8
13	do.	1500	Disintegrated
14	Fe_2O_3	1000	22.0
15	do.	1250	20.0
16	do.	1500	Disintegrated
17	63% Fly ash—37% Fe_2O_3	1000	6.1
18	do.	1250	8.1
19	do.	1500	34.0
20	do.	1500	26.0
21	87% Fly ash—13% Fe_2O_3	1000	4.4
22	do.	1250	9.8
23	do.	1500	22.0

Table V. H_2S absorbing capacities of sintered pumice stone.

Test No.	Material	Temp., °F	Capacity, g Sulfur / 100 g Absorbent
24	Pumice, granular, −4 +8 mesh	1000	0
25	do.	1250	1.4
26	do.	1500	3.7
27	87% Pumice—13% Fe_2O_3	1000	4.7
28	do.	1250	6.3
29	do.	1500	8.5
30	66% Pumice—34% Fe_2O_3	1000	7.2
31	do.	1250	8.4
32	do.	1500	12.3
33	do.	1500	13.3
34	40% Pumice—60% Fe_2O_3	1000	23.3
35	do.	1000	20.4
36	do.	1250	26.8
37	do.	1500	27.6
38	do.	1500	30.6

Table VI. H_2S absorbing capacities of brown and red mud.

Test No.	Temp., °F	Mud No.	g of Sulfur: Capacity from Quantity H_2S Absorbed	g of Sulfur: 100 g Absorbent from Quantity SO_2 Evolved	Percent Error in Sulfur Balance
39	1000	1	16.2	16.0	1.2
40	1250	1	25.6	24.0	6.0
41	1500	1	52.7	45.1	14.4
42	1000	2	1.6	1.5	6.0
43	1250	2	6.1	6.6	7.6
44	1500	2	28.2	26.4	6.6
45	1000	3	13.7	12.2	11.0
46	1250	3	14.9	13.7	8.1
47	1500	3	34.0	37.6	9.6
48	1000	4	5.9	6.6	10.6
49	1250	4	14.6	13.2	9.6

Gas chromatographic analyses of both influent and effluent gas streams were made (when using sintered fly ash-ferric oxide) to determine if rearrangement of the gas composition occurs and to determine if gaseous sulfur compounds are formed which are not detected by titration for H_2S. At 1500°F, water vapor and a small concentration of methane (0.4%) were formed, but no other gases were detected that were not present in the influent gas. The influent gas contained the impurities SO_2 and methyl mercaptan in low concentrations (45 and 16 ppm, respectively), but these are not found in the effluent.

Conclusions

Hydrogen sulfide can be removed from hot producer gas in the 1000° to 1500°F temperature range by reaction with a metallic oxide, such as Fe_2O_3 (a material which has long been used to absorb H_2S from producer-type gases at low temperatures), but the material must be incorporated into a semifused porous matrix of other metallic oxides to prevent dust formation and loss of absorption material. This research shows that such a material can be made by mixing Fe_2O_3 with fly ash and sintering the mixture, or by sintering red mud residues from aluminum refining. In all cases, the mixture contains alumina and silica, which may act as matrix formers, and alkali metal oxides which could act as fluxes to reduce temperature required to sinter the materials.

Absorbents were regenerated to an essentially fresh condition by passing air through the bed at a temperature of 1000° to 1200°F. Sulfur dioxide was liberated and the reactive metallic oxides were re-formed. Small quantities of elemental sulfur and sulfuric acid were formed during regeneration.

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