

DESULFURIZING FUEL VIA METAL OXIDES

R. K. Bhada and W. L. Sage

The Babcock & Wilcox Co.
Research Center
Alliance, Ohio

INTRODUCTION

One concept for desulfurization of fuel involves conversion of the sulfur to hydrogen sulfide via partial oxidation with subsequent removal by reaction with a metal oxide to form a metal sulfide. The sulfide could then be regenerated with preheated air to produce a stream of concentrated sulfur dioxide. This scheme is illustrated in Figure 1. Such a scheme may be used in several processes. One such process for a two-stage combustion power cycle is illustrated in Figure 2.

While the concept appears attractive, very little is known about the reaction rates and limitations of desulfurization and regeneration. In order to obtain some preliminary data regarding these, bench-scale experiments were made using a synthetic gas. Temperature and gas flow velocity were varied. Based on results of these bench-scale experiments, a small pilot plant was built and tested employing coal gasification and a cyclic sulfur removal system. Iron oxide was selected because of its low cost and ease of availability. However, other oxides, such as zinc oxide, would probably be just as effective.

This paper describes our experiments and their results pointing to the utility of this desulfurizing concept.

APPARATUS AND PROCEDURE

Bench-Scale Experiments

A schematic diagram of the bench-scale experimental system is shown in Figure 3. Gas or air (depending on whether it is an absorption or regeneration cycle) flows at a controlled and measured rate through a quartz preheater into the reactant furnace. The furnace containing the reactant cell (details described later) is maintained so that the reactant surface temperature is constant at a predesigned value. The exit gases are cooled, analyzed, and vented through a stack.

High-temperature thermocouples are imbedded in the following five places to trace the temperature profile through the system: preheater, inlet to reactant furnace, surface of reactant, exit of reactant furnace, and exit of cooler (just prior to analysis). The flow rate is measured before preheating.

The hydrogen sulfide or sulfur dioxide is analyzed by a colorimetric method (modified Reich method) where the H_2S or SO_2 is reacted with a slightly acidic iodine solution. Additionally the other gaseous constituents of interest such as sulfur trioxide, carbon monoxide, carbon dioxide, and oxygen are periodically analyzed.

Two reactant materials were utilized: (1) sintered iron powder and (2) plain carbon steel. The sintered iron powder surface was fabricated in the form of cells of 0.25-inch inside diameter and reacting surface area of approximately 0.06 square foot. Each cell was formed by packing a tube with fine iron powder using a carbon rod to create the bore. The cells were then placed in a furnace at 70 F and raised to 1800 F at a rate of about 900 F per hour. The cells were held at 1800 F for 3 hours and then cooled gradually for 16 hours.

The plain carbon-steel surface was tested in two arrangements. The first arrangement was in the form of an annulus, and the second was in the form of a long single tube with three passes in the furnace. The first arrangement had a 3/8-inch diameter threaded rod in a 1/2-inch inside diameter pipe and was 21 inches long; the active surface was approximately 0.38 square foot. The second arrangement was 6.5 feet long, made of 0.269-inch inside diameter pipe; the reactant surface was thus approximately 0.45 square foot.

All tests were started with the oxidation cycle. Air at a controlled rate (set so that the velocity in the reactant cell was between 5 and 30 fps) was started through the system. The preheater temperature was then slowly raised, followed by raising the reactant furnace temperature. All thermocouples were continuously monitored. The cooling water was regulated to hold the stack gas temperature below about 150 F. After a sufficient oxidation period (greater than 1 hour), the air was turned off, and the gas was started. A synthetic gas, containing* approximately 1% H₂S, 12% CO, 8% CO₂, 1% CH₄, and the balance N₂, was started through the system at a controlled rate (set for a fixed velocity through the reactant cell). The exit gas was continuously analyzed for H₂S, and a record was also maintained of the temperature readings of the various thermocouples, the flow rate, and the CO and CO₂ contents of the exit gas. The synthetic gas flow was maintained until an appreciable breakthrough of H₂S was observed, usually about 1 hour, after which the gas was switched off and the air flow was started for regeneration. SO₂ was analyzed continuously, and temperatures, flows, and oxygen content were monitored intermittently.

After the regeneration, the absorption cycle could be started again. Several absorption and regeneration cycles were conducted in series to obtain some idea of the effect of cycling and continuous operation. At the end of the tests, the reaction cells were cut open and examined.

Pilot Plant Tests

The test equipment used is shown schematically in Figure 4, and a photograph is shown in Figure 5.

Coal is charged to a gasification chamber of 1-foot diameter and 10-foot length. This chamber is refractory lined to minimize heat losses. The make-gas from the gasifier passes through a one-stage cyclone chamber with an expected efficiency of 80 to 90% for particulate removal.

* Essentially the same composition as that of a synthetic gas from a gasifier.

The removal of hydrogen sulfide from products of combustion is accomplished by reaction on the iron oxide surface. The absorption cells were designed, employing a carbon-steel surface, to handle approximately 400 lb of gas flow per hour.

The arrangement of an absorbent cell is shown on Figure 6. The grid surface is made of 0.25-inch diameter carbon-steel rods. There are 1780 1-foot long rods in each cell providing 116 square feet of surface. The rods are staggered on 0.375-inch centers covering a 12-inch by 12-inch opening 18 inches deep. The cells are refractory lined with 2 inches of Kaocrete "D" to reduce heat loss.

A secondary furnace and combustor receives sufficient air to complete the combustion of make-gas, unreacted carbon, and auxiliary natural gas. The heat from the flue gas is absorbed by an air heater before the gases pass out the stack.

Air flow to the gasifier, secondary combustor, and cell regeneration is controlled by remote pneumatically operated dampers. Flow rates are determined by orifice meters, pressures by manometers or gages, and temperatures by well-type thermocouples. The fuel feeds are determined as follows: natural gas by orifice meter and coal from a calibration of feeder speed versus coal rate.

The method of gas analysis was the same as that in the bench-scale tests. Additionally the Barton Electrolytic Titrator was used for hydrogen sulfide detection at the exit, and a UV sulfur dioxide detector was used to closely follow the regeneration.

All shakedown and preliminary tests were started with the oxidation cycle. Combustion air to the primary combustor was set at a controlled rate to maintain a desired gas flow through two absorbent cells until steady-state conditions were established. The unit was heated up using natural gas by first placing the secondary combustor in service and then the primary. As the combustion air temperature was raised, the desired operating parameters were set in preparation for gasification and the absorption cycle. The combustion air temperature to the secondary and primary combustors was limited by the available air heater surface, resulting in a steady-state air temperature of 650 to 700 F during gasification. The pulverized coal was fed at approximately 50 pounds per hour for gasification. This gasification coal was transported by compressed air flowing at approximately 100 pounds per hour.

The gas leaving the absorption cells was continuously analyzed for H_2S , and the resulting data was recorded until significant breakthrough or saturation was apparent. After this occurred, regeneration was started, and the idle cell was placed in service on the absorption cycle. Normally, two of the cells were continuously on absorption while one of the three was on regeneration.

After the regeneration, the absorption cycle could be started again if desired. Absorption and regeneration cycles were conducted in parallel in order to obtain a better idea of the effect of cycling and continuous operation.

RESULTS

Bench-Scale Experiments

The following parameters were examined with the sintered iron oxide cells:

Cell dimensions: 0.25-inch inside diameter and 10.5 inches long
Cell surface temperature: 825 and 1200 F
Gas velocity: 7 to 18 fps

With the carbon-steel surface (annular and tubular arrangements), the following were the parameters:

Cell dimensions:

1. 3/8-inch threaded rod in 1/2-inch pipe, 21 inches long for the annular arrangement
2. 0.269-inch inside diameter and 6.5 feet long for the tubular arrangement

Cell surface temperature: 1200 and 1600 F
Absorption gas velocity: 7 to 20 fps

Time, temperature, and gas composition were obtained and are summarized in Tables 1 and 2.

The data in Tables 1 and 2 does not include intermediate sulfur concentrations during absorption and during regeneration.* For one set of parameters (1200 F cell temperature and 0.064 scfm flow during adsorption using the tubular heater of 0.45-square-foot surface) the concentration-time curves are shown in Figures 7 and 8; these are typical results and are similar to the behavior observed under other operating conditions.

A microscopic examination was also made of the specially-prepared tube, cut open after an absorption cycle. The main purpose was to determine whether iron sulfide was formed, and if so, whether the reaction was primarily at the surface or throughout the wall. The microscopic examination revealed that the reaction was primarily at the surface, as evidenced by Figure 9.

An odd phenomenon was observed at 1600 F cell temperature, both during absorption and during regeneration. It was found during absorption that more than 99% of the H₂S was absorbed with no breakthrough (or reactant saturation), even after 2 hours of absorption. However, regeneration with air was unsuccessful since surface deformation or deposition caused the flow passage to be blocked. An unusually large amount of internal heat caused the reaction tube to bend.

* Periodic Orsat gas analysis showed no change in composition of the other gas constituents during absorption, nor did it show any oxygen in the regenerated stream during the peak period of regeneration.

Pilot Plant Tests

A plot of pertinent data for a typical cycle employing cell No. 1 with a full grid and cell No. 2 with a half grid is shown on Figure 10. The free flow area through the grids was 0.33 square foot per grid. Make-gas flows were obtained by summing the air flow to the gasifier, the natural gas, and 50% of the coal. On this basis make-gas flows ranged from 350 to 500 lb/hr. An assumed make-gas temperature of 1000 F resulted in gas velocities of 5 to 8 fps using two grids or 10 to 16 fps using one grid, both ranges being well above the gas velocities employed for electrostatic precipitators. Inlet H₂S concentrations were varied from 1000 to 7500 ppm by volume using sulfur addition for the higher values. These concentrations would be obtained from 0.6 to 4.5% sulfur coal (based on 50% theoretical air).

The efficiency* of H₂S removal is plotted in Figure 11, which indicates that:

1. Removal efficiency is favored by operation at higher temperatures.
2. Removal increases with contact time. Contact times for the three curves are in the order of 0.25 sec for two cells, 0.12 sec for one cell, and 0.06 sec using half of the grids in one cell.

Note: Since total gas flow was constant the upper and center curves show a 2 to 1 velocity effect; however, the middle and lower curves have only retention time.

The cells were normally regenerated using preheated air (500 to 650 F) at flows ranging from 90 to 165 lb/hr. The grids appeared dark in color following the H₂S removal cycle and seemed to have some carbon deposition on the surface. Following regeneration the surface assumed a reddish, rust colored appearance. Using the last 120 minutes of data shown on Figure 10 and calculating on the basis of 6500 ppm removed from a gas throughput of 450 lb/hr, yields an hourly removal rate of 40 scf of H₂S. On the basis of the 90 lb/hr regeneration rate employed, an average 3.3% SO₂ content would provide a sulfur balance. This value appears to be a reasonable summation of the area under the SO₂ regeneration curves.

CONCLUSIONS

The following pertinent conclusions may be drawn from the results of the bench-scale and the larger-scale experiments:

1. The concept of absorption of H₂S by iron oxide and subsequent regeneration as a concentrated (12 to 15%) stream of SO₂ is technically feasible in the temperature range of 800 to 1200 F. The absorption does not decrease due to carbon particles in the gas. However, to avoid pluggage it is desirable to operate the absorption unit at 1100 to 1200 F.

* Efficiency is defined as H₂S removed/H₂S inlet x 100.

2. The overall desulfurizing reaction, $\text{H}_2\text{S} + \text{FeO} \rightarrow \text{FeS} + \text{H}_2\text{O}$, is extremely rapid and occurs at the iron oxide surface. The reaction appears limited only by surface saturation. This saturation limit lies above 25 scf of H_2S per 100 square feet of surface. Reaction rate and saturation limit are favored by the higher temperatures.
3. The overall regeneration reaction, $\text{FeS} + \text{O}_2(\text{in air}) \rightarrow \text{FeO} + \text{SO}_2(\text{in air})$ is also extremely rapid in the temperature range of 800 to 1200 F.

On the whole the preliminary experiments reported in this paper indicate that the absorption and regeneration reaction rates are rapid. Diffusion, rather than reaction, will control the design parameters. The surface saturation limit will determine the cycling period.

DISCUSSION

The initial intent of this work was to establish the technical feasibility of this concept of controlling sulfur emission from fossil fuel fired power plants. This feasibility has been established. The second objective was to obtain sufficient performance data to permit making a conceptual plant design and an economic evaluation. These are currently underway. No attempt was made to establish the precise reaction mechanism or the kinetics of the reactions.

TABLE 1. SUMMARY OF RESULTS WITH SPECIALLY-PREPARED SURFACE

Cycle	Diam, inches	Cell Wall Temp, F	Flow Rate, scfm	Velocity in Cell, fps	Length of Cycle, min	Exit Gas Sulfur Concentration**	
						At Start, ppm	At End, ppm
Absorption	0.25	1200	0.112	17.5	7	270 H ₂ S	1870 H ₂ S
Regeneration	0.25	1200	0.111	17.4	3	Large SO ₂ *	0 SO ₂
Absorption	0.25	1200	0.114	17.8	7	~200 H ₂ S	3300 H ₂ S
Regeneration	0.25	1200	0.117	18.3	2	Large SO ₂	0 SO ₂
Absorption	0.25	1200	0.114	17.8	7	~200 H ₂ S	5000 H ₂ S
Regeneration	0.25	1200	0.114	17.8	3	29000 SO ₂	0 SO ₂
Absorption	0.25	1200	0.064	10.0	10	~200 H ₂ S	3170 H ₂ S
Regeneration	0.25	1200	0.064	10.0	5	Large SO ₂	0 SO ₂
Absorption	0.25	1200	0.064	10.0	9	330 H ₂ S	1650 H ₂ S
Regeneration	0.25	1200	0.064	10.0	3	Large SO ₂	0 SO ₂
Absorption	0.25	825	0.064	7.75	9	220 H ₂ S	1700 H ₂ S
Regeneration	0.25	825	0.064	7.75	3	Large SO ₂	0 SO ₂
Absorption	0.25	825	0.064	7.75	9	220 H ₂ S	710 H ₂ S
Regeneration	0.25	825	0.064	7.75	2	Large SO ₂	0 SO ₂
Absorption	0.25	825	0.114	13.8	6	460 H ₂ S	1780 H ₂ S
Regeneration	0.25	825	0.114	13.8	2	Large SO ₂	0 SO ₂
Absorption	0.25	825	0.114	13.8	6	640 H ₂ S	1900 H ₂ S
Regeneration	0.25	825	0.114	13.8	2	Large SO ₂	0 SO ₂

* Due to rapid evolution of SO₂ it was not possible to measure exact amount.

** Inlet sulfur concentration was 10,000 ppm H₂S during absorption and approximately 0 ppm SO₂ during regeneration.
SO₂ exit concentration shown was after an initial transient period.

TABLE 2. SUMMARY OF BENCH-SCALE RESULTS WITH STEEL SURFACE

Cycle	Cell Type	Cell Wall Temp, F	Flow Rate, scfm	Velocity in Cell, fps	Length of Cycle, min	Exit Gas Sulfur Concentration*	
						At Start, ppm	At End, ppm
Absorption	Annular	1200	0.120	10.5	9	320 H ₂ S	2760 H ₂ S
Regeneration	"	1200	0.026	2.3	12	96500 SO ₂	0 SO ₂
Absorption	"	1200	0.060	7.0	33	120 H ₂ S	2740 H ₂ S
Regeneration	"	1200	0.026	2.3	17	151000 SO ₂	0 SO ₂
Absorption	"	1200	0.060	7.0	30	90 H ₂ S	2000 H ₂ S
Regeneration	"	1200	0.026	2.3	12	122000 SO ₂	0 SO ₂
Absorption	"	1200	0.120	10.5	8	110 H ₂ S	2660 H ₂ S
Regeneration	"	1200	0.027	2.4	7	96000 SO ₂	0 SO ₂
Absorption	"	1200	0.120	10.5	8	305 H ₂ S	2200 H ₂ S
Regeneration	"	1200	0.027	2.4	10	133000 SO ₂	0 SO ₂
Absorption	"	1615	0.060	8.8	128	<100 H ₂ S	No Breakthrough
Regeneration	"	1615	0.027	4.0	Large	0 SO ₂	0 SO ₂
Absorption	Tubular	1200	0.064	8.5	13	65 H ₂ S	3100 H ₂ S
Regeneration	"	1200	0.027	3.6	5	10100 SO ₂	0 SO ₂
Absorption	"	1200	0.064	8.5	17	50 H ₂ S	1210 H ₂ S
Regeneration	"	1200	0.031	4.1	5.2	13100 SO ₂	0 SO ₂
Absorption	"	1200	0.064	8.5	20	40 H ₂ S	1280 H ₂ S
Regeneration	"	1200	0.032	4.2	5.8	13100 SO ₂	0 SO ₂
Absorption	"	1200	0.062	8.2	24	45 H ₂ S	1400 H ₂ S
Regeneration	"	1200	0.028	3.7	8.3	12700 SO ₂	0 SO ₂
Absorption	"	1200	0.120	15.9	20	60 H ₂ S	1600 H ₂ S
Regeneration	"	1200	0.038	5.0	12	14300 SO ₂	0 SO ₂
Absorption	"	1200	0.120	15.9	24	90 H ₂ S	750 H ₂ S
Regeneration	"	1200	0.037	4.9	14	16000 SO ₂	0 SO ₂
Absorption	"	1600	0.120	19.7	80	50 H ₂ S	No Breakthrough
Regeneration	"	1600	0.027	4.4	Large	0 SO ₂	0 SO ₂

* Inlet sulfur concentration was 10,000 ppm H₂S during absorption and approximately 0 ppm SO₂ during regeneration.
SO₂ exit concentration shown was after an initial transient period.

FIGURE 1. HIGH TEMPERATURE SULFUR REMOVAL CONCEPT

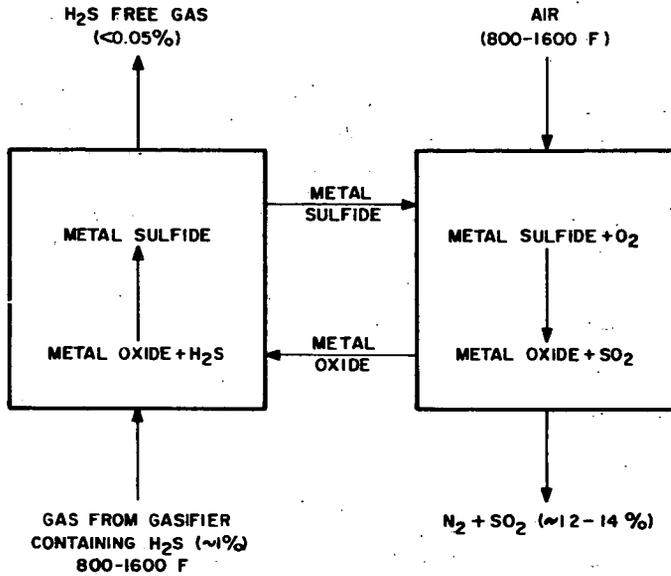


FIGURE 2. TWO-STAGE COMBUSTION POWER CYCLE

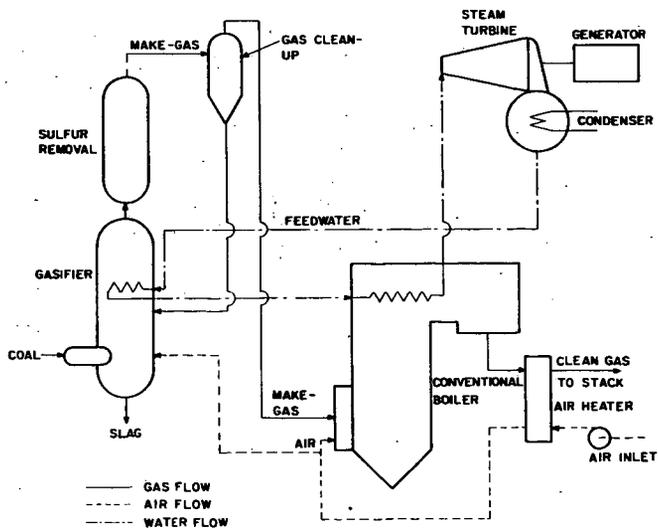


FIGURE 3. SCHEMATIC DIAGRAM OF BENCH SCALE EXPERIMENT

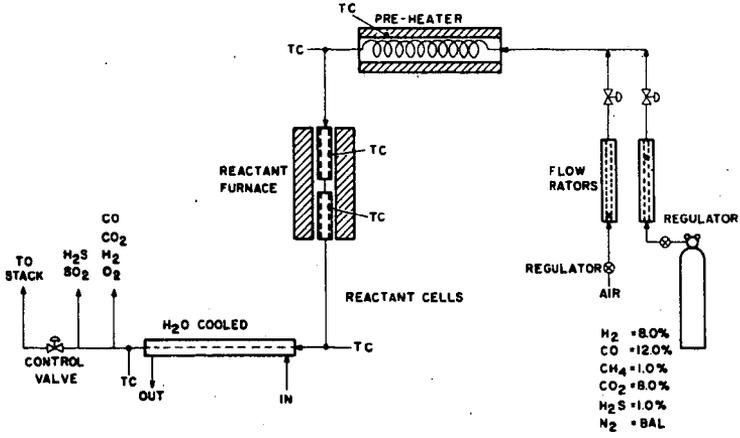


FIGURE 4. SCHEMATIC OF LARGE SCALE TEST ARRANGEMENT

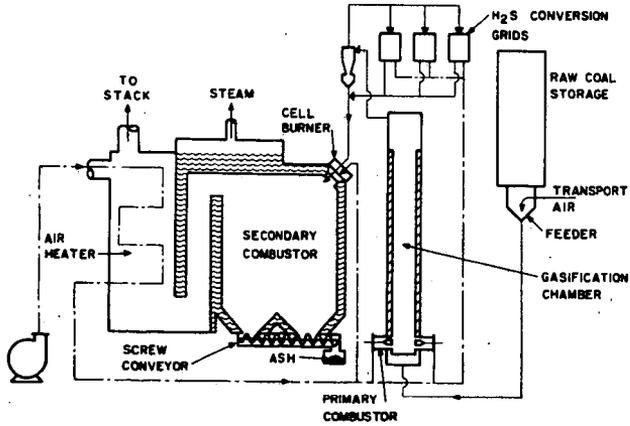


FIGURE 6. ARRANGEMENT OF ABSORPTION CELL FOR LARGE SCALE TESTS

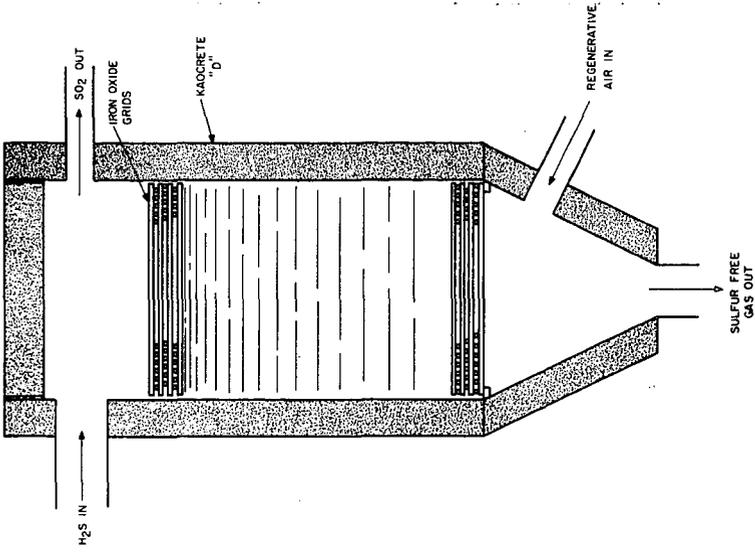


FIGURE 5. PHOTOGRAPH OF PILOT PLANT

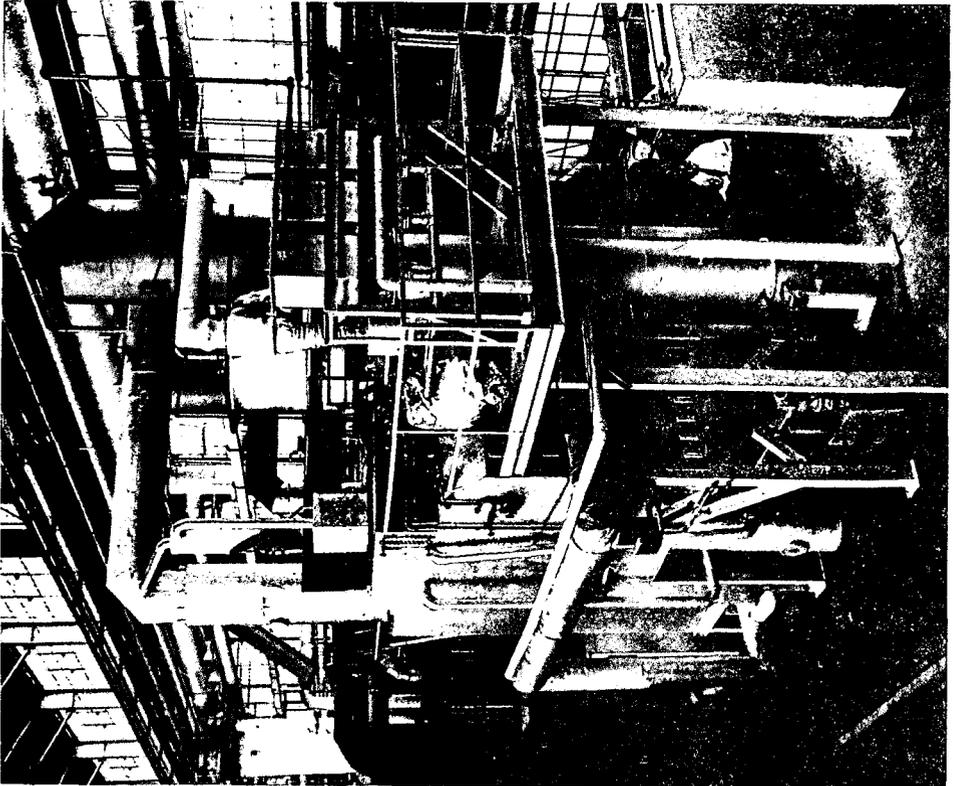


FIGURE 7. TYPICAL H₂S CONCENTRATION VS TIME CURVE DURING ABSORPTION FOR BENCH SCALE TESTS

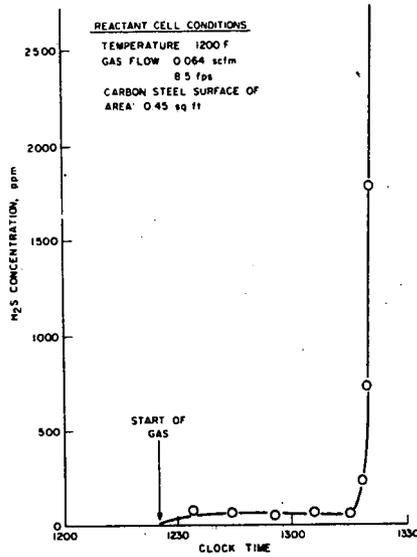


FIGURE 8. TYPICAL H₂S CONCENTRATION VS TIME CURVE DURING REGENERATION FOR BENCH SCALE TESTS

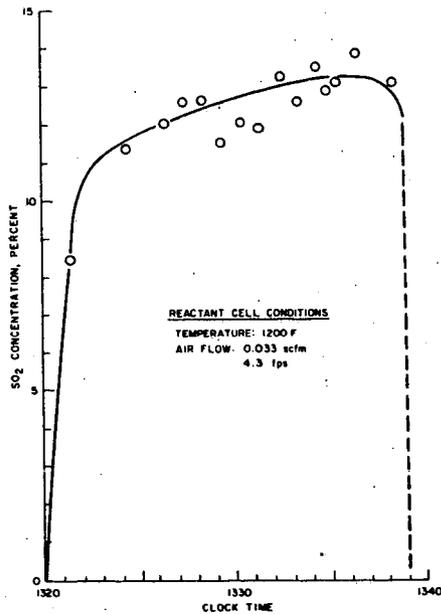


FIGURE 10. PERFORMANCE OF CELLS NO. 1 (NORMAL GRID SURFACE) AND NO. 2 (ONE-HALF GRID SURFACE)

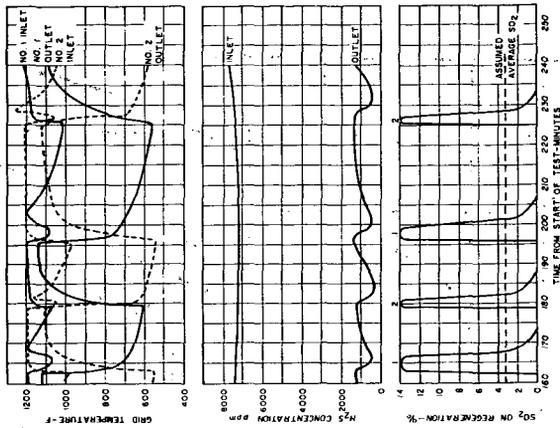
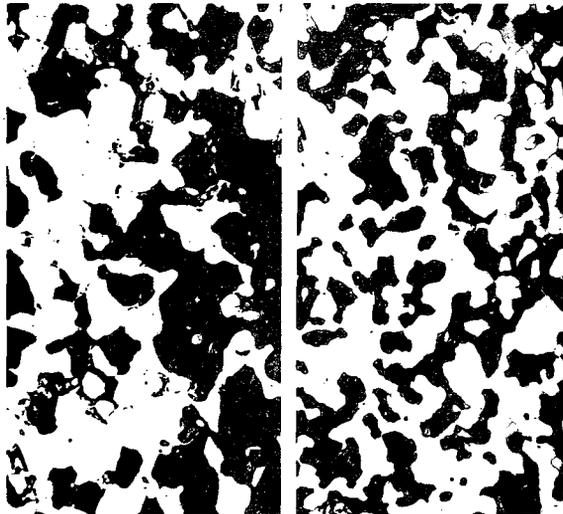


FIGURE 9. PHOTOMICROGRAPH OF REACTANT AFTER ABSORPTION CYCLE



Light network is FeS.
 Gray areas, high in FeO content, appear to contain FeS also.
 Near Surface

White areas are Fe.
 Gray areas are FeO, with little, if any, FeS.
 Interior of Wall

250X Magnification

FIGURE 11. H₂S REMOVAL EFFICIENCY FOR LARGE SCALE TESTS

