

REMOVAL OF SULFUR DIOXIDE FROM POWER PLANT
STACKS BY A MODIFIED CLAUS PROCESS

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A large amount of research and development is being conducted both by government and industry to develop processes for removal of SO_2 from power plant stack gases. These efforts have been stimulated by the activity of the Federal Government in suggesting to local, state and interstate air pollution control agencies that stringent standards be set up on the maximum permissible ground level concentration of SO_2 . The suggested criterion¹ calls, for example, for a maximum ground level concentration over a 24-hour period of 0.1 ppm of SO_2 . It is difficult to relate this criterion to a maximum permissible level of SO_2 in a typical power plant stack since this depends on many factors such as stack height, presence of other pollution sources, meteorological conditions, etc. However, in many instances this would require reduction of the SO_2 content in the stack to a level corresponding to the combustion of a fuel containing much less than 1% sulfur.

There is no doubt that wherever such stringent air quality standards may become legally required, power plant operators will be forced either to install SO_2 -removal equipment or to switch to low-sulfur fuels (if such should be available).

The situation is of particular concern to the coal industry, since over 50% of its production is used for power generation and only a small fraction of the coal produced in the Eastern United States is low enough in sulfur to meet the stringent standards mentioned above.

The most feasible solution to the problem for a coal burning utility at the present time is the installation of SO_2 -scrubbing facilities since removal of sulfur from the coal to the level required is a much more difficult task.

The first system for flue gas cleanup to undergo trial operation on a full commercial-scale is the combined limestone injection and wet scrubbing process offered by Combustion Engineering.² The above system does not produce any valuable by-products and incurs a cost debit for limestone purchase and spent calcium sulfate slurry disposal.

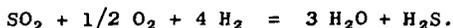
A number of developments is in progress aimed at reducing the net cost of SO_2 scrubbing by sale of by-products, usually either sulfuric acid or sulfur. Some processes are also aimed at the production of either $(\text{NH}_4)_2\text{SO}_4$ or liquid SO_2 as by-products, but these are not of general interest because of restricted markets.

The production of sulfuric acid has a somewhat broader market potential. Two processes are being offered for commercial use, i.e., Monsanto's³ Cat-Ox process and Lurgi's Sulfacid process.⁴ The high cost of shipping sulfuric acid to consuming points, however, also restricts the number of plants to which this approach is applicable.

The production of elemental sulfur on the other hand, considerably broadens the market potential due to its low cost of shipping relative to sulfuric acid. Considerable research and development is underway, therefore, directed at SO_2 scrubbing processes which yield elemental sulfur as a by-product. None of these, however, is as yet available for commercial use.

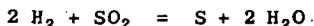
Most of these processes are based on the use of an "alkaline type" absorbent either in form of an aqueous⁵ or molten carbonate⁶ or an alkalized solid support such as alkalized alumina.⁷ The absorption process is associated with unavoidable oxidation, if it is conducted at high temperatures, such that large amounts of alkali sulfate are generally formed. The regeneration system, in general, involves reduction of the alkali sulfate with CO and H₂ mixtures, and recovery of the sulfur as H₂S which is subsequently converted to sulfur in a conventional Claus plant.

This type of process requires more than 3 and as many as 4 mols of CO plus H₂ reductant per mol of sulfur recovered, as typified by the equation below describing the overall process,



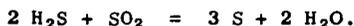
The most convenient way of generating the CO plus H₂ reductant is by way of steam-methane reforming. The thermal efficiency of such plants may be taken as equal to about 70%, based on natural gas feed. It is readily computed on the above basis that the natural gas requirement, where 4 mols of CO + H₂ reductant are required per mol of elemental sulfur recovered, amounts to 48 MM Btu/long ton of sulfur. Present prices for natural gas at most locations in north eastern United States, i.e., in the range of 35-45¢/MM Btu, are such that the reductant cost (\$17-21/long ton of sulfur for a 4/1 mol ratio) places a very high economic burden on such a process even without considering the capital and other significant operating costs of the gas generation and reagent regeneration processes.

It is clear, therefore, that a very large incentive exists to reduce the reductant cost to the theoretical minimum of 2 mols/mol of sulfur recovered as typified by the overall reaction,



or roughly half, as compared with the schemes discussed above.

One method that has been proposed which accomplishes this objective is to inject H₂S into the flue gas and reduce the SO₂ in situ, to produce sulfur by a Claus type process, i.e.,



Two thirds of the recovered sulfur are reduced to H₂S and reinjected into the flue gas. This process, in principle, then produces sulfur with a consumption of only 2 mols of reductant/mol of sulfur produced.

The conventional Claus process is usually operated with concentrated gases using an alumina catalyst at sufficiently high temperatures, usually 400-450°F, such that the sulfur vapor produced does not condense on the catalyst.

Thermodynamic limitations in the case of flue gas, however, preclude such a type of operation. This is illustrated by the equilibrium calculations for a typical flue gas to which 2 mols H₂S/mol SO₂ have been added as illustrated in Figure 1. These calculations were made utilizing the most modern available thermodynamic data.⁸ Data are also shown, for an artificial case, where water is removed from the flue gas to illustrate the adverse effect of water vapor on the equilibrium.

It is seen from Figure 1 that efficient removal of SO₂ from flue gas by the modified Claus technique requires operation at temperatures well below those utilized in the standard Claus process. This is necessitated to a large degree, as shown in Figure 1, by the adverse effect of water vapor on the equilibrium. It should be remembered also, that because of the more noticeable odor of H₂S, the permissible level

of sulfur compounds in the stack should probably be held to a level well under that for SO_2 alone. Thus, operation at very low temperature, i.e., below about 240°F is indicated. Under these conditions, more than 98.5% of the sulfur produced will condense on the catalyst. It is clear, therefore, that either a cyclic or moving-burden process is required to periodically remove the deposited sulfur from the catalyst.

The first attempt to apply such a process to gas purification was made to coke oven gas by Audas.⁹ In this case, the process was applied in reverse, i.e., SO_2 was added to the H_2S -containing gas, and the modified low temperature Claus process was conducted with condensation of the sulfur on the alumina catalyst and its subsequent regeneration.

Application of the concept to flue gas treating was proposed by Kerr¹⁰ in a patent assigned to Peter Spence, Ltd. In both the Audas and Kerr processes, the sulfur-fouled catalyst is cycled through a thermal regeneration step where the sulfur is removed by distillation at about $900\text{--}950^\circ\text{F}$.

More recently, Princeton Research has undertaken work to develop this type of process¹¹ under the auspices of the National Air Pollution Control Administration. Little information is available, however, about the results of their work at this time.

The Consolidation Coal Company undertook evaluation of the "modified Claus Process" in its laboratories since it appears to be potentially one of the most attractive processes for treating flue gas. The work soon showed that the alumina catalyst was rapidly poisoned on cycling through the process, largely due to formation of aluminum sulfate.

A two-step regeneration process now under development is described herein which removes this poison and recovers 93% of the sulfur as elementary sulfur and 7% as ammonium sulfate. The tail gas from the process contains less than 50 ppm of H_2S and SO_2 .

EXPERIMENTAL

The apparatus used is shown in Figure 2. A fixed bed of catalyst is supported on quartz chips in a heated tube through which the simulated stack gas flows. The gases are preheated by passage through Pyrex wool and quartz chips. A central thermo-couple well with adjustable couple position is used to measure the bed temperature. The controlled temperature is taken as the hottest spot in the bed. Water is added to the incoming gases by bubbling one of the gas streams through a water bath held at the proper temperature. Under the conditions used here, elemental sulfur remains on the catalyst and the tail gases pass out through a soda lime trap before being metered. At regular intervals, part of the tail gas is diverted through an iodine scrubber to analyze for H_2S and SO_2 . Catalyst bed depths of one and three inches were used, and a reactor pressure of 810 mm Hg absolute.

Thermal regeneration of the catalyst is carried out by passing nitrogen at 1 to 4 SCFH over the catalyst as it is heated above the boiling point of sulfur to distill off sulfur. The exit gases pass through a sulfur trap (dotted line on Figure 1) and then through the iodine scrubber to analyze for H_2S and SO_2 liberated during stripping. The analysis for H_2S and SO_2 is based on their reactions with iodine as was previously described by Doumani.¹²

Three different aluminas were used as catalysts in these tests. Catalyst A is a commercial dessiccant alumina which contains 1.6% alkali and 2.0% silica. The others are purer, more expensive aluminas with properties given in Table I.

DISCUSSION OF RESULTS

Table II shows the results of short term tests at 300°F (149°C) feeding the stoichiometric ratio: $H_2S/SO_2 = 2$. With neither oxygen or water vapor present, the reaction goes nearly to completion and reaches the thermodynamic equilibrium predicted by Figure 1. With added oxygen, results are nearly equivalent. The presence of both steam and oxygen gives much poorer results (last line, Table II). The thermodynamic equilibrium values of Figure 1 were not approached indicating that the presence of steam has an adverse effect on both the kinetics and equilibrium in the Claus reaction. Results of similar experiments to test the effect of oxygen and steam at higher temperatures, i.e., 360°F, can be seen in Figure 3. The right hand figure gives the results in the absence of oxygen, showing that at this temperature, the reaction, after an initial induction period, gives a tail gas having an even lower content of $H_2S + SO_2$ (900 ppm) than the predicted thermodynamic equilibrium value of 1100 ppm in Figure 1. The low initial SO_2 content of the tail gas is probably due to absorption of SO_2 on the catalyst. When free oxygen is present (as it always is in power plant stacks), the results shown in the left hand half of Figure 3 are obtained. Although the SO_2 concentration was erratic, the rapidly increasing level of H_2S shows how the catalyst became quickly poisoned. Following this test, an appreciable amount of sulfate was found on the catalyst. It is thus clear that undesirable oxidation of SO_2 is taking place.

The next tests were made at the lower temperatures of 212°F (100°C) in an attempt to minimize sulfate formation and to improve the completeness of the reaction. The first cycle of this test (Figure 4) showed surprisingly that the reaction was very fast at this low temperature and that nearly sulfur-free tail gas could be obtained at this temperature, as predicted by the equilibrium curve of Figure 1. Some H_2S breakthrough occurred in the early part of the run and both gases broke through due to filling of pores with product sulfur after about 60 grams of sulfur had been fed per 100 grams of catalyst. During the early period when considerable H_2S breakthrough was observed, it is noted again that no SO_2 broke through. This again is likely due to adsorption of SO_2 by the alumina catalyst.¹³ The adsorptive capacity of alumina for SO_2 is taken advantage of in the Audas⁹ process previously cited. After this "break-out," the run was stopped and the catalyst heated to 950°F in a stream of nitrogen to remove sulfur. The simulated stack gas was then fed over the catalyst again and the process repeated through four cycles. Results from the last cycle (right half of Figure 4) show that the capacity to completely remove SO_2 had been reduced from 60 to less than 10 grams of sulfur fed per 100 grams of catalyst. This loss of capacity was found again to be due to formation of sulfate poisons even at the low temperature of 212°F. The origin of the sulfate is not wholly clear at the present time as it was found that some sulfate is formed at 212°F even when oxygen is excluded from the flue gas. This problem is being investigated further at this time.

Several attempts were made to remove sulfur from the catalyst by means of organic solvents, such as toluene and carbon disulfide, in order to avoid the thermal stripping. Other aqueous solvents, such as ammonium hydrosulfide solutions, with the potential of removing both sulfates and sulfur, also were tested. With all of these solvents the catalyst particles were disintegrated or weakened so that mechanical handling would be impossible.

The final regeneration process which was successful in maintaining activity consists of two stages: 1) heat the sulfur-laden catalyst to strip off sulfur, and 2) treat the stripped catalyst with aqueous ammonium hydroxide to remove sulfates and regenerate an active alumina surface.

The second stage was accomplished by dropping the cooled catalyst (after stripping) into about 50 times its weight of 2% NH_4OH at 75°F. After soaking 15 minutes, the catalyst was removed and rinsed four times with distilled water. After air drying, the catalyst was recharged to the reactor and heated to 400°F in nitrogen to remove ammonia.

Figure 5 shows the results of the first and fifth cycles using the new two-stage catalyst regeneration. Although results of the first cycle are erratic (the SO₂ breakthrough suggests that the feed ratio probably was not exactly at the stoichiometric ratio) it is clear that after five cycles there had been no deterioration. In addition, the initial break-in period with high H₂S values had been eliminated, so that right from the start there was no detectable H₂S or SO₂ until breakthrough at 24 grams of sulfur fed per 100 grams of catalyst. The uneven results thereafter represent attempts to explore the effects of changing the H₂S/SO₂ feed ratio slightly on both sides of 2.0.

No change in catalyst size or weight was detectable after five cycles. After stripping off sulfur, the cooled catalyst was tested for hardness in the Hardgrove Grindability Machine (A.S.T.M. Method D-409). The used catalyst was slightly stronger than fresh catalyst.

Figure 6 shows how the two-stage regeneration has eliminated the poisoning problem. The upper graph shows how the catalyst capacity dropped rapidly when only thermal removal of sulfur was used. The lower graph shows that capacity gradually increased through five cycles with the two-stage regeneration. This may be attributable to precipitation of fresh alumina in the ammonia wash. The overall lower capacity shown by the lower graph is a function of the catalyst used. The catalyst, H, has a pore volume of 0.77 versus 0.55 cc/g for catalyst A. It is also noteworthy that the percentage of sulfur in the products which was recovered as elemental sulfur also gradually increased from cycle to cycle: from 92.2 in Cycle 1 to 95.0 in Cycle 5.

Based on results of Cycle 5, the steady-state sulfur balance for the process would be as follows:

<u>In (As Gases)</u>	<u>Percent of Sulfur Fed to Reactors</u>	
SO ₂ in Stack Gas	31.8	
SO ₂ Recycled from Stripping	1.5	
H ₂ S Recycled from Stripping	1.5	
H ₂ S Made from S Produced	<u>65.2</u>	
	100.0	
<u>Out (On Catalyst)</u>		
Elemental Sulfur	95.0	
Sulfate	2.0	
H ₂ S	1.5	
SO ₂	<u>1.5</u>	
	100.0	
<u>Net Products</u>	<u>Percent of Sulfur Fed in Stack Gas</u>	
Elemental Sulfur	29.8	93.7
Sulfate	<u>2.0</u>	<u>6.3</u>
	31.8	100.0

It should be noted that the process also would handle the small amount of SO₃ present in stack gases, giving a slightly higher yield of sulfate.

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TABLE ICatalyst Analyses

Catalyst Composition, ppm	A	C	H
Na	11,900 ⁽¹⁾	5	180
Si	9,300 ⁽¹⁾	< 100	560
Fe	840	40	280
Ca	--	37	9,100
Al	Balance	Balance	Balance
Surface Area m ² /g	390	200	218
Pore Volume, cc/g	0.55	0.42	0.77
Bulk Density, Lb/CF	54	--	32

(1) This corresponds to 2% SiO₂ and 1.6% Na₂O.

TABLE IIThe Effect of Water and Oxygen on Reaction Efficiency

Conditions: Catalyst C

Temperature 300°F

VHSV = 4200

Bed Height = 1 Inch

<u>Feed Gas Composition, Vol %</u>				<u>Tail Gas Composition, ppm</u>	
SO ₂	H ₂ S	O ₂	H ₂ O	SO ₂	H ₂ S
0.163	0.325	0	0	< 50	< 50
0.159	0.317	1.23	0	< 50	50
0.307	0.614	2.40	6.0	700	1400

Figure 1

EQUILIBRIUM CONCENTRATION IN TAIL GAS AND PERCENT OF SULFUR FORMED WHICH CONDENSES vs OPERATING TEMPERATURE

<u>VOL. %</u>	<u>NORMAL-○-</u> <u>WET FEED</u>	<u>DRY FEED -△-</u>
H ₂ S	0.6	0.6
SO ₂	0.3	0.3
H ₂ O	6.0	0.0
OTHER	93.1	99.1

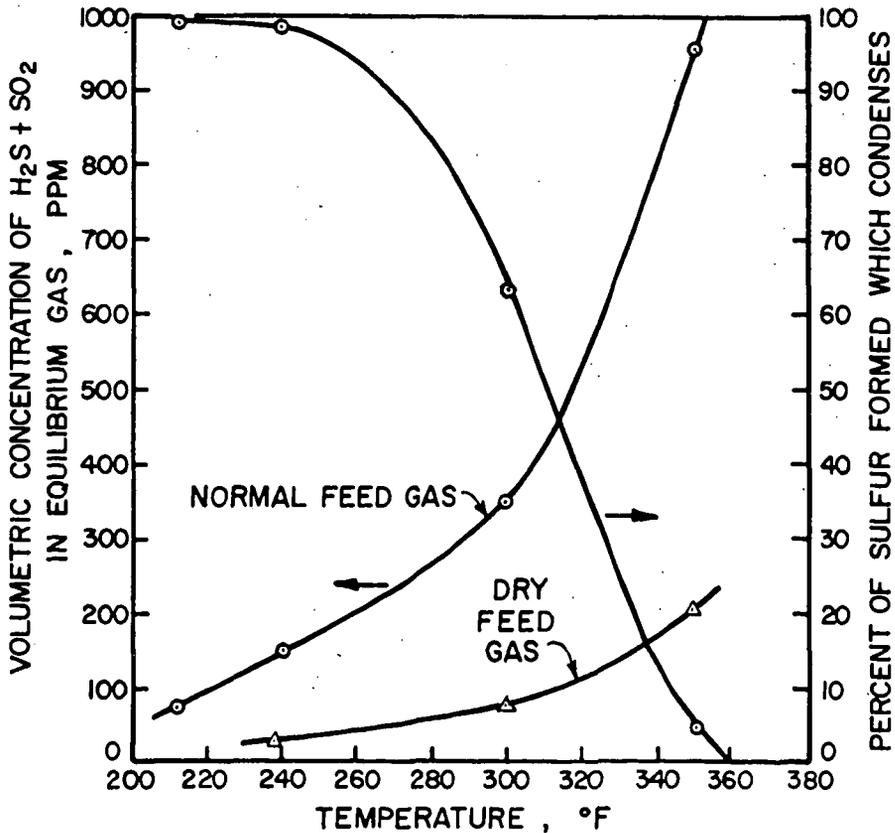


Figure 2

EXPERIMENTAL APPARATUS

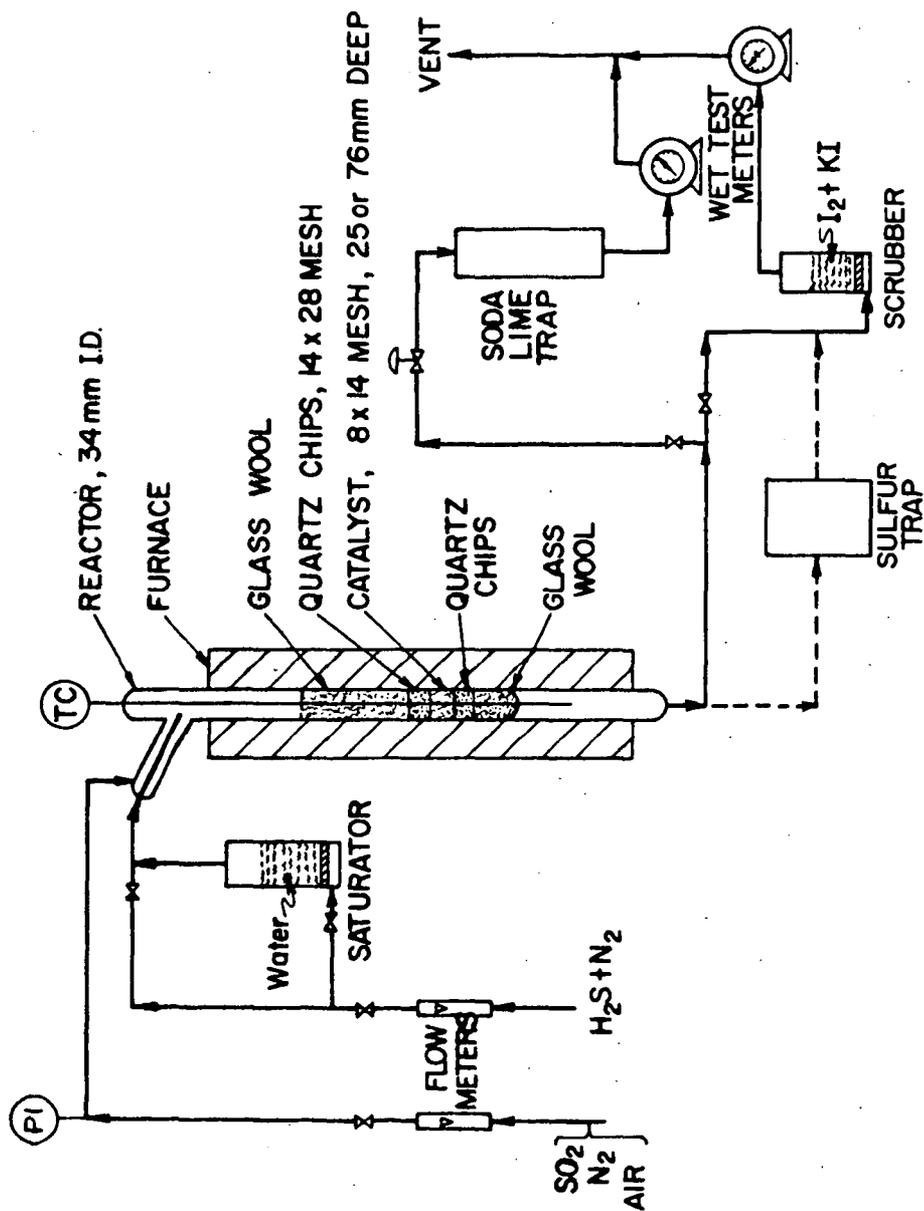


Figure 3

THE EFFECTS OF OXYGEN AT 360°F

CONDITIONS: CATALYST H
 TEMP. 360°F
 VHSV 1500

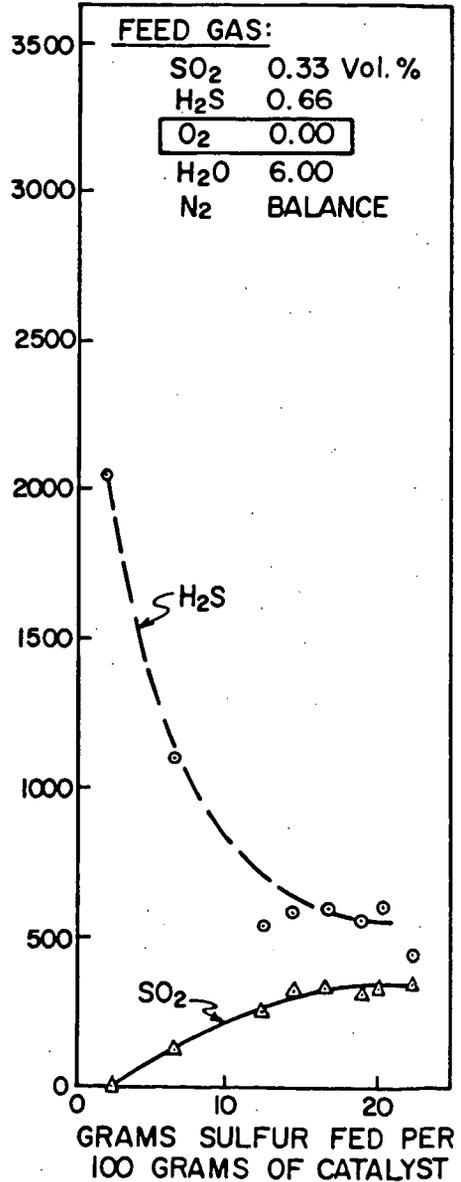
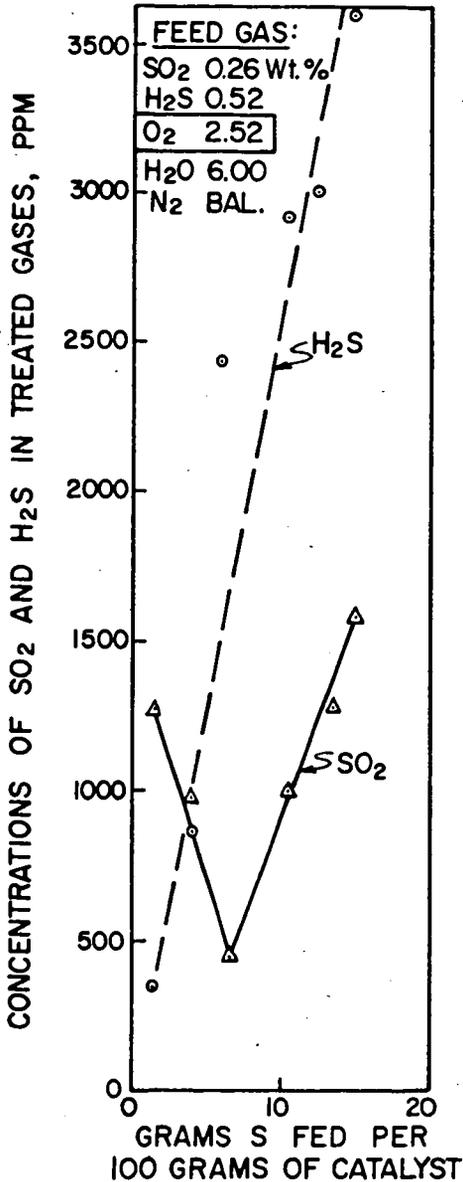


Figure 4

DECREASE IN CATALYST ACTIVITY USING SINGLE-STAGE THERMAL REGENERATION

CONDITIONS:

CATALYST	H
REACTION TEMP.	212°F
VHSV	1425
REGENERATION IN N ₂	950°F

FEED GASES:

SO ₂	0.24 Vol. %
H ₂ S	0.46
O ₂	2.01
H ₂ O	6.00
N ₂	BALANCE

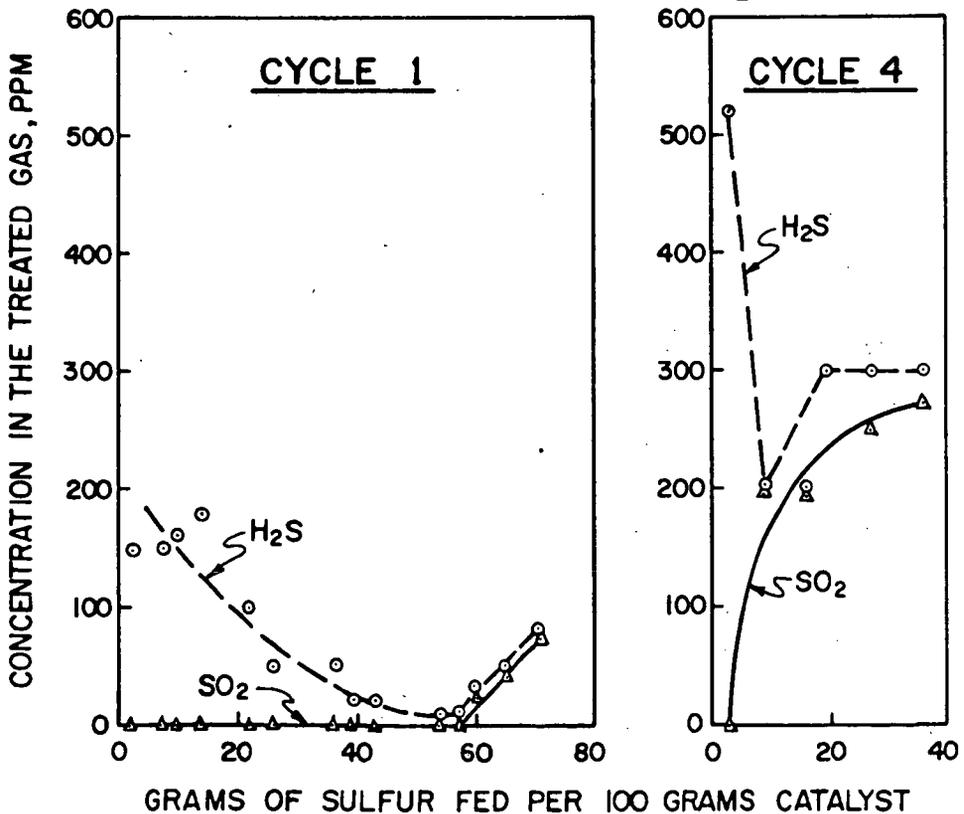


Figure 5

CATALYST ACTIVITY USING THE CONSOL TWO-STAGE REGENERATION

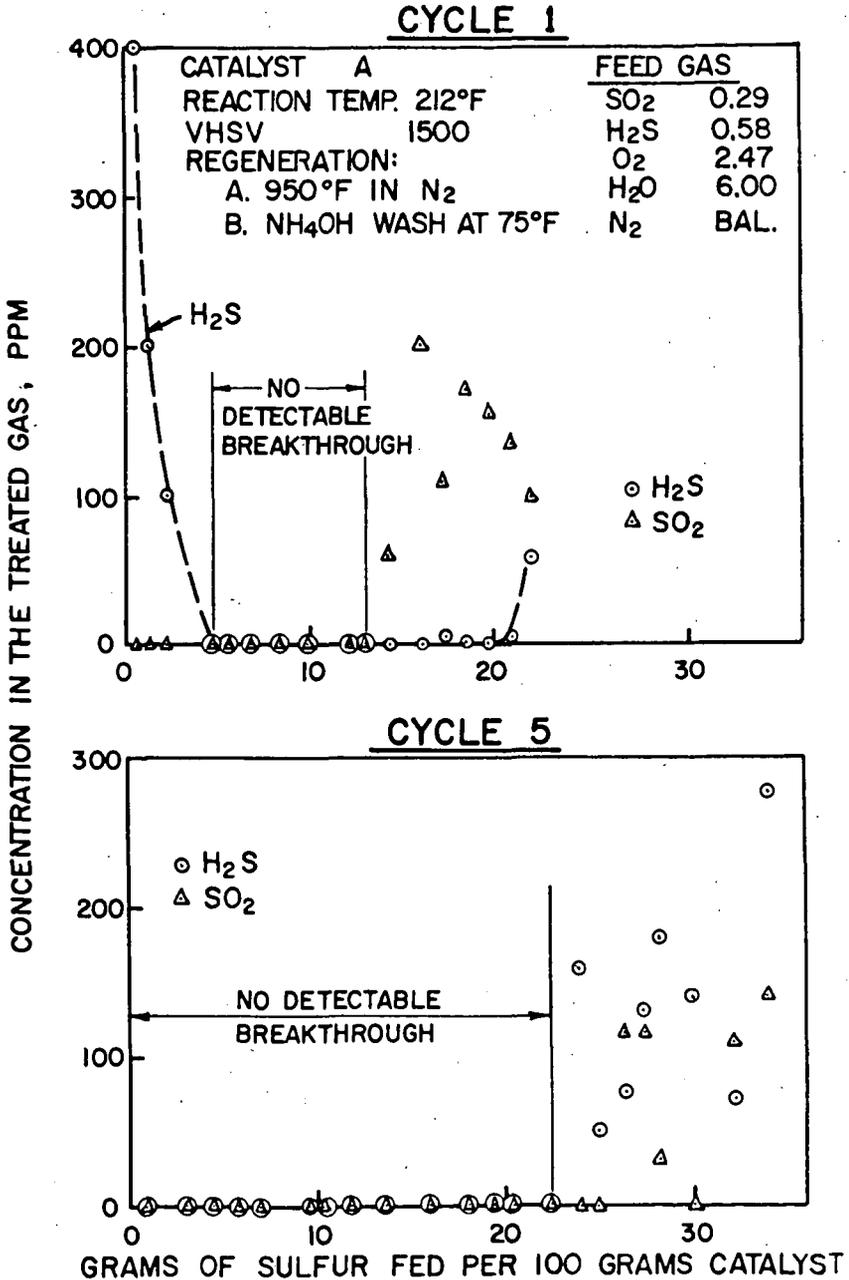


Figure 6AMOUNT OF STACK GAS FED PRIOR TO SULFUR DIOXIDE BREAKTHROUGH