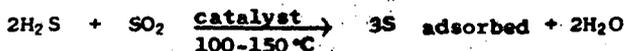


THE RECOVERY OF SULPHUR FROM SULPHIDE ORE
SMELTER WASTE GASES, CONTAINING LOW CONCENTRATIONS OF SO₂

R.G.W. Laughlin, F. J. Hopton and V.B. Sefton

ABSTRACT

A low temperature (100-120°C) Claus reaction is suggested as the basis of a recovery process to obtain sulphur from waste gases, containing low concentrations of sulphur dioxide, emitted during sulphide ore smelting. The catalyst for the reaction acts as an adsorbent for the sulphur produced.



A hot reducing gas passed through the loaded catalyst strips off the sulphur and also regenerates the catalyst for further reaction and adsorption. After condensation, two thirds of the sulphur is used to produce hydrogen sulphide for the Claus reaction and the remainder may be sold to defray expenses. Several methods for hydrogen sulphide production have been examined and the reactions between natural gas and producer gas with sulphur or sulphur dioxide are discussed. Tests of the process on site at a smelter indicate that the process would work successfully to desulphurize gases containing 1-2% sulphur dioxide by volume. Two major process flow schemes are considered, one suitable for a smelter where a strong 10-15% sulphur dioxide stream is available for hydrogen sulphide production, the other where no such stream exists. Preliminary process economics are discussed.

1. INTRODUCTION

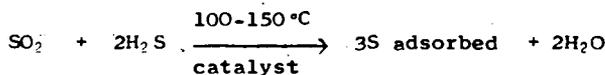
Sulphur dioxide is now universally recognized as a harmful air pollutant. The use of tall stacks, and the existence of reasonable weather patterns, have generally minimized the effect of SO₂ on people, buildings, and plants. Unusual geographic and weather conditions have lead to several catastrophes attributable to SO₂, e.g. Donora, Pennsylvania (1948)(1); and London, England (1952).

Two major sources of SO₂ pollution are coal and residual oil fired thermal electric generating stations and sulphide ore smelting operations. These sources account for 50% of the 15-20 million tons of sulphur(2) emitted to the atmosphere in North America each year. The concentrations of SO₂ in the effluent gases from these operations are 0.1-0.3% by volume SO₂ from generating plants and 1.0-15.0% from smelters. In Ontario 150,000-200,000 tons per year of sulphur are emitted from generating stations, and 1.5-2 millions tons/year from smelting operations.

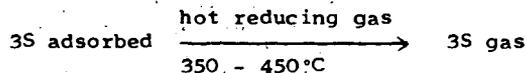
In late 1966, the Ontario Research Foundation initiated an investigation into an SO₂ removal scheme, which would be applicable to both generating plants and sulphide ore smelters. The process was aimed at both air pollution abatement and resource conservation. It was considered essential to recover sulphur in the elemental form, since this incurs minimum transportation costs per unit weight of sulphur. Ontario is already well supplied with sulphuric acid manufactured from high strength SO₂ streams being emitted from the Sudbury complex of nickel smelters. Any further sulphur recovered in Ontario would, therefore, have to be transported away from the province, thus the minimum transportation cost is essential.

The O.R.F. process(3,4) is based on a low temperature Claus reaction(5). The SO₂ in the effluent is catalytically reduced to sulphur with H₂S; a portion of the sulphur is retained as product and the balance is converted to H₂S and recycled. Fig. 1 shows a simple flow sheet for the process. The chemistry of the process is summarized in the reactions given below:

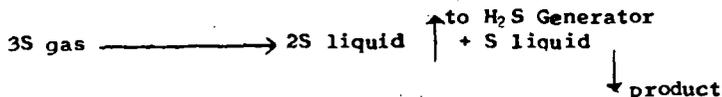
i) Reduction and Adsorption



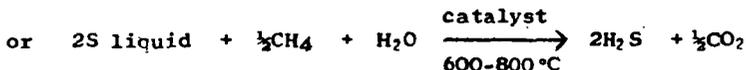
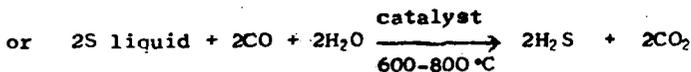
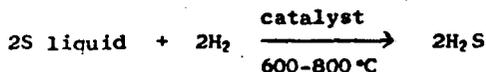
ii) Catalyst Regeneration



iii) Sulphur Condensation and Splitting



iv) H₂S Production



2. CATALYST SELECTION

The properties required for a successful catalyst/adsorbent in this process are:-

- i) High catalytic efficiency for the H₂S/SO₂ reaction in the presence of both oxygen and water.
- ii) High adsorptive capacity for sulphur.
- iii) Long active catalytic life.
- iv) High mechanical strength, low attrition loss potential.
- v) Low cost.

Tests in the laboratory were carried out using a 1% SO₂ and 2% H₂S stream passing over 10 grams of some 30 different catalysts with a gas contact time of 0.3 seconds. The results showed that the three following catalysts exhibited the best potential for fulfilling the first two required properties. Activated aluminas (Kaiser Chemicals KA-201 and Alcoa F-1) and a treated Bauxite (Engelhard Porocel SRC). All three catalyzed the reaction of H₂S with SO₂ preferentially to the reaction between H₂S and oxygen at low temperatures (<150°C). At higher temperatures the oxidation of H₂S to water and SO₂ was favored as would be expected.

Subsequent tests showed that Kaiser KA-201 activated alumina was the best catalyst for sulphur loading, mechanical strength, and maintenance of catalytic activity, over several loading and regenerating cycles. The efficiencies of the three catalysts for the H₂S-SO₂ reaction at increasing sulphur loadings are shown in Fig. 2.

Analyses of the gas streams in the laboratory tests were made using a Perkin Elmer 154L gas chromatograph with a polypropylene glycol on chromosorb W column. This instrument was also used in the subsequent field tests.

3. FIELD TESTS

Having shown the feasibility of the reduction step in the laboratory, and having defined the optimum range of operating conditions, it was decided that some field tests should be carried out.

Two series of tests were arranged, one at an Ontario Hydro Generating Station, the other at a nickel/copper smelter in Ontario

3.1 Tests at the Generating Station

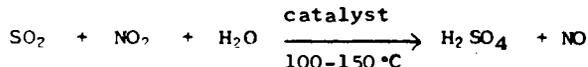
A small reactor containing KA-201 catalyst was set up and gas pulled through it by a pump at a controlled rate from a duct downstream of the electrostatic precipitators used in this station. The composition of this gas stream was:

SO ₂	1400-1500 ppm
NO _x	150-300 ppm
P ₂	3%
H ₂ O	10%
CO ₂	12-13%
N ₂	Balance

H₂S from a gas cylinder was bled into the gas stream upstream of the reactor to give a concentration of 2800-3000 ppm.

The results of these tests were extremely poor. Very low efficiency for SO₂ removal was found and very low sulphur loadings obtained. Several different catalysts were tried, but with no improvement of results.

A tentative explanation for this failure is offered. It is suggested that the NO_x in the gas stream causes poisoning of the catalyst by oxidizing SO₂ to SO₃ on the catalyst surface in the presence of moisture.



It is speculated that the H₂SO₄ on the surface inhibits the reaction between H₂S and SO₂. The extent of the inhibition was so great that further work on the application of the process to generating stations was terminated. The identification of NO_x as the cause of reaction inhibition was made by carrying out tests in the laboratory with and without 100 ppm to NO_x in the gas stream. Results of these laboratory tests were similar to those obtained during the field tests.

3.2 Tests at the Smelter

With the higher sulphur dioxide concentrations (>1.0%) expected in the smelter gases and much lower NO_x concentrations, it was thought that the poisoning process would be less likely to inhibit the H₂S-SO₂ reaction.

The composition of the gas streams tested at the smelter were as follows:-

	<u>From the Converters</u>	<u>From the Roasters</u>
SO ₂	0.2 - 2.2% mainly 0.8-1.1% mean 0.9%	0.9 - 1.4% - 1.2%
NO ₂	< 20 ppm	< 20 ppm
SO ₃	~150 ppm	~150 ppm
O ₂	~17%	17%
H ₂ O	~1%	2%
Nitrogen	Balance	Balance

A 50 gram catalyst bed of Kaiser KA-201 was used to test the effectiveness of SO₂ reduction and sulphur adsorption. The results agreed well with those found in the laboratory with simulated gas mixtures. The catalyst was regenerated using a reducing gas mixture of hydrogen and nitrogen. The catalytic activity was completely restored, and the catalyst was reloaded. This adsorption-regeneration cycle was repeated 10 times with no apparent loss in catalytic activity.

A problem encountered working with the smelter stream was the extreme variability in SO₂ concentration. In order to ensure that H₂S is not released into the atmosphere it will probably be necessary to run the process with a deficiency of H₂S. One set of loading-regeneration runs was carried out using approximately 60% of the theoretical H₂S required. No drop in efficiency was observed. It should, therefore, be quite possible to run the process with 90 or 95% of the theoretical H₂S requirement. Fig. 3 shows the variation of the SO₂ concentration with time in the gas stream from the converters. H₂S injection into the gas stream in the plant would have to be controlled by an SO₂ detector upstream of the catalytic reactor.

4. PRODUCTION OF H₂S

All the laboratory and field tests of the reduction step used pure H₂S from a gas cylinder.

H₂S could be produced in many ways for this process. A number of plausible reactions were examined experimentally in the laboratory.

4.1 Production of H₂S in the Catalyst Regeneration Step

This method of H₂S production does not fit into the general flow sheet shown in Fig. 1. It is shown diagrammatically in Fig. 4. A hot gas stream containing CO, H₂ and steam, such as might be produced from the partial oxidation of natural gas, is passed through the sulphur laden catalyst bed, heating the catalyst to about 400°C. Part of the sulphur is converted to H₂S and COS. The stream is then passed over a second catalyst bed of Harshaw Fe-0901 sulphided iron on alumina catalyst, at 350°C. The remaining sulphur, CO, H₂ and steam react together to give hydrogen sulphide and traces of carbonyl sulphide. The quantities of reducing gases used to regenerate the catalyst would be sufficient to reduce only two-thirds of the sulphur on the catalyst. Thus, one-third of the sulphur is stripped from the catalyst unreacted. This is condensed to give a marketable liquid or solid sulphur product.

4.2 Production of H₂S by Direct Reaction of Sulphur with Methane



Tests were made using several catalysts. Kaiser KA-201 and Harshaw H-151 activated aluminas gave the best conversion. Fig. 5 shows the relationship between temperature and contact time for complete reaction of methane and sulphur. Also shown is the effect of a 10% excess of sulphur on the required contact time. As can be seen, a substantial reduction in temperature, for complete reaction of methane is achieved by using a greater than stoichiometric quantity of sulphur. It may be more economical to operate the H₂S production unit in this manner, constantly recycling the small excess of sulphur.

4.3 Production of H₂S by Reaction of SO₂ with Methane

H₂S may be synthesized by the direct reduction of SO₂ with methane⁽⁶⁾ i.e.



This reaction requires a suitable catalyst to occur at reasonable temperatures, i.e. about 700°C.

Our investigations showed that nickel sulphide supported on Harshaw H.151 Alumina was a suitable catalyst for this reaction. Complete reaction of methane was achieved at 720°C with a methane to SO₂ ratio of 0.75 and a gas contact time of 0.56 sec.

The Texas Gulf Sulphur Co. have a patent⁽⁷⁾ on the reaction of sulphur dioxide with methane. This examines the reaction with a methane to SO₂ ratio of 0.5.



This reaction was found to be only 60-70% complete at 800°C over an alumina catalyst.

The reason for examining the possibility of producing H₂S directly from SO₂ is because some of the waste streams in the smelter contain 10-15% SO₂ with very little oxygen. If this stream can be directly reduced by methane, savings are realized on two counts.

1) The reaction:



is exothermic ($\Delta H^{700^\circ\text{C}} = -15,500$ B.T.U./16 mole H₂S produced)

while the reaction:



is endothermic ($\Delta H^{700^\circ\text{C}} = +31,000$ B.T.U./16 mole H₂S produced)

Thus, the additional heat produced in the CH₄ - SO₂ reaction may be utilized to raise the temperature of catalyst and gases towards the necessary reaction temperature of 700°C. For the CH₄-S reaction, additional methane would have to be combusted to provide this heat.

While it appears from the equations that the CH₄-S reaction requires one-third as much methane to produce the same amount of H₂S, it must be remembered that two-thirds of the contained sulphur is recycled. Hence the amount of methane per unit of product sulphur is the same for both reactions.

2) Use of the CH₄-SO₂ reaction to produce H₂S decreases the heat requirement per unit of sulphur product, for heating the catalyst and stripping the sulphur in the regeneration step, since all of this sulphur is product sulphur. Also, the amount of catalyst recycled per unit of sulphur product is reduced to one-third, thus decreasing catalyst loss due to attrition and deactivation.

4.4 Production of H₂S by Reaction of Methane with a Mixture of Sulphur and SO₂

In a practical situation part of the required H₂S may be produced by direct reduction of SO₂, but it may be necessary to supplement this by H₂S from sulphur. An experiment was run using a mixture of SO₂ and sulphur (SO₂, 44% of total sulphur) over Kaiser KA-201 catalyst. Fig. 6 shows that higher temperatures were required for this mixed reaction. No explanation of the inhibition phenomena which must exist is offered at this time. The results suggest that it would be preferable to run the two reactions separately.

5. PROCESS FLOW SHEETS AND PRELIMINARY ECONOMICS

The flow sheets shown in Figs. 7 and 8 are based on the concentrations, flow rates, and gas temperatures of streams from an Ontario smelter.

The waste gas flows from this smelter are as follows:

Converters - 1,770,000 a.c.f.m. at 256°F total gas flow
1.12% SO₂
36.4 tons/hour sulphur

Fluid bed roasters - 190,000 a.c.f.m. at 256°F total gas flow
13% SO₂
45.6 tons/hour sulphur

Total annual sulphur production 700,000 tons

Flowsheet "A" considers combining these two streams and treating them both in the reactor. H₂S is then manufactured from two-thirds of the sulphur condensed from the regenerator.

Flowsheet "B" considers using the 12% SO₂ stream from the fluid bed roasters to produce H₂S by direct reduction with natural gas; savings in heat requirement, catalyst circulation, and reactor size are realized.

Detailed capital cost estimation is difficult at this stage, before a comprehensive pilot plant study has been completed.

A brief discussion of each of the major plant items is given below:

i) The Reactor

It is envisaged that a fluidized bed reactor will be used. Because of the huge volumes of gas to be handled, a series of fluid bed reactors will be used in parallel. For the combined stream using a flow velocity of 3 ft/sec., a total reactor area of 12,500 ft² is needed; this would be equivalent to 6 or 7 50' diameter reactors. The minimum bed depth required at this flow rate would be 1.2 feet, based on experimental data for 100% H₂S removal at a 60 grams sulphur per 100 grams catalyst loading. This would involve a pressure drop of 10-12 inches of water across the bed.

Water sprays would be incorporated into the bed for temperature control. The H₂S/SO₂ reaction is exothermic, and if the temperature is allowed to rise too far, oxidization of H₂S by air begins.

Cyclone separators would be used to remove fines entrained in the exit gas.

ii) The Regenerator

Much smaller volumes of gas are involved in the regeneration step. Either fluidized or fixed bed operation could be considered for this operation. It is probable that a fluidized bed will be preferred for temperature control, and a lower pressure drop across the bed.

iii) The H₂S Producer

Again, a fluidized bed comparable in size to the regenerator will be used. A fairly deep bed will be required to achieve the contact time needed for complete reaction. This vessel will require ceramic lining to withstand the high temperatures and corrosive conditions encountered in this step.

5.1 Costs

The capital costs for the 700,000 tons of sulphur per year application discussed above, has been estimated from the data presently available to be of the order of \$25,000,000 - \$30,000,000. Our best estimate of costs per ton of sulphur produced is given in Fig. 9; processes based on both Flow Sheet A and Flow Sheet B are considered. Scheme B shows markedly better economics than scheme A.

Another way of reducing costs would be an upgrading of the gas stream from 1% SO₂ to 4 or 5% SO₂, thus reducing the volume of gas and cutting down the size of reactor required to a quarter or a fifth of what is needed now. This upgrading could probably be achieved by better hooding and control of dilution air.

The costs of \$20 - \$28 per ton of sulphur produced looked most encouraging, when this work was started, since the price of sulphur at that time was \$30 - \$40/ton. The present \$8 - \$10 per ton for sulphur makes the process economics much less attractive, but it compares very favourably with other proposed processes for treating dilute SO₂ streams.

6. MAJOR CONCLUSIONS AND THE STATUS OF THE PROCESS

6.1 Conclusions

Small scale field and laboratory tests have shown that:

- a) SO₂ from an actual smelter gas containing ~1% SO₂ by volume can be reduced to sulphur and adsorbed on a catalyst bed at 100 - 150°F, by adding H₂S to the gas stream.
- b) The sulphur can be removed from the catalyst and condensed to give a liquid or solid sulphur product.

- c) The catalyst can be completely regenerated for reuse in the reduction-adsorption step at 350-450°C.
- d) Hydrogen sulphide for the reduction step, can be produced by the catalytic reaction of methane with sulphur or with a fairly concentrated (>10% by volume) SO₂ stream at 650-800°C.
- e) The information available from the small scale tests is sufficient to begin the design and building of a pilot plant.

7. ACKNOWLEDGEMENT

The authors gratefully acknowledge that the work described above was supported in part by Canadian Industries Ltd.

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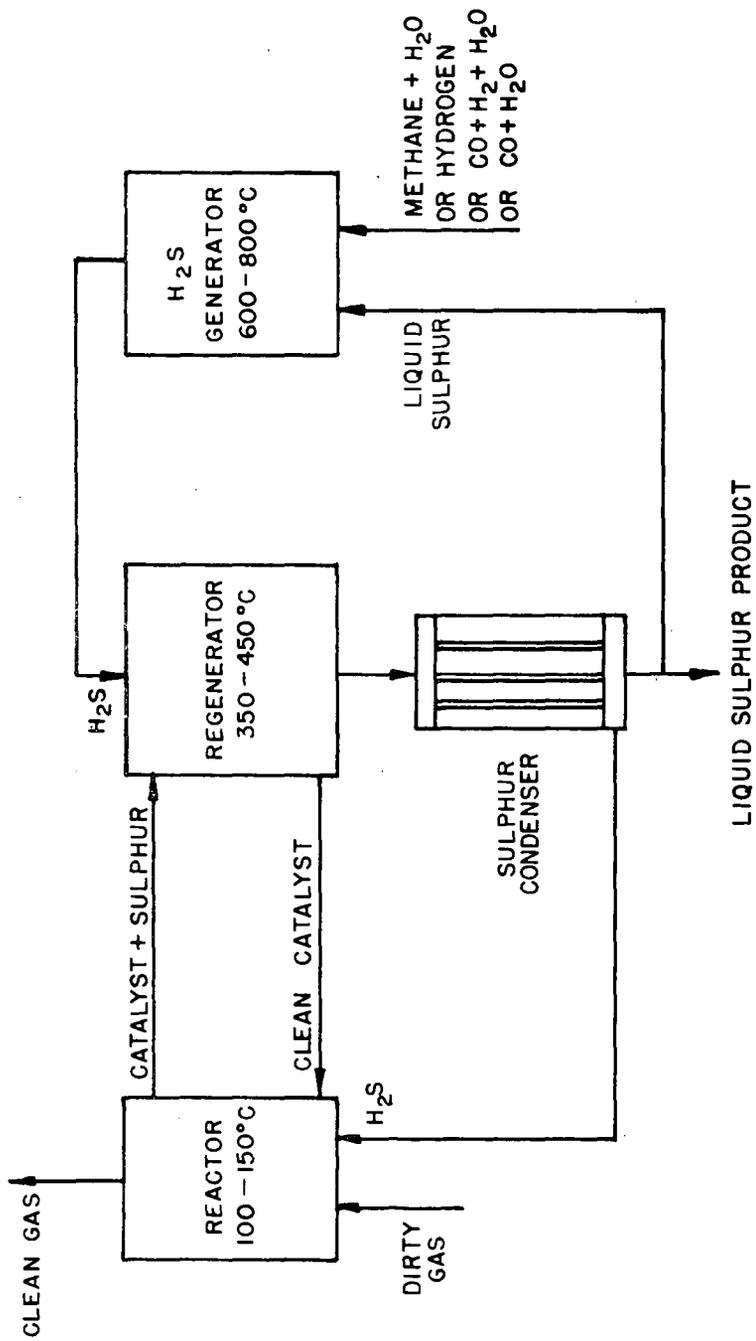


FIG. 1. GENERAL BLOCK DIAGRAM OF THE PROCESS

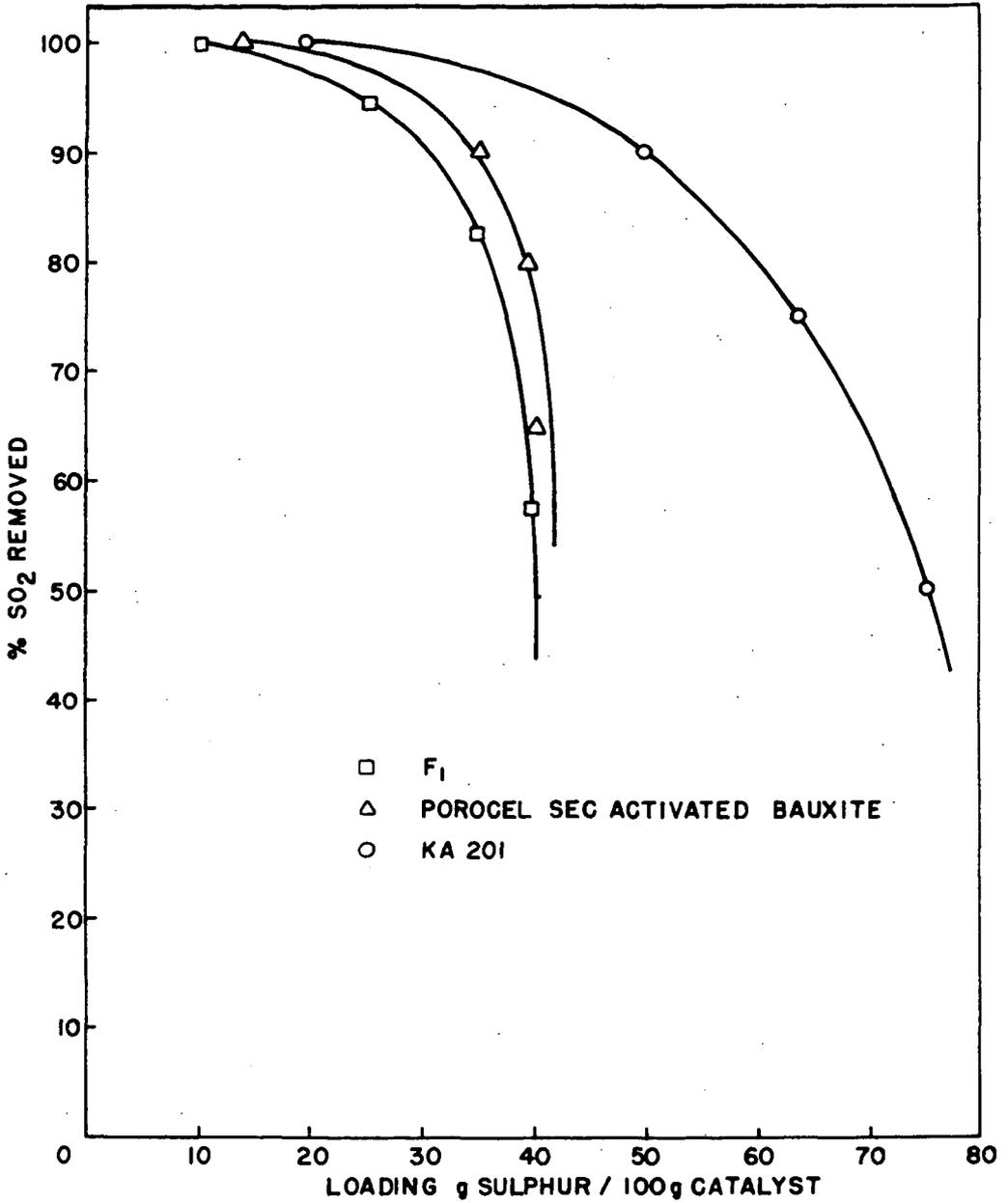


FIG. 2

THE EFFECT OF SULPHUR DEPOSITION ON CATALYTIC EFFICIENCY

REACTION TEMP. 120°C. GAS CONTACT TIME 0.3 SECS

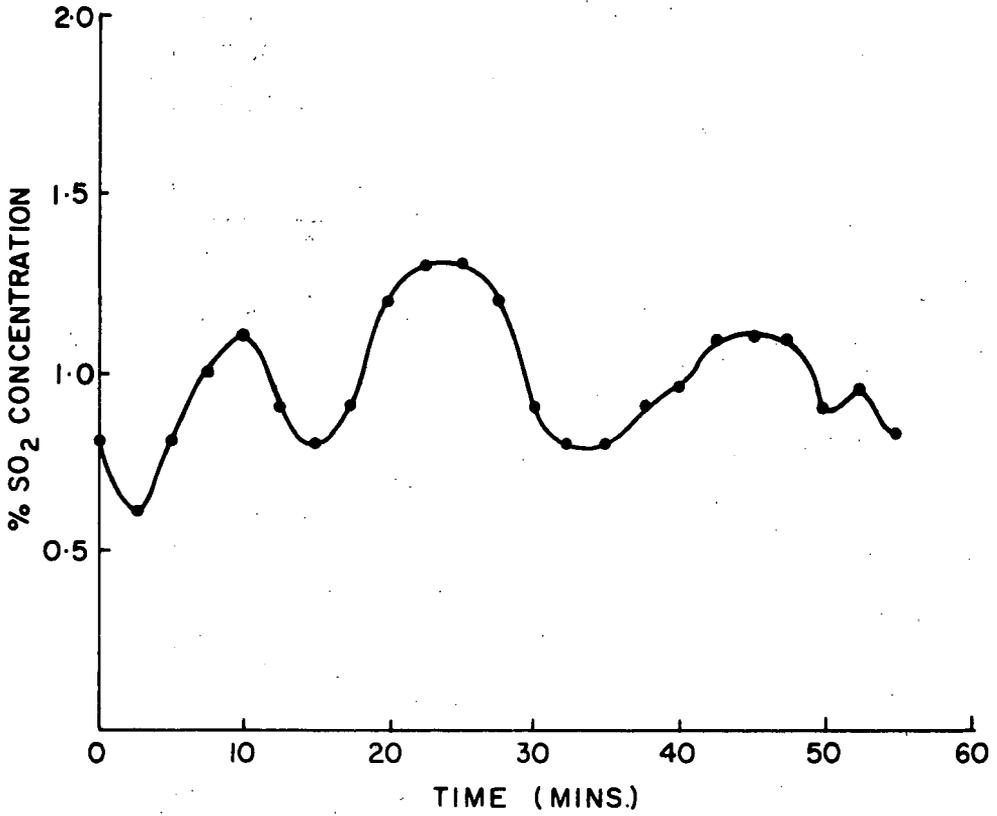


FIG. 3.

TYPICAL VARIATION OF SO₂ CONCENTRATION IN THE WASTE GASES FROM THE CONVERTERS

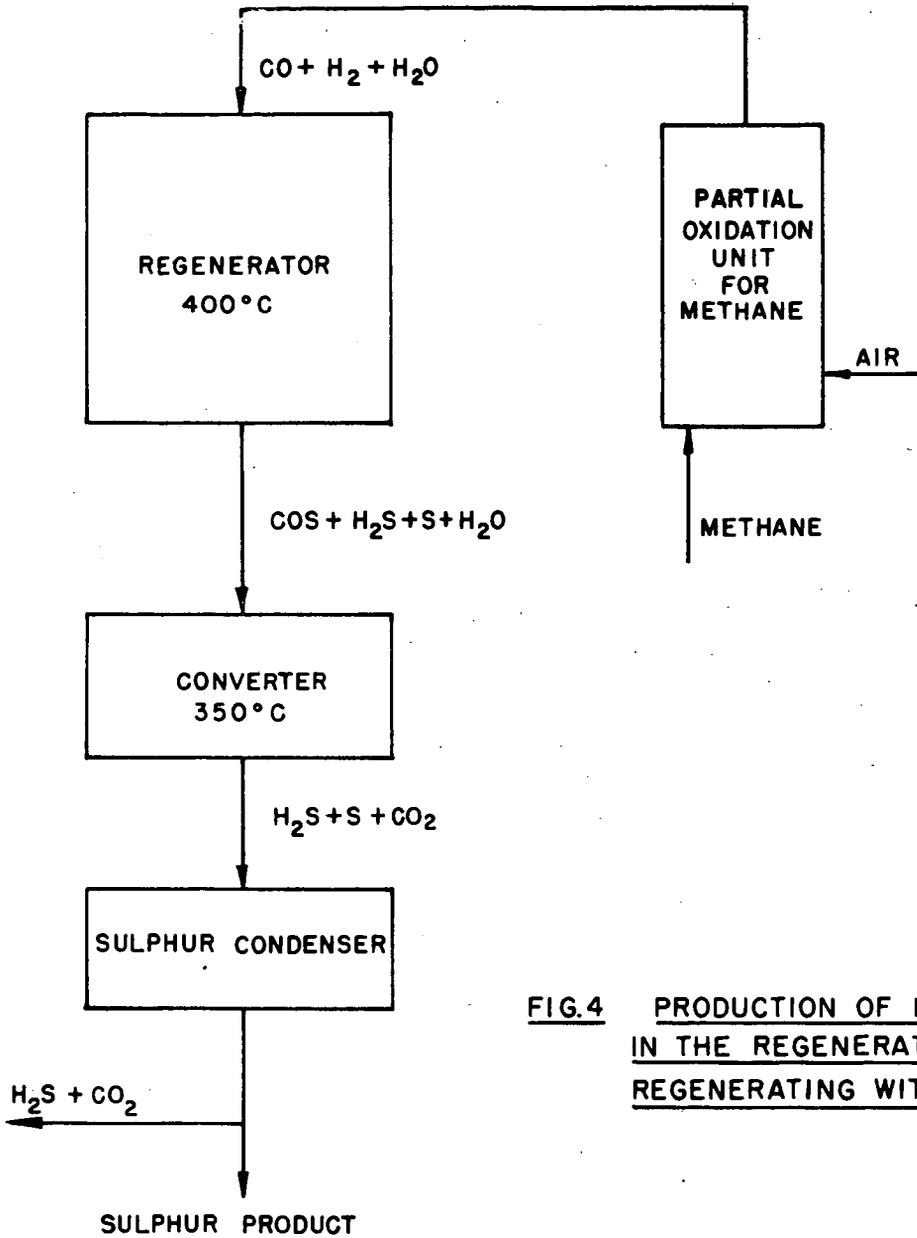


FIG.4 PRODUCTION OF H_2S
IN THE REGENERATOR BY
REGENERATING WITH CO/H_2

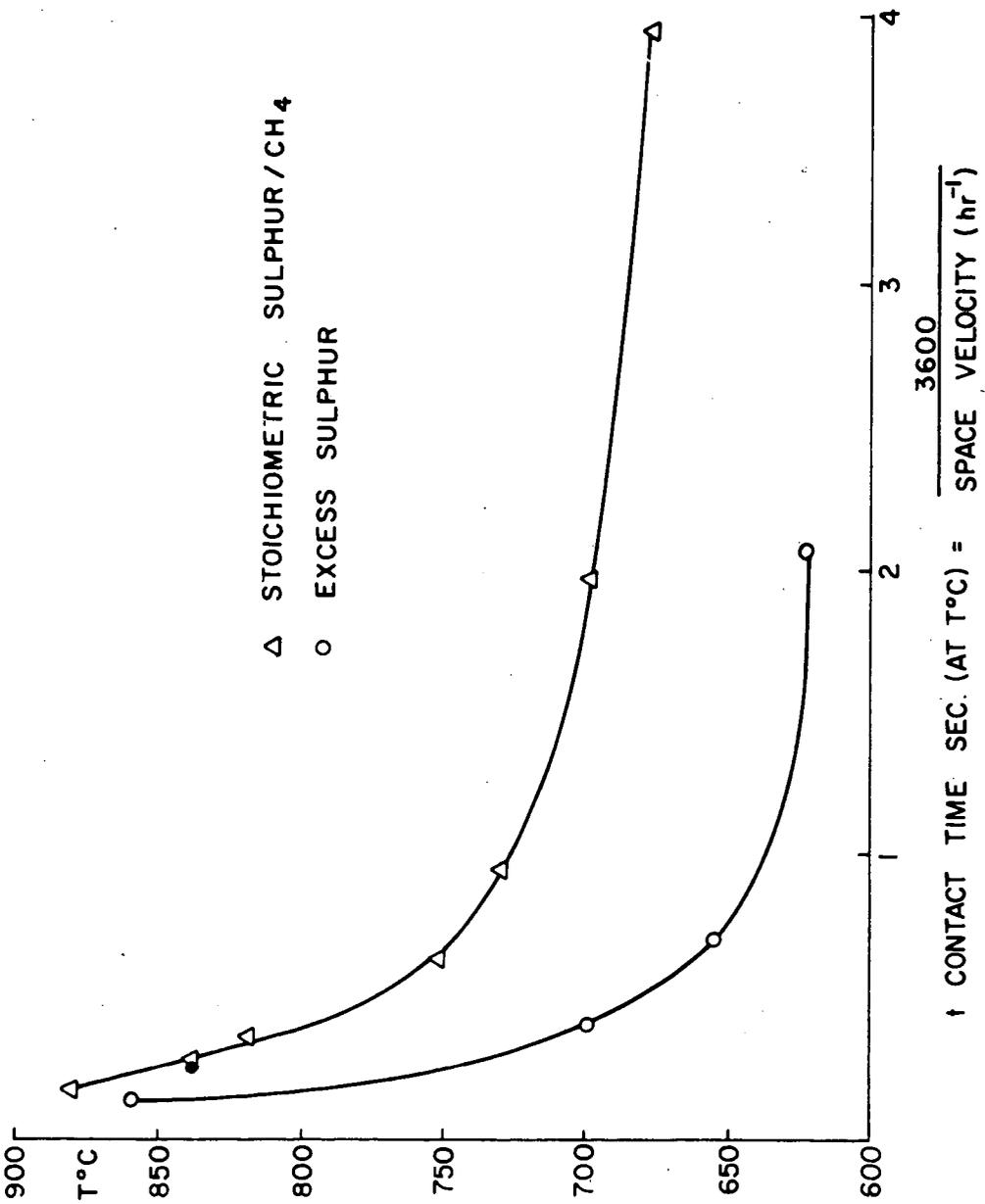


FIG. 5

THE EFFECT OF CONTACT TIME ON THE MINIMUM TEMPERATURE FOR COMPLETE REACTION OVER KA-21 CATALYST (8-16 MESH)

$$\uparrow \text{ CONTACT TIME SEC. (AT } T^{\circ}\text{C)} = \frac{3600}{\text{SPACE VELOCITY (hr}^{-1}\text{)}}$$

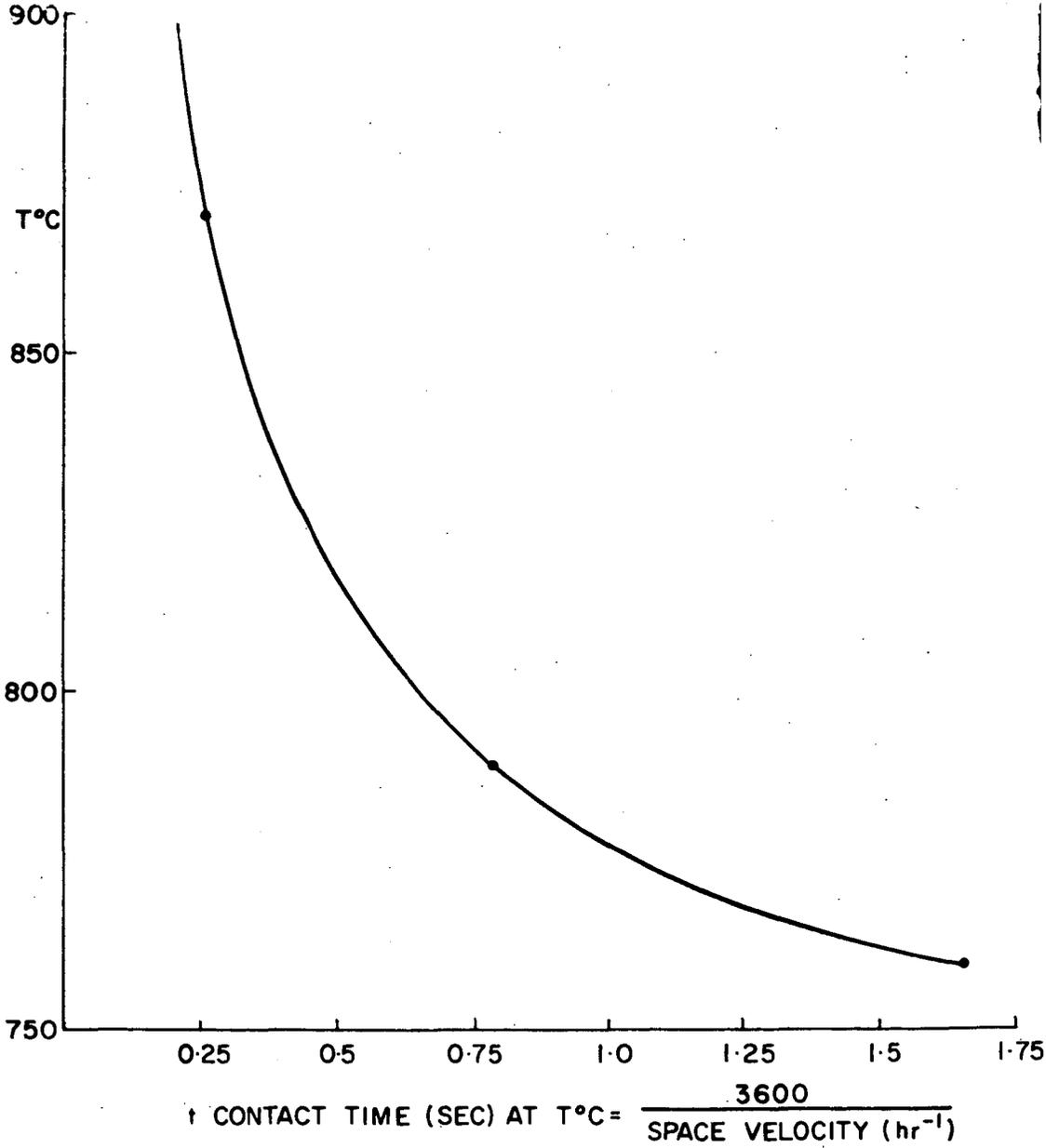


FIG. 6

THE EFFECT OF CONTACT TIME ON THE MINIMUM TEMPERATURE FOR COMPLETE REACTION (MIXED S/SO₂ + CH₄) OVER KA-201 CATALYST (8-16 MESH)

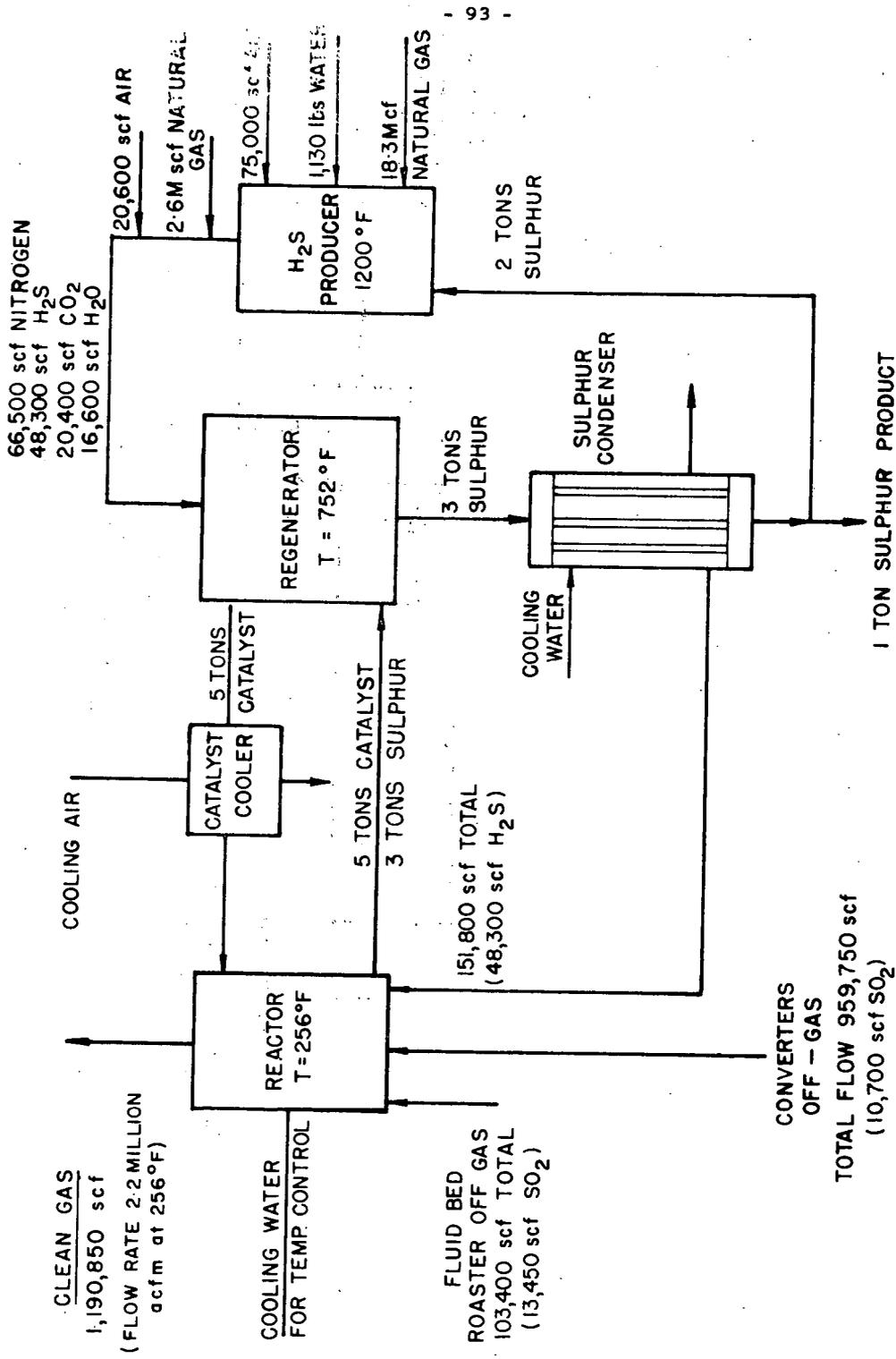


FIG.7 FLOW SHEET "A"

CONVERTER AND ROASTER STREAMS TREATED IN THE REACTOR
BASIS 1 TON SULPHUR PRODUCT

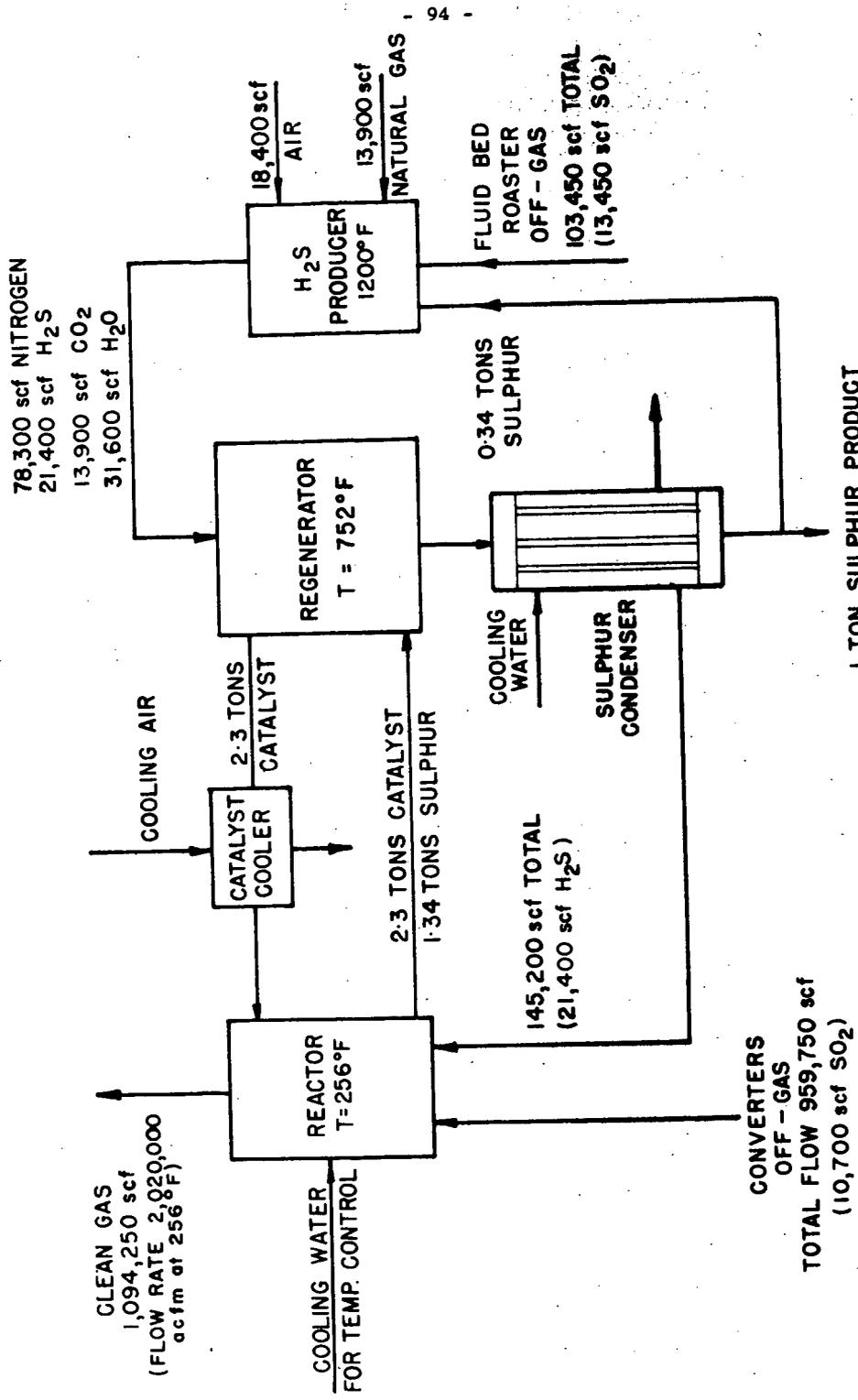


FIG.8 FLOW SHEET "B"
 FLUID BED ROASTER STREAM USED FOR H₂S PRODUCTION
 BASIS 1 TON SULPHUR PRODUCT

FIG. 9 ESTIMATED PROCESS COSTS

BASIS COSTS PER TON OF SULPHUR PRODUCED (NO CREDIT FOR SULPHUR SALES.)

PRODUCTION RATE 82 tons SULPHUR / hour .

	<u>SCHEME A</u>	<u>SCHEME B</u>
CAPITAL CHARGES (25% of investment Depreciation 10 % Interest 8 % Maintenance 4.5 % Taxes + Insurance 2.5 %)	8.90 - 10.70	8.90 - 10.70
NATURAL GAS COST (at 50¢/M.C.F.)	10.20	7.00
CATALYST REPLACEMENT (0.2 % cycle at \$ 300/ton)	3.00	1.40
LABOUR (4 men/shift at \$ 5.00/man - Supervision at \$ 7.00/man - + 50 % overhead)	.50	.50
UTILITIES (Power at 0.8¢/KWhr Cooling water at 5¢/1000 gals.)	3.00	2.50
	<hr/>	<hr/>
	\$ 25.60 - \$ 27.40	\$ 20.30 - \$ 22.10