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Mines Branch Information Circular IC 243

THE HYDROGEN SULPHIDE ROUTE TO SULPHUR
RECOVERY FROM BASE METAL SULPHIDES

PART II: THE RECOVERY OF SULPHUR
FROM GASES CONTAINING H_2S

by

R.F. Pilgrim* and T.R. Ingraham**

ABSTRACT

A review has been made of the many variations of
the Claus reaction for recovering sulphur from hydrogen
sulphide. The variations include wet and dry processing in
the presence and absence of a variety of catalysts. Simult-
aneous separate reviews have also been made of means for
generating hydrogen sulphide from pyrrhotite and for recovering
an iron product from the ferrous chloride solutions.

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51 pp.

Direction des mines

Circulaire d'information IC 243

RÉCUPÉRATION DU SOUFRE DES SULFURES DE MÉTAUX COMMUNS
PAR LA VOIE DE L'ACIDE SULFHYDRIQUE

PARTIE II: RÉCUPÉRATION DU SOUFRE À PARTIR
DES GAZ À BASE DE H_2S

par

R.F. Pilgrim* et T.R. Ingraham**

RÉSUMÉ

Les auteurs ont étudié les nombreuses variantes
de la réaction de Claus, qui sert à récupérer le soufre de
l'acide sulfhydrique, y compris le traitement à sec ou par
voie humide, avec ou sans divers catalyseurs. Ils ont aussi
passé en revue les moyens de produire de l'acide sulfhydrique
à partir de la pyrrhotine et de récupérer un produit de fer
des solutions de chlorure ferreux.

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INTRODUCTION

In one of its aspects, the Mines Branch Environmental
Improvement Program is concerned with the reduction of sulphur
dioxide pollution of the air utilized for the combustion of
fossil fuels and for the pyrometallurgical treatment of sulphide
minerals. The Program at the present time involves a multi-
faceted attack on the problems associated with both of these
major sources of sulphur dioxide emissions.

In this report series on "The Hydrogen Sulphide Route
to Sulphur Recovery from Base Metal Sulphides", an examination
is made of the various steps that might be involved in recovering
sulphur directly from sulphide minerals via the intermediate step
of generating hydrogen sulphide. Alternative methods by which
sulphur may be recovered directly from sulphur dioxide have been
reviewed[1-8]. The hydrogen sulphide route was selected for study
because of its inherent flexibility. Sulphur may be recovered
directly from hydrogen sulphide by the Claus reaction, in which
the H_2S is oxidized with precisely the stoichiometric amount of
oxygen:
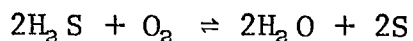
$$2H_2S + O_2 \rightleftharpoons 2H_2O + 2S \qquad [1]$$

Or, as an alternative, the H_2S may be used to reclaim the sulphur from the sulphur dioxide produced by pyrometallurgical methods of treating sulphide ores:

$$2H_2S + SO_2 \rightleftharpoons 2H_2O + 3S \qquad\qquad [2]$$
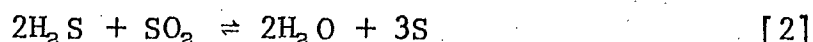
The technology for sulphur recovery from hydrogen sulphide is well established. The reactions are virtually quantitative and they are effective with both strong and dilute gas mixtures.

The inherent flexibility of the hydrogen sulphide route for producing sulphur is attractive at the present time when attempts are being made to reduce sulphur dioxide pollution levels.

In this series of reports, the methods of generating hydrogen sulphide from sulphide ores are examined and, based on the assumption that the chloride systems are favoured, an examination is made of the methods of recovering iron products and of regenerating hydrogen chloride. In the present report, the second of the series, a detailed examination is made of the Claus reaction and the variety of its applications.

THE ORIGINAL CLAUS PROCESS

A patent was issued to C.F. Claus in 1883[9] for a
process to recover sulphur from calcium sulphide "alkali waste"
from the Leblanc process for manufacturing soda. "Sulphuretted
hydrogen" (H_2S), released by carbonic acid dissolution of the
CaS, was reacted with oxygen or air over a catalyst to produce
S according to Equation 1. The principal requirement was that
the molar ratio H_2S/oxygen be very nearly stoichiometric, that
is, 2:1.

The first practical application of Claus's invention
was worked out by A.M. Chance and J.F. Chance in 1887[10]. The
main function of the process was the controlled oxidation of H_2S
in the presence of a catalyst, and it is this phase of the original
Claus patent which is, to this day, identified as the Claus or the
Claus-Chance process.

Figure 1 is a block diagram of the original Claus process
as constructed by the brothers Chance[10]. The H_2S and air were
premixed and the reaction took place in the "Claus kiln", which
contained a bed of powdered catalyst. Liquid sulphur was with-
drawn from the run-off chamber, and finely divided solid sulphur
was collected in a series of settling chambers. The effluent

FIGURE 1: Original Claus Process
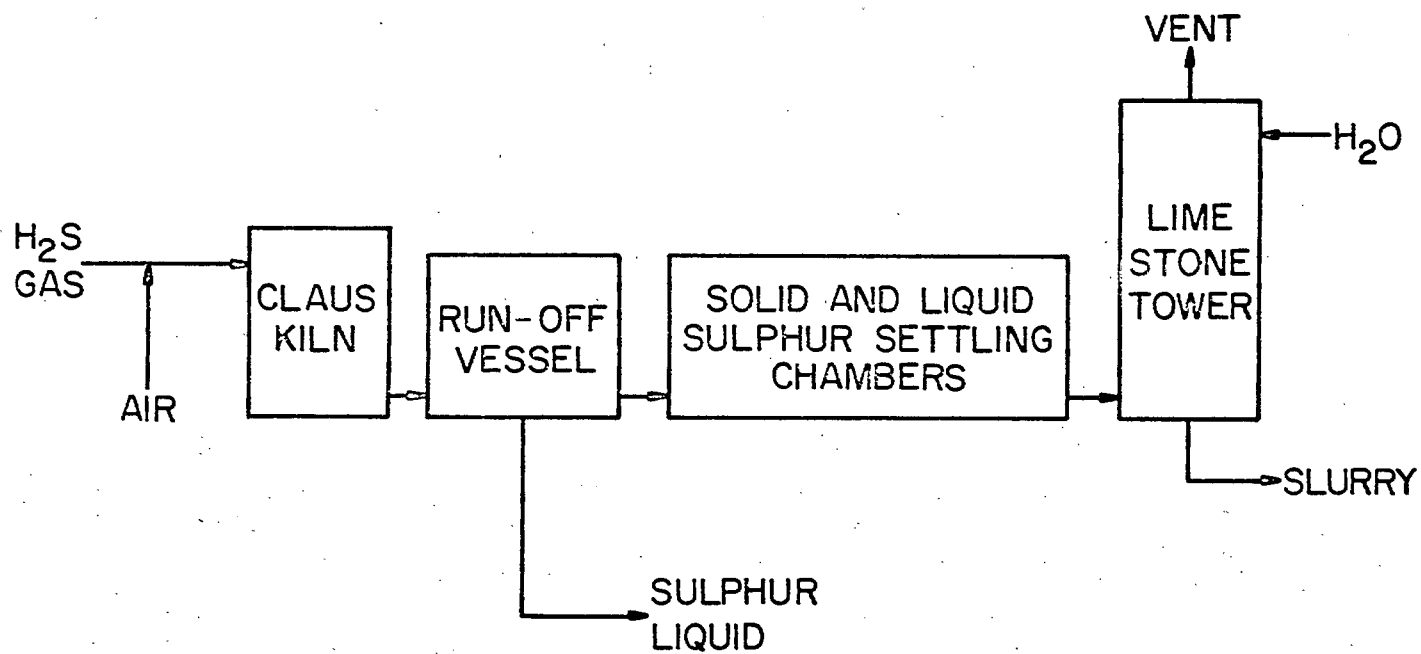
gases containing residual SO_2 were washed in a limestone tower before being discharged to the atmosphere.

The combustion reaction (Equation 1) was highly exothermic. This posed a considerable problem, since it was found that optimum H_2S to S conversion efficiency was obtained at an exit gas temperature of 500°F (260°C). In the original process this temperature was controlled by adjusting the input gas flow. When the temperature became too high, it was necessary to discontinue the flow completely. For maximum flow of gas the kiln was built as large as possible to give the maximum heat radiation.

THE DEVELOPMENT OF CLAUS MODIFICATIONS

The history of the development and use of the Claus process has been described by Lunge[11], Gamson and Elkins[12], Graff[13], Sawyer et al.[14], and Blohm[15]. Beginning as a means of treatment of air-polluting flue and coke-oven gases containing H_2S, the method was quickly adopted by the natural and petroleum gas industry as a means of recovering sulphur from acid gas produced in gas-sweetening plants.

There was, as well, an economic incentive because in the late 1940's and early 1950's there was a shortage of sulphur and some indication that Frasch deposits (of brimstone) were becoming depleted. The resulting high prices and ready sulphur market led to expansion of "recovered" sulphur production and also to improved process designs.

This recovered sulphur production has continued to expand. In 1950, 95% of the North American sulphur and 82% of the world production came from Frasch deposits[16]. By 1969 Frasch sulphur accounted for only 33% of the free world sulphur production[17]; the remainder was obtained from various fuel and metallurgical recovery processes, many of which make use of the Claus process or one of its modifications.

As was pointed out in discussing the original Claus design, the principal difficulties arose from the need to control the temperature of large volumes of gas containing varying concentrations of H_2S under conditions which were highly exothermic. At high temperatures the side reaction

$$S + O_2 \rightleftharpoons SO_2$$

is favoured and results in a reduction in sulphur recovery. The sulphur species present also depend on temperature. Sawyer et al.[14]

noted that lower temperatures prevented the undesirable reaction:

$$S + 2CO_2 \rightleftharpoons 2CO + SO_2$$
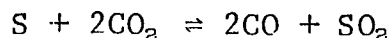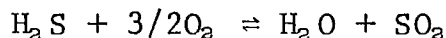
when one of the dilutants in the H_2S is CO_2 .

Figure 2 shows a modification of the original process which permitted a measure of temperature control by recirculating part of the stack gases to the reactor input[18]. Although this provided a more efficient conversion of H_2S to S, by preventing the high-temperature formation of SO_2, there was little or no increase in the volume throughput of input gas. The only way to accomplish this seemed to be by increasing the size of the kiln.

A significant advance in the art was made by I.G. Farbenindustrie in Germany in 1937. In a patent issued to Baehr and Mengdehl[19], and to Barkholt[20] in 1939, a process was described in which one third of the H_2S was burned completely to SO_2 under a waste-heat boiler. This was then reacted with the remaining two thirds of the H_2S over a catalyst at a comparatively low temperature, 700-750°F. Gamson and Elkins[12] demonstrated the improvement made by this "split-flow" modification by comparing the heats of reaction:

In the waste-heat boiler
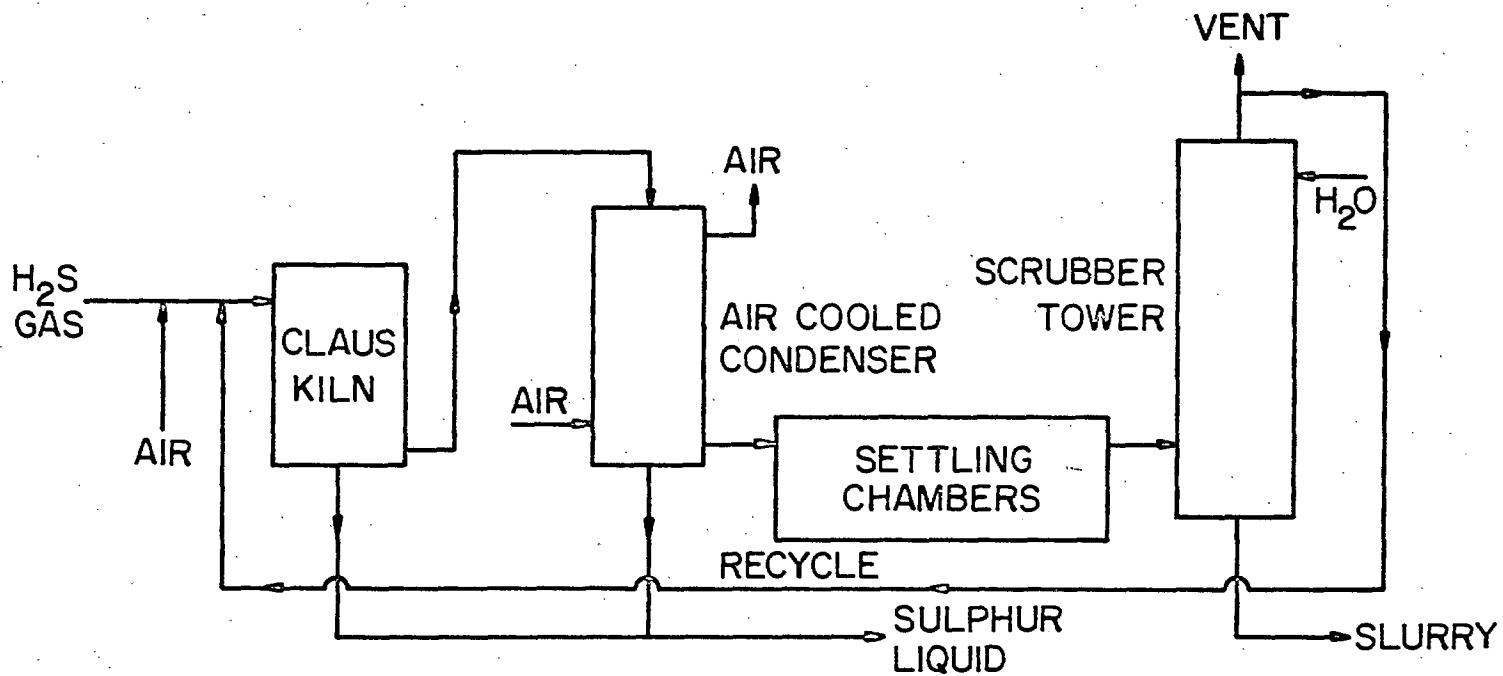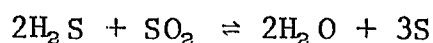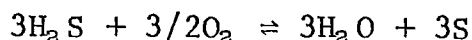$$H_2S + 3/2O_2 \rightleftharpoons H_2O + SO_2$$
$$\Delta H = 124\text{-}138 \text{ kcal;}$$

FIGURE 2: Modified Claus process, in which part of the stack gases are recirculated to provide control of the combustion temperature

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In the catalytic converter

$$2H_2S + SO_2 \rightleftharpoons 2H_2O + 3S$$

$$\Delta H = 21\text{-}35 \text{ kcal};$$

For over-all combustion in a single reactor

$$3H_2S + 3/2O_2 \rightleftharpoons 3H_2O + 3S$$

$$\Delta H = 145\text{-}173 \text{ kcal}$$

Thus, only about one fifth of the total heat of reaction was given out in the catalytic converter. This permitted the maintenance of lower temperatures in the principal reactor and greatly increased the "space velocity" in the system. (The space velocity is generally given in cu ft of H_2S converted to elemental sulphur per cu ft of catalyst per hour[13].) A diagram of this modification is shown in Figure 3. In the usual application of this modification, sufficient oxygen or air was supplied in the combustion of one third of the H_2S to convert all the H_2S to S according to Equation 1.

Another modification was based on a patent by Baehr and Braus[21] and is shown diagrammatically in Figure 4. All of the H_2S-containing gas was burned in a free flame with an amount of oxygen insufficient to form SO_2 but sufficient to convert the H_2S to free sulphur. About 60% of the sulphur was separated in this way in a high-temperature, non-catalytic reactor. The

FIGURE 3: Modified Claus process, split-flow design
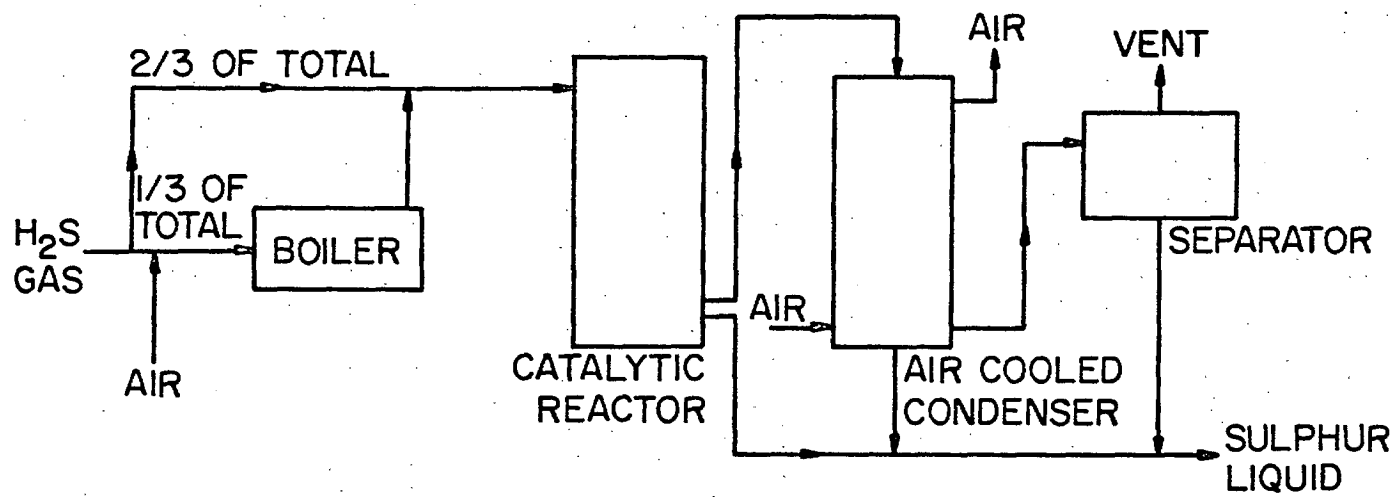
FIGURE 4: Modified Claus process, in which all the gas is burned in free flame combustion for the recovery of 60 to 70% of the sulphur before the gases enter the catalytic reactor

FIGURE 4: Modified Claus process, in which all the gas is burned in free flame combustion for the recovery of 60 to 70% of the sulphur before the gases enter the catalytic reactor
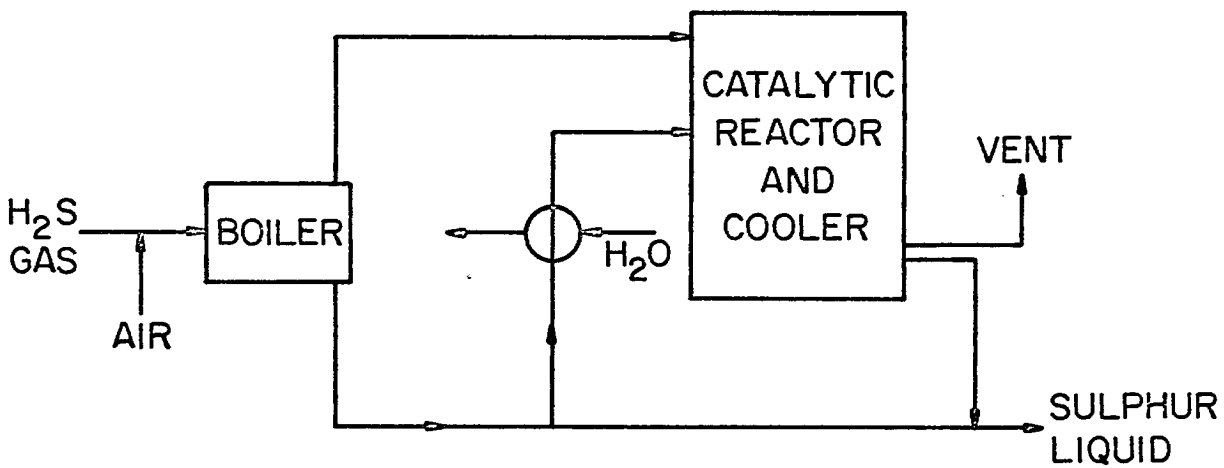
sulphur was condensed and collected as liquid sulphur[22]. The residual gases containing H_2S, and oxygen or SO_2, were then reacted over a catalyst to recover most of the remaining sulphur. In a more recent patent[23], Gamson claimed a greater than 75% yield of sulphur with a non-catalytic system. Carlson's modification[24] involved the use of less than three quarters of the stoichiometric oxygen in the primary combustion step. In this way a somewhat lower temperature could be maintained. After condensing and withdrawing some of the sulphur formed, the remaining air was added and reacted over a catalyst.

Gamson and Elkins[15] noted two advantages of this "straight-through" design over the split-flow method. Firstly, 90 to 95% of the heat of reaction was liberated prior to the catalytic conversion stage. This had the effect of greatly increasing the space velocity in the system. Secondly, the high percentage conversion to sulphur prior to the catalytic reactor stage caused a lowering in the maximum sulphur dewpoint.

The dewpoint is the temperature at which sulphur condenses, and it is necessary to operate the reactors at temperatures above this point to prevent fouling of the catalyst by the sulphur. In this straight-through modification it was found that, with a pure

H_2S feed, the dewpoint was lowered from 280°C to 235°C. When the tail gases were also recycled, as in the Claus modification shown in Figure 2, Gamson and Elkins stated that the reactor could be operated at 210°C with considerable increase in primary conversion and almost complete conversion in two catalytic stages. The diagram for such a design is shown in Figure 5.

When the H_2S gas stream contains carbon dioxide or light hydrocarbons, it is necessary to alter the process[12,14] because carbonyl sulphide, sulphur, sulphur dioxide, water and nitrogen may all appear at the combustion temperature (1000°C). The COS and SO_2 react to form sulphur according to the equation

$$2COS + SO_2 \rightleftharpoons 3/2S_2 + 2CO_2 \qquad [3]$$
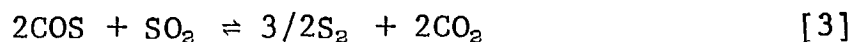
The reaction is similar to the H_2S-SO_2 reaction given in Equation 2. However, a higher temperature, about 400°C, was required for complete conversion of the COS. Therefore, to prevent a low sulphur conversion when the formation of COS is involved, two catalytic reactors were used: the first was operated at 400°C to ensure complete reaction in accordance with Equation 3, and the second at a temperature just above the sulphur dewpoint to give high H_2S conversions[12,14,25].

FIGURE 5: Modified Claus process, straight-through design

- 14 -
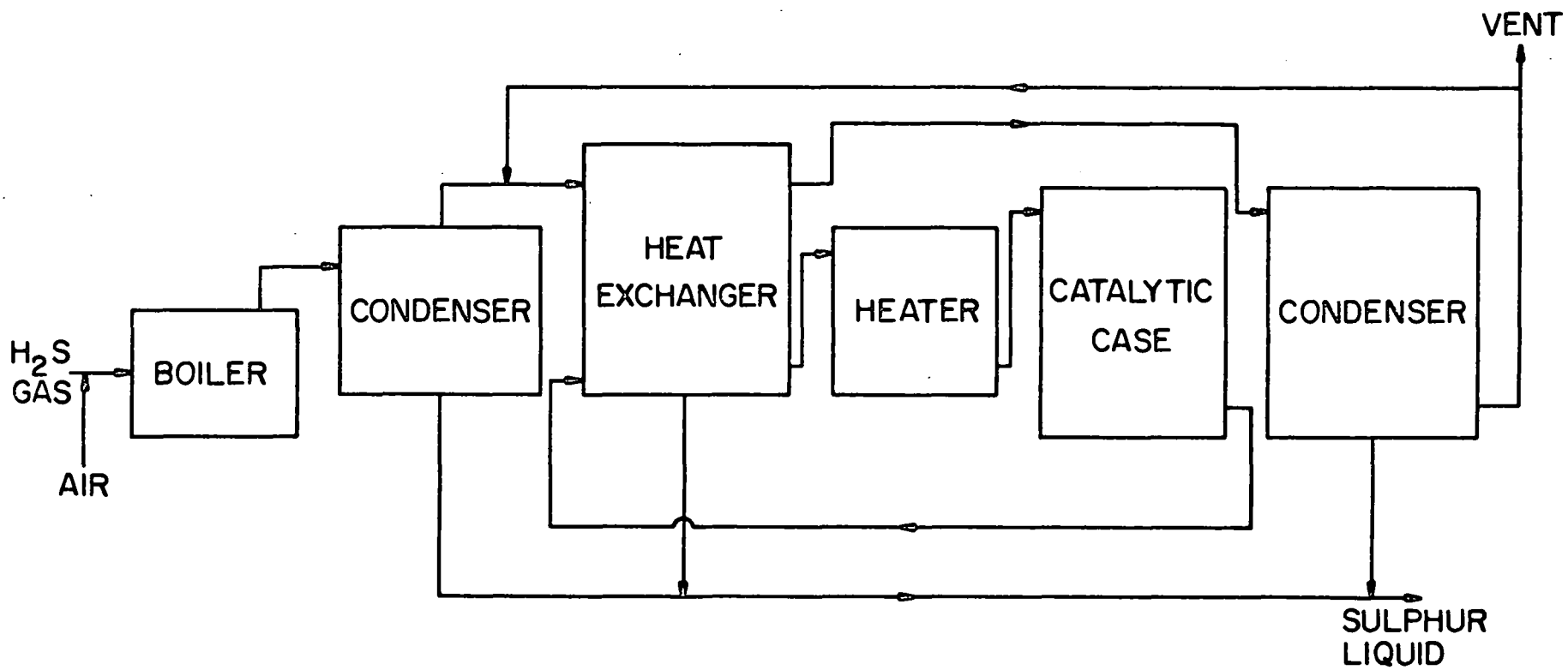
For the recovery of sulphur from gas streams where the H_2S content is too low to support combustion, or where the H_2S is diluted with a high percentage of CO_2, it may be necessary to apply some type of preheating to bring the gases to the reaction temperature. One way in which this was done[12] is shown in Figure 6. External preheaters were used for both H_2S and air prior to the catalytic reactor.

Another preheating method is shown in Figure 7[12]. Some of the collected sulphur was burned in a waste-heat boiler to form SO_2. The preheated SO_2 and dilute H_2S were then reacted in catalytic reactors. The residual gases were scrubbed with liquid S before being exhausted to the atmosphere.

Valdes[26] described three methods for preheating or reheating gases prior to the catalytic reactors. In case 1, heat from the primary combustion boiler was used to raise the gas temperature from the sulphur condensation temperature to that for optimum conversion in the catalytic reactors. In case 2, reheaters were used to accomplish the same purpose. These reheaters consisted of small burners fed by some of the H_2S feed plus a small amount of air. In case 3, the heat developed in each converter was recycled to preheat the feed gas to the converter. Gas-to-gas heat exchangers were used.

FIGURE 6: Acid gas and air preheaters prior to catalytic reactor

- 16 -
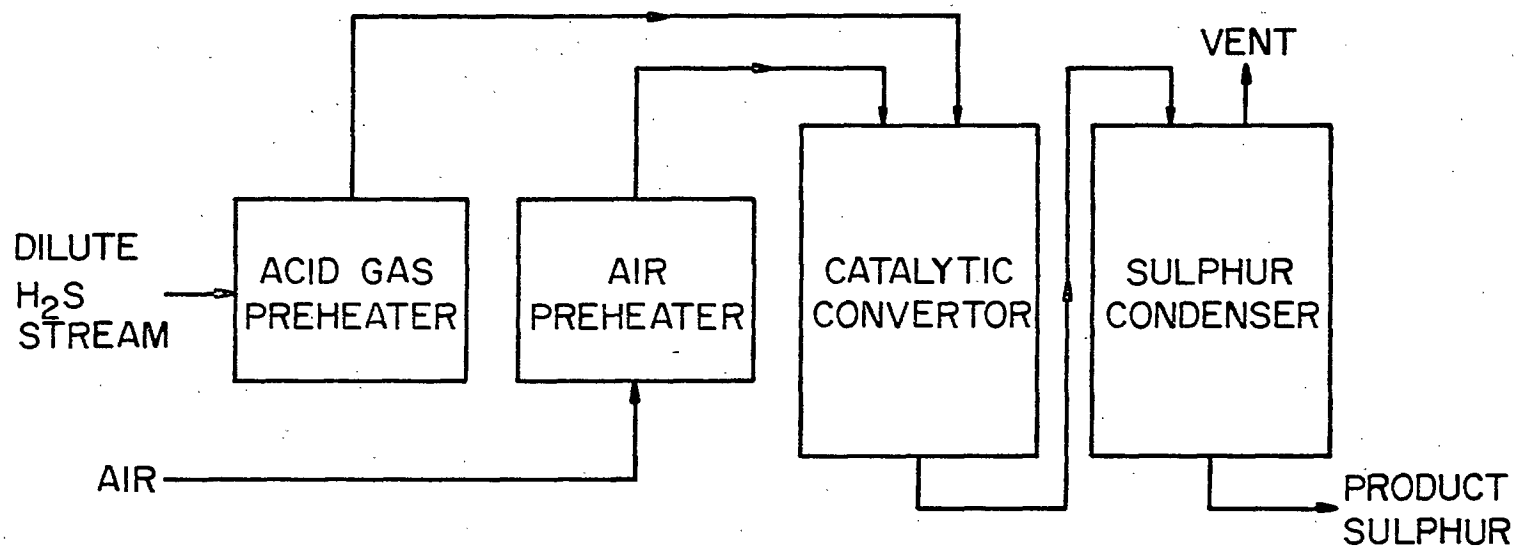
FIGURE 7: Liquid sulphur burned in air to provide preheated SO_2 to react with dilute H_2S in catalytic reactor
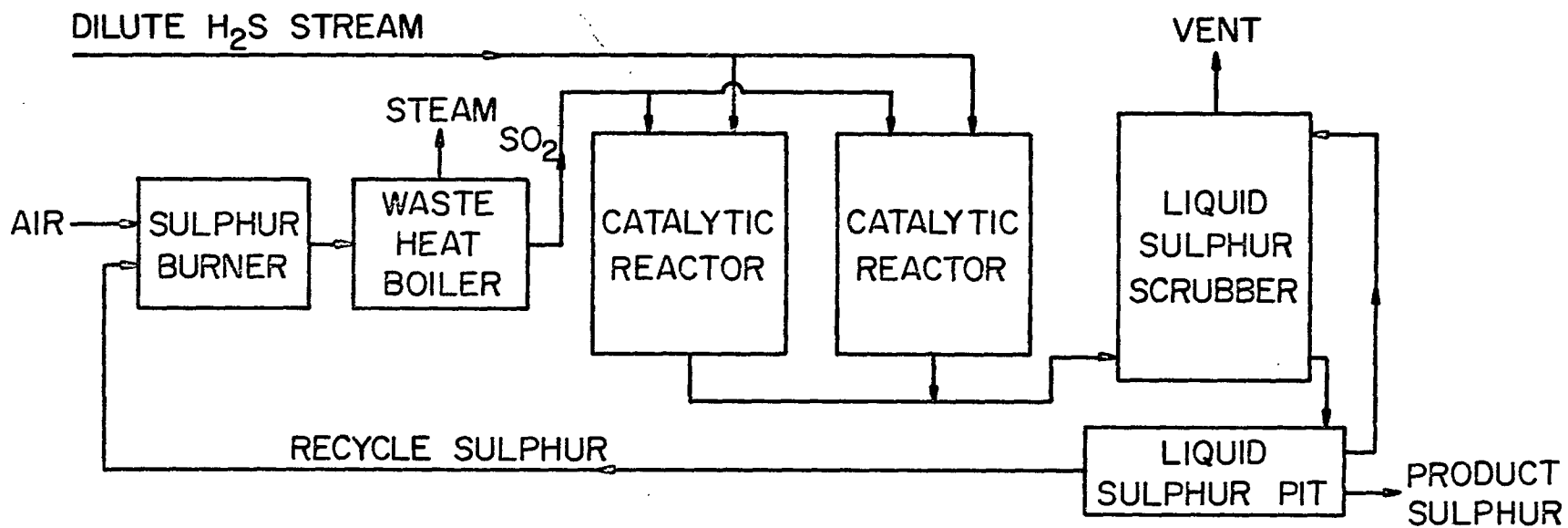
DILUTE H₂S STREAM

VENT

STEAM

SO₂

AIR → SULPHUR BURNER

WASTE HEAT BOILER

CATALYTIC REACTOR

CATALYTIC REACTOR

LIQUID SULPHUR SCRUBBER

RECYCLE SULPHUR

LIQUID SULPHUR PIT → PRODUCT SULPHUR

A considerable saving in preheating was obtained by use of the "direct oxidation" method described by Grekel[27]. A typical flowsheet is shown in Figure 8. The high-temperature combustion step was eliminated and there were two catalytic oxidation steps in series operating at temperatures much below 1000°F. Grekel claims that the economy over the split-flow process is up to 40%, but that this advantage is lost when the H_2S concentration exceeds 25%, thus necessitating another catalytic reactor to obtain an acceptable S recovery.

There are several other Claus modifications and innovations which are worthy of note: Patents by Catchpole and Cuddington[28] describe a modification for reacting H_2S with SO_2 stoichiometrically, using three catalytic reactors. One was held at 300°C or higher, one was kept near 150°C (that is, below the sulphur dewpoint), while the third was used when the low-temperature reactor, which had become fouled with liquid sulphur, was being regenerated by distillation. A similar process is described by Thumm et al.[29].

For H_2S-containing gases mixed with gaseous nitrogen compounds--cyanides, cyanogens, ammonia, etc.--relatively high combustion temperatures were required[30,31] to decompose the nitrogen compounds. The air intake was kept low to prevent the formation of SO_2.
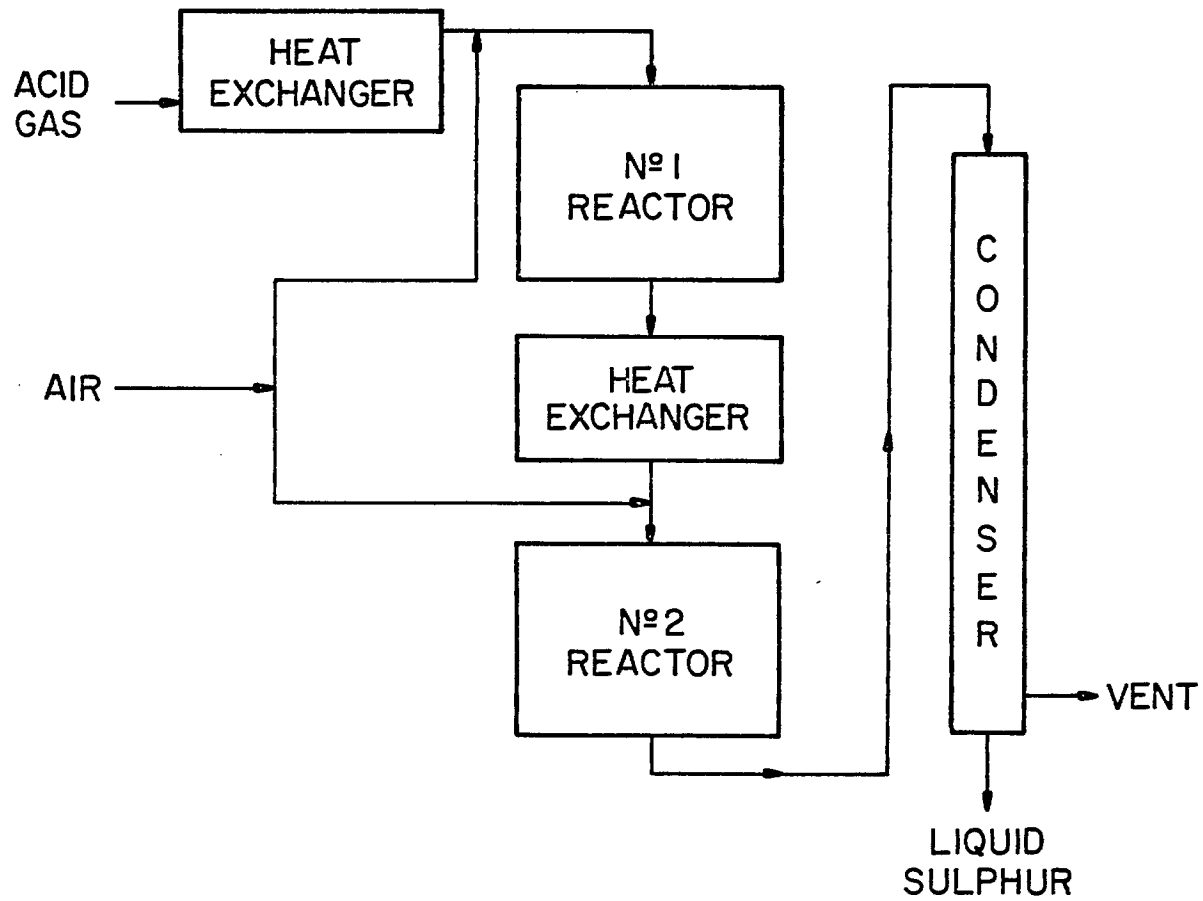
FIGURE 8: Modified Claus process, direct oxidation design with two stages of heat exchanging

Patents by Stirlen[32], Bärn[33] and Bahr[34] describe the recovery of sulphur from the exhaust of an internal combustion engine using an H_2S-containing gas as fuel and a controlled air intake. A condensation step before and after a catalytic reactor removed the sulphur from the exhaust gases.

Conroy et al.[35] developed a cyclic process for desulphurizing hydrogen sulphide gas. Air and SO_2 were mixed and reacted with the H_2S in a combustion chamber to produce S according to Equations 1 and 2. The unreacted H_2S and uncondensed S were then reacted with air in a secondary combustion chamber to produce SO_2. This was absorbed in a liquid, stripped from it by air injection, and then reacted with the incoming H_2S.

A more recent patent[36] describes the recovery of S from residual gases from a conventional Claus plant. After first cooling the gases to condense out any elemental S, air or oxygen are added at a temperature just above the S dewpoint in a bed of activated carbon. The sulphur formed is deposited on the C, desorbed later by a hot inert gas or with steam, and returned to one of the cooling stages or to the catalytic conversion stage. The off-gas is claimed to be completely free of sulphur.

Methods for recovering elemental sulphur as solid flakes, rather than molten or solidified block sulphur, are described by Miller[37].

THE DEVELOPMENT OF COMPACT
SULPHUR PLANTS

Efforts to reduce the capital and operating costs of sulphur plants have emphasized preheating, reheating and heat exchanging. Some of the design considerations for a sulphur plant were listed in 1964 by Valdes[26]. The need for economy was two-fold. Firstly, with the increasing public awareness of air pollution more stringent regulations on flue gases were imposed. These required higher conversions from H_2S to S in sulphur plants and generally required another catalytic reactor to accomplish this. Both capital and operating expenses increased[26]. Secondly, there was a need for small sulphur plants to treat gases low in H_2S.

In general, conventional Claus plants with capacities less than 20 tons of sulphur per day were considered uneconomic[38,39,40]. Parker[41] in 1952 made some cost estimates on sulphur plants and showed that under highly favourable conditions--plant location, labour, markets, H_2S content of gas treated, price of sulphur, etc.--it might be possible to make a slight profit producing 5 tons of sulphur per day. Weber[42] described the 10-tons-per-day plant built by Lion Oil Company which operated economically under some such ideal conditions.

Franklin et al.[39] described a simplified design which used a compact furnace-cooler-condenser unit, a pair of catalytic reactors in a single shell, and a compartmented liquid sulphur storage tank. These were built and licensed by Pan American Petroleum Company in 1957. By 1961 there were eight such economy plants in operation, ranging in size from 6 to 70 tons per day in recovered sulphur capacity[43]. By 1965 there were 49 Pan-Am package sulphur plants in use. They had capacities from 1 to 700 long tons per day and were situated in eleven different countries[44].

Other compact sulphur plants for desulphurizing petroleum gases were built by the Ralph M. Parsons Company and are based on the experience gained in designing and building more than 100 conventional sulphur installations in various countries around the world[45]. These include, for example, the 877-tons-per-day Petrogas plant near Calgary[46]. The Parsons "packaged" plants have capacities from 5 to 50 long tons of sulphur per day. Chute[43] lists some of the advantages such compact plants have over conventional plants. They are economic in both installation and operation; replacement parts are standardized and interchangeable; and there are fewer equipment elements to maintain. As a result there is considerably less down-time. Chute notes, however, that packaged plants have one

disadvantage compared with those that are designed specifically for a particular case. Some over-capacity is inevitably built into these designs, causing lack of flexibility and somewhat lower efficiencies.

Three of the standard Claus modifications already described are used for these compact plants, depending on the H_2S concentration. The first of these is the straight-through process which is used for high concentrations. The conventional flowsheet is shown in Figure 5, whilst Figure 9 is a diagram of the compact design[44]. In this design the complete acid gas flow is reacted with stoichiometric air in a combustion zone. This is followed by condensation of the sulphur, reheating of the unreacted gas, and catalytic oxidation in two stages each of which is followed by sulphur condensation.

The second design is the split-flow modification which is used for somewhat lower H_2S concentrations. The principle is that already described and shown in Figure 3, in which one third of the H_2S is reacted in a combustion zone with sufficient air to oxidize all of the H_2S. The SO_2 formed is then reacted with the other two thirds of the H_2S over a catalyst to form sulphur. The compact design of this modification is shown in Figure 10[44].

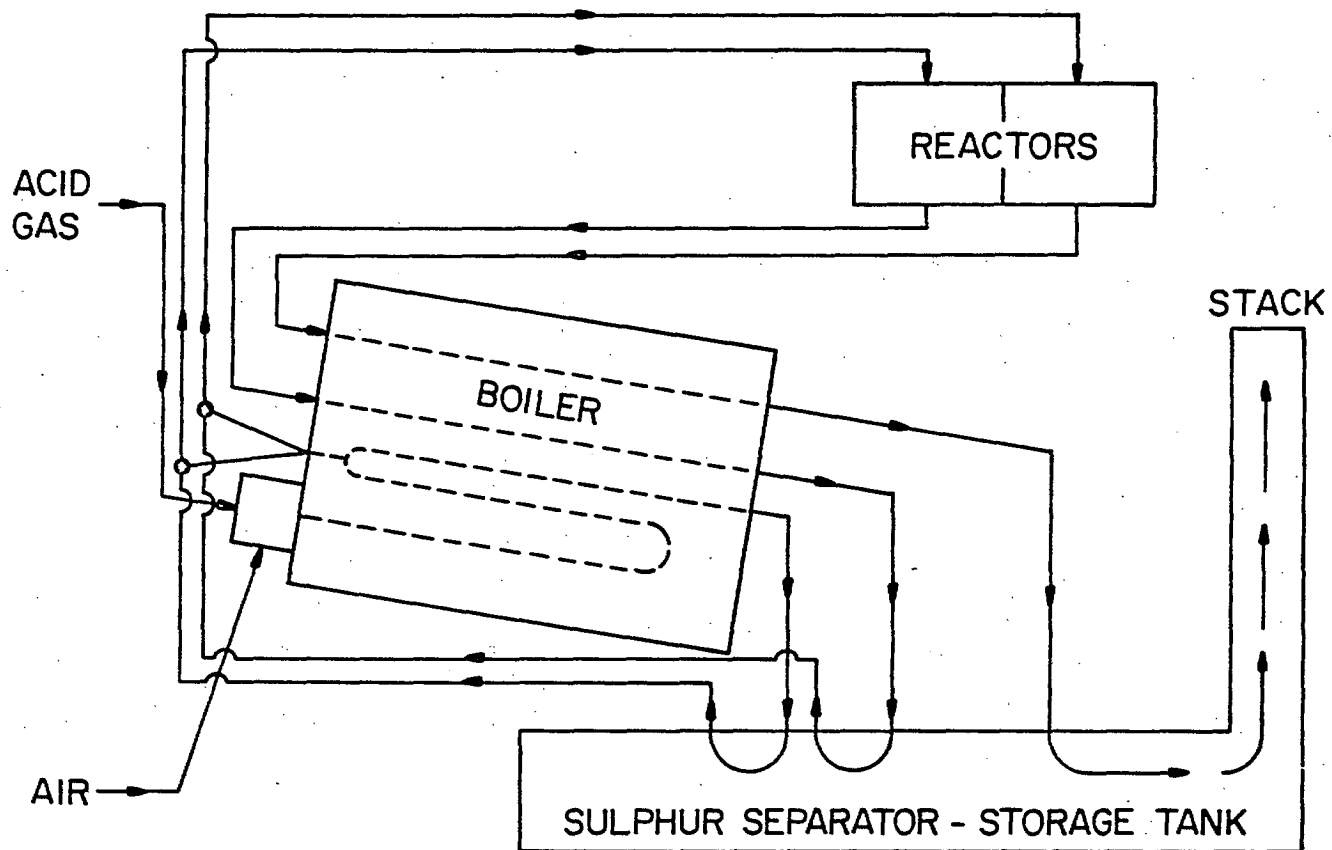FIGURE 9: Straight-through package plant design

ACID GAS

REACTORS

STACK

BOILER

AIR

SULPHUR SEPARATOR - STORAGE TANK

FIGURE 10: Split-flow package plant design

REACTORS

STACK

ACID GAS

2/3

1/3

BOILER

AIR

SULPHUR SEPARATOR - STORAGE TANK

- 25 -
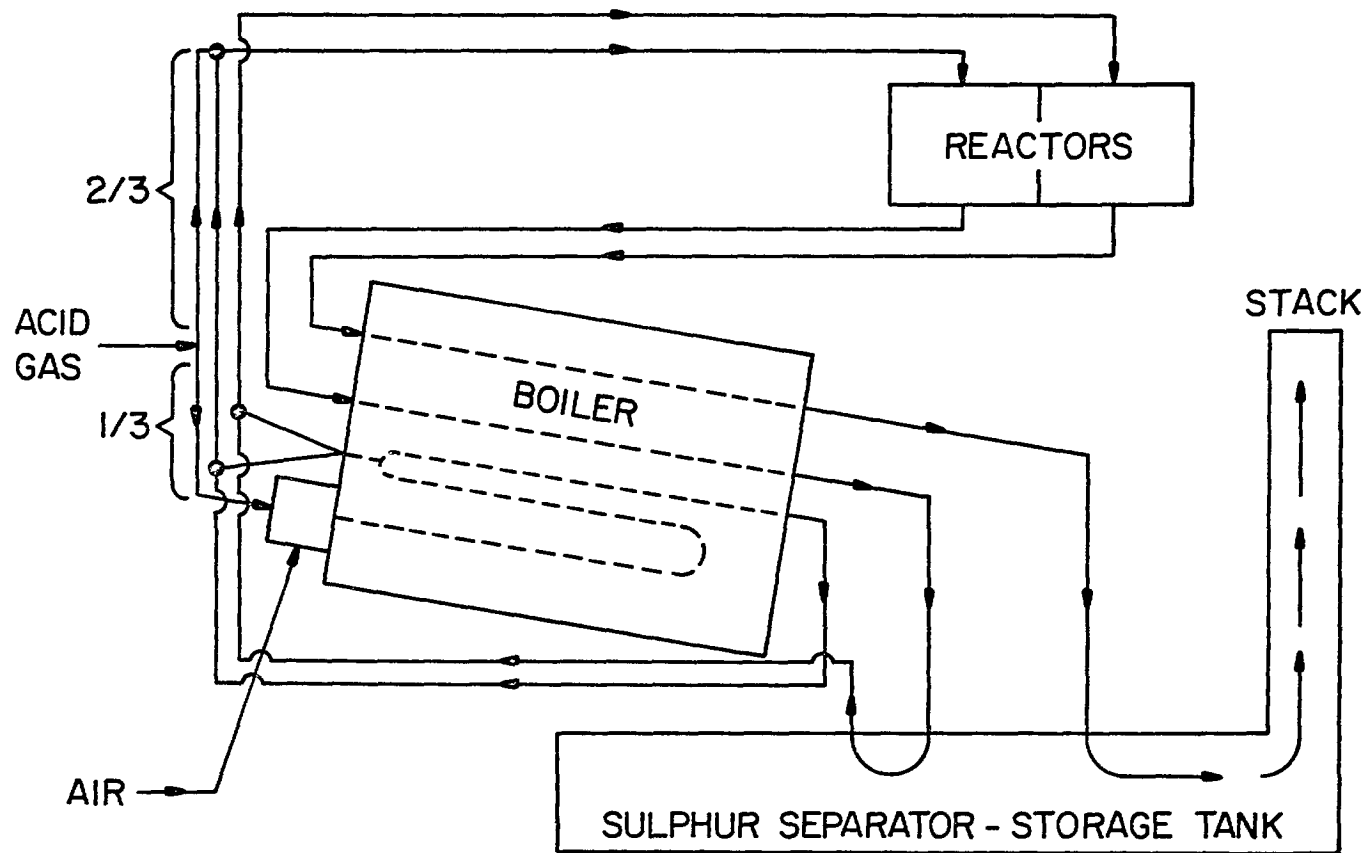
The third of these compact designs is the direct-oxidation modification and is used for low H_2S concentrations. Grekel's design[27] has already been discussed. A diagram of the packaged plant is shown in Figure 11.

CLAUS CATALYSTS

In his original patent[9], Claus listed the following possible catalysts: brick, iron oxide, manganese oxide, asbestos, alumina, zinc oxide, lime, or calcium carbonate. The most widely used is alumina in one of its forms - natural bauxite, activated alumina, etc. Graff[13] noted that high surface activity was desirable in a sulphur catalyst. Natural bauxite mixed with 10 to 15% of hydrated iron oxide was commonly used[13,29] and permitted space velocities of the order of 100. At the McKamie, Ark. sulphur plant of the Mathieson Chemical Company, the catalyst used was Porocel, a high-iron, activated bauxite[14]. A French patent describes the method for activating bauxite[47]. Catalysts of this type were found to be mechanically strong, economical to install and long-lasting in activity.

Several other catalysts have been used or suggested in the literature. Lindblad and Herneryd[48] used portland cement,

FIGURE 11: Direct oxidation package plant design

AIR

FUEL GAS

ACID GAS

PREHEATER

REACTORS

CONDENSER

STACK

SULPHUR SEPARATOR - STORAGE TANK
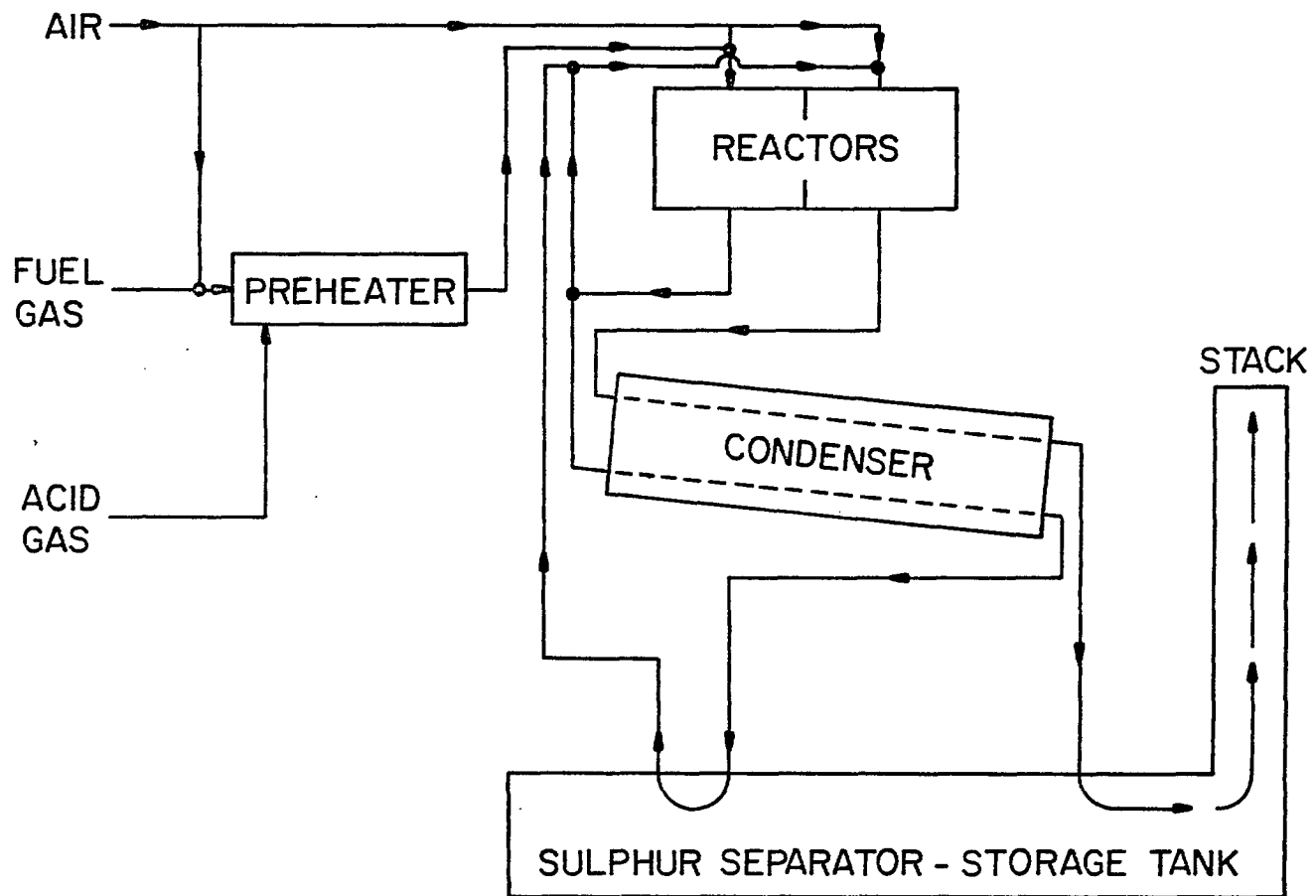
smelter cement or gypsum, mixed with pyrite or pyrites con-
centrate. Münz and Cramer[49] claimed 10 to 15% improvement
over a natural bauxite catalyst by using pelletized clay and
kaolin. To obtain higher porosity they mixed granular
naphthalene with their pellets and burned it off at a low
temperature. Carbonaceous materials such as active lignite coke,
peat coke or charcoal, pretreated with superheated steam at
700-900°C, were used as sulphur catalysts by Bankowski
et al.[50,51].

Griffith et al.[52] found that nickel or cobalt
sulphides were true catalysts for H_2S to S conversions. They
could be used in several forms: shaped pieces, broken or graded
coke, as a powder suspension, or deposited on a carrier. Space
rates up to 1100 were obtainable, and low operating temperatures
(<100°C) were possible. In patents by Spillane[53], H_2S-to-S
catalysts were formed from a mixture consisting of an alkali
sulphide (20 to 40%) and one or more metal sulphides (Ni, Co,
Mn, Cd, Sn, Al) supported on a carrier. Conversion temperatures
were from 80 to 400°C. Rottig and Hanisch[54] describe the use
of a Ni sulphide catalyst deposited on an inert carrier. A
temperature of 150-300°C was used, thus maintaining sulphur in
the molten state. The nickel sulphide was prepared by reducing

oxides, salts and ores of nickel with hydrogen and sulphiding them with H_2S. Marsh and Newling[55] found that any readily-sulphidable material, as well as activated carbon, was a suitable sulphur catalyst. In another patent[56], aqueous solutions of aluminum salts - $AlCl_3$ or $Al_2(SO_4)_3$ - were deposited on or mixed with natural or synthetic Al_2O_3 or bauxite containing water of hydration.

Mel'nikova et al.[57] studied the change in activity of various catalysts with time in a Claus reactor used to desulphurize gases produced by roasting sulphide ores. After several hours of deterioration in service, the catalyst became stabilized. They suggested that the initial decrease was due to thermal dehydration of the complex hydrated alumina silicates. This caused some loss in catalytic activity. The stabilization was probably caused by the opposing effect of metal sulphide catalytic activity.

A recent French patent describes the use of ammonia gas or aqueous ammonia solution to reactivate alumina or bauxite catalysts[58].

In summary, then, it would appear that economy has dictated the choice of a readily available and relatively cheap catalyst such as bauxite or alumina. It seems clear too that a

porous, open structure is desirable to obtain high space velocities. Methods for obtaining this are available, but their use is related to cost. The need to regenerate catalysts which became fouled with sulphur would seem to obviate the use of catalytic reactor temperatures below the sulphur dewpoint.

OPTIMIZATION AND CONTROL IN
CLAUS PLANTS

The principal controls required to optimize the recovery of S from H_2S by the Claus method are involved in maintaining the very accurate 2:1 ratio between the H_2S and the oxygen, according to Equation 1. Valdes[59] and Smalley and Klohr[60] have shown the serious reductions in conversion efficiency caused by even small deviations from the stoichiometric 2.

Anderson[61] noted, however, that control of the H_2S/O ratio at the combustion stage was difficult because of variations in H_2S content, gas flow rates, amount of diluting hydrocarbons and CO_2, etc. Also, as pointed out previously, the combustion step is highly exothermic and temperature control which would permit accurate gas-ratio control was difficult. He noted that, when H_2S was added to SO_2 below a H_2S/SO_2 ratio of 2, an

abnormal increase in temperature occurred that was proportional to the oxygen content. Similarly, there was a sharp decrease in temperature, proportional to oxygen content, when the ratio was greater than 2. Anderson's patent made use of these relationships to control the air flow inputted to the combustion stage.

Karasek[62] describes a flow sheet in which the flow of gases into and out of the catalytic reactor and from the stack is monitored and used to control the input air flow to the waste heat boiler. A gas chromatographic analyzer for use in such a system was described by Fraade[63]. He pointed out the importance of steam-jacketting the analyzer to keep the sulphur in the liquid state. Hensley's patent[64] used control valves that were responsive to temperature, pressure and flow, to maintain a constant reaction temperature of 475 ± 5°F (246°C) and an accurate 2:1 ratio of input H_2S to SO_2.

The instrumentation required for controlling conditions in a split-flow sulphur plant was described by Jones[65]. Two aneroid-type ratio flow controllers were used to maintain the two-thirds/one-third separation of the input H_2S and also the stoichiometric 2:1 H_2S to O_2 ratio. These controllers were easily adjusted to compensate for changes in pressure, gas composition, etc. A temperature controller was used to maintain the optimum

temperature of the liquid sulphur produced.

With regard to the optimum temperature for handling liquid sulphur, Smalley and Klohr[60] call attention to the sharp increase in sulphur viscosity that occurs at about 300°F. McCarthy[66] gives the limit as 328°F. Overheating of the liquid sulphur must be avoided to prevent difficulties in liquid transport. These same authors show, however, that the increase in viscosity is not as great when some H_2S is dissolved in the liquid sulphur.

A computer system for optimization of some of the basic Claus modifications has been given by Opekar and Goar[67]. In their system, computation of the individual steps in the process, i.e. burner, converter, condenser, etc., were combined to give a calculated percent conversion. Another complex system has been described by Carmassi[68] to obtain optimum recovery of sulphur and minimum air pollution, i.e. minimum SO_2 or H_2S in the stack, in a French Claus plant.

In summary, then, the standardized design of Claus plants appears to lend itself to automation and the use of control equipment and computerization.

SULPHUR REMOVAL FROM H_2S IN LIQUID MEDIA

A number of methods for recovering sulphur from hydrogen sulphide involve the Claus reactions (Equations 1 and 2) in a liquid medium. Historically these methods have, for the most part, originated from the sweetening treatment of natural or petroleum gases containing varying amounts of H_2S. Many of these processes have been reviewed in papers by Sawyer et al.[14], Blohm[15], Zurcher[25], and Parker[41].

It has been common practice to use an absorbent to remove the H_2S from sour gas and then to recover sulphur from the desorbed H_2S by the conventional Claus process. However, since the absorption step is generally done in a liquid, it has been found possible, in some cases, to recover at least part of the sulphur in the absorbing liquid or in the step through which the absorbent is regenerated.

The Thylox process[69] is an example of this latter system. Sodium thioarsenate is the absorbent for H_2S and it is regenerated by oxidation to form sulphur, which is then recovered by filtration. The Giammarco-Vetrocoke and Stretford processes are also of this type[70]. Patents by Udy[71] describe the use

of alkali metal sulphite solutions for the recovery of sulphur
from H_2S and SO_2.

Another example is the work of Townend, Arlington and
Kelly[72], who bubbled SO_2 into an aqueous solution of 0.5 to
5% $Al_2(SO_4)_3$ and 1 to 5% H_2SO_4. Sulphur was precipitated when
the solution was contacted with the input H_2S, at the same time
regenerating the sulphate solutions. Some of the sulphur that
formed was burned in air to produce SO_2 to recycle. A French
patent[73] used an aqueous solution of ferric chloride, acetic
acid and calcium citrate to wash an H_2S-containing gas to recover
elemental sulphur. The solution was regenerated by bubbling-in
oxygen gas at 50°C.

A somewhat similar approach is described in a paper
presented at a recent meeting of the Mining Society of the AIME[74].
The process used a sodium acetate solution to absorb SO_2. Sulphur
was formed when H_2S was reacted with this solution. The sulphur
was filtered and the solution recycled. When the process was
used to desulphurize SO_2 gas, H_2S was generated by reacting some
of the sulphur with methane and steam. A German patent[75]
described the use of an alkali polythionate solution in which the
Claus off-gases (H_2S + SO_2) were reacted in a spray nozzle. The
sulphur formed was removed by filtration.

In another approach, oil refinery gases containing H_2S were partly oxidized to form a stoichiometric mixture of H_2S and SO_2, and then cooled to 100°-150°F[76]. After reacting in H_2O at 70°-130°F, molten sulphur was separated by heating to 250°-300°F under pressure. Mathieu[77,78] found that sulphur could be precipitated from H_2S and SO_2 in a neutral aqueous solution of salts of univalent ions such as NaCl, KCl and NH_4Cl. Lesser amounts of multivalent ions such as Mg^{++}, Ca^{++}, Al^{3+}, SO_4^{--}, SO_3^{--} and PO_4^{3-} were required for precipitation. It was noted that sea water supplied the proper salt concentrations, and good recoveries of sulphur could be obtained. It was found necessary, however, to neutralize the sea water with an insoluble alkali before recycling.

A patent by Butler et al.[79] describes the "submerged" combustion of H_2S-containing gases in either sulphur or water baths. The sulphur bath was maintained at 230°-320°F. The new sulphur formed was mixed with the bath and some of it was continuously withdrawn. Solid colloidal sulphur was obtained from a water bath operated at a temperature below the melting point of sulphur and at a pressure between 1 and 10 atmospheres. In an Italian patent[80], H_2S was permitted to react with water in which SO_2 was dissolved. The precipitated sulphur was removed

by filtration and the water recycled. Sato and Ishizuha[81] absorbed H_2S in water and described apparatus by which the solution was sprayed in fine droplets into air. Colloidal sulphur was formed and was accumulated in CS_2. Schallis[82] and Ross and Wilde[83] found that, when H_2S and SO_2 in a 2:1 molar ratio was bubbled into a cold water-acid solution, the resulting sulphur was mostly insoluble in CS_2. Another patent by Wilde[84] described a method for ensuring the formation of crystalline sulphur. This was accomplished by keeping the H_2S to SO_2 ratio between 3 and 15 times the stoichiometric 2:1 requirement.

Organic liquids have also been employed as absorbents for H_2S[85] and SO_2. The Townsend process[86,87,88] is an example. It made use of aqueous solutions, containing less than 10 per cent H_2O, of di- or triethylene glycol, propylene glycol or their ethers or esters, as both reaction media and catalysts. A conventional split-flow system, in which one third of the H_2S was burned in air to form SO_2 and mixed with the remaining two third of the H_2S, provided a stoichiometric H_2S-SO_2 gas mixture. The reaction of this gas in the organic solution produced sulphur. The solution was decanted and regenerated by heating to remove dissolved SO_2 and excess H_2O formed in the

reaction. The sulphur was heated above its melting point and collected as liquid sulphur.

Deschamps[89] found that the use of a catalyst improved the efficiency of the glycol method. The catalysts tested were alkali mono- or dialkylphosphates, used either in solution or on solid carriers. Andreev[90] has examined some of the characteristics of the glycol method. High-purity sulphur is produced, essentially free from arsenic which may be a contaminant when the Thylox method is used. A finely dispersed sulphur may be obtained without further size reduction. He points out, however, that, because of the necessity of recovering excess SO_2 from the solution and from the sulphur, there is little advantage in using more than one reactor.

In a series of patents by Urban, Stolfa et al.[91,92,93,94], processes are described in which aqueous organic liquids (esters, carboxamides, or soluble aliphatic alcohols) containing up to 40% of H_2O by volume, were reacted with H_2S and SO_2. Crystalline sulphur was precipitated and the H_2O produced in the reaction was removed by distillation from the organic solution before the latter was recirculated.

Gurevich[95] passed H_2S and SO_2 through molten naphthalene; the sulphur was recovered by using an organic

solvent. Wierwiorowski[96] used an ethylenediamine (or similar nitrogen-containing compound) as catalyst to promote the reaction between H_2S and SO_2 in molten sulphur. Partially water-soluble tetra-substituted urea was used as reaction medium by Metallgesellschaft A.-G.[97].

A recent review[98] briefly describes some of the currently-used solvent processes for gas sweetening, many of which yield a sulphur product. In particular, attention is drawn to the use of molecular sieve compounds with liquid media[99,100].

The use of liquids as media for reaction between H_2S and SO_2 has permitted a study of the mechanisms involved, using radioactive tracers. Van der Heijde and Aten[101] used S^{35} to label alternatively the H_2S and the SO_2 for the cases in which either components was in excess. The specific activity of the sulphur obtained in the reaction was measured and compared with that of the labelled reaction partner. The results showed that the main portion of the elemental sulphur was formed by means of the 2:1 stoichiometric ratio H_2S to SO_2 of Equation 2. There seemed to be no indication of the formation of intermediate compounds during the time that sulphur was being formed.

In this part of the report, a number of methods for recovering sulphur from H_2S gas, by the Claus method in liquid

media, have been examined. There is, however, very little information on which to base a comparison or to estimate their relative merits. The Townsend glycol process[86] is claimed to be more economical that the gaseous Claus process and to produce comparable yields and purity of sulphur. The sodium citrate method[74] appears attractive since it has been well worked out and can be used for the treatment of either H_2S or SO_2. The use of a widely available medium like sea water[78] is certainly an interesting possibility.

CONCLUSIONS

Modifications to the Claus process, by which elemental sulphur is recovered from a stoichiometric 2:1 mixture of H_2S and oxygen or SO_2, are available for mixtures having low, medium or high concentrations of H_2S as well as varying proportions of diluting gases such as CO_2, mercaptans, etc. Both high-temperature (dry) processes and those in which sulphur is precipitated in inorganic solutions or in organic liquids (wet processes) have also been devised. High percentage recoveries of sulphur are possible in both systems and a high-purity product may be obtained. Compact sulphur plants have been designed to permit efficient economical recovery of sulphur from small deposits.

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