

SECTION 22

Sulfur Recovery

Sulfur is present in natural gas principally as hydrogen sulfide (H_2S) and, in other fossil fuels, as sulfur-containing compounds which are converted to hydrogen sulfide during processing. The H_2S , together with some or all of any carbon dioxide (CO_2) present, is removed from the natural gas or refinery gas by means of one of the gas treating processes described in Section 21. The resulting H_2S -containing acid gas stream is incinerated, or fed to a sulfur recovery unit. This section is concerned with recovery of sulfur by means of the modified Claus and Claus tail gas clean-up processes. Redox processes are touched upon. For a discussion and description of other sulfur recovery processes, see Maddox.¹

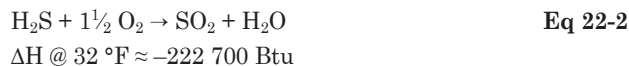
THE CLAUSS PROCESS

The Claus process as used today is a modification of a process first used in 1883 in which H_2S was reacted over a catalyst with air (oxygen) to form elemental sulfur and water.

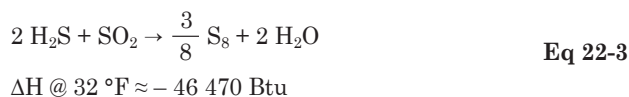


Control of this highly exothermic reaction was difficult and sulfur recovery efficiencies were low. In order to overcome these process deficiencies, a modification of the Claus process was developed and introduced in 1936 in which the overall reaction was separated into (1) a highly exothermic thermal or combustion reaction section in which most of the overall heat of reaction (from burning one-third of the H_2S and essentially 100% of any hydrocarbons and other combustibles in the feed) is released and removed, and (2) a moderately exothermic catalytic reaction section in which sulfur dioxide (SO_2) formed in the combustion section reacts with unburned H_2S to form elemental sulfur. The principal reactions taking place (neglecting those of the hydrocarbons and other combustibles) can then be written as follows:

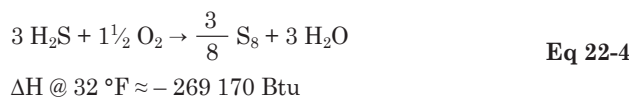
Thermal or Combustion Reaction Section



Combustion and Catalytic Reaction Sections



Overall Reaction



Hydrogen Sulfide Cracking

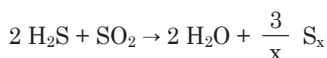


This is a simplified interpretation of the reaction actually taking place in a Claus unit. The reaction equilibrium is complicated by the existence of various species of gaseous sulfur (S_2 , S_3 , S_4 , S_5 , S_6 , S_7 , and S_8) whose equilibrium concentrations in relation to each other are not precisely known for the entire range of process conditions. Furthermore, side reactions involving hydrocarbons, H_2S , and CO_2 present in the acid gas feed can result in the formation of carbonyl sulfide (COS), carbon disulfide (CS_2), and carbon monoxide (CO). Gamson and Elkins² cover the basic theory involved in the Claus process; however, they ignore the many potential side reactions and also the existence of S_3 , S_4 , S_5 , and S_7 .

FIG. 22-1

Nomenclature

H = heat content or enthalpy, Btu/lb or Btu/lb-mole
 K_p = equilibrium constant
 For the low pressure, vapor phase Claus reaction



$$K_p = \frac{(P_{\text{H}_2\text{O}})^2 (P_{\text{S}_x})^{3/x}}{(P_{\text{H}_2\text{S}})^2 (P_{\text{SO}_2})}$$

$$= \frac{[\text{Mols H}_2\text{O}]^2 [\text{Mols S}_x]^{3/x}}{[\text{Mols H}_2\text{S}]^2 [\text{Mols SO}_2]} \left[\frac{\pi}{\text{Total Mols}} \right]^{\frac{3}{x} - 1}$$

LT/D = long ton per day. A long ton is 2240 pounds.
 P = partial pressure, atmospheres
 π = total pressure, atmospheres

DEFINITIONS OF WORDS AND PHRASES USED IN SULFUR RECOVERY

Acid gas: feed stream to sulfur recovery plant consisting of H_2S , CO_2 , H_2O , and usually less than 2 mol % hydrocarbons.

Claus process: a process in which $\frac{1}{3}$ of the H_2S in the acid gas feed is burned to SO_2 which is then reacted with the remaining H_2S to produce sulfur. This is also referred to as the modified Claus process.

Residence time: the period of time in which a process stream will be contained within a certain volume or piece of equipment, seconds.

Tail gas cleanup unit: a process unit designed to take tail gas from a Claus sulfur recovery plant and remove additional sulfur with the goal of meeting environmental sulfur emission standards.

For the usual Claus plant feed gas composition (water-saturated with 30–80 mol % H_2S , 0.5–1.5 mol % hydrocarbons, the remainder CO_2), the modified Claus process arrangement results in thermal section (burner) temperatures of about 1800 to 2500 °F. The principal molecular species in this temperature range is S_2 (Fig. 22-21) and conditions appear favorable for the formation of elemental sulfur by direct oxidation of H_2S (Equation 22-6) rather than by the Claus reaction (Equation 22-7).



$$\Delta H @ 32^\circ \text{F} = -135\,000 \text{ Btu}$$



$$\Delta H @ 32^\circ \text{F} = +20\,230 \text{ Btu}$$

However, both laboratory and plant measurements indicate the more highly exothermic oxidation of H_2S to SO_2 (Equation 22-2) predominates and the composition of the equilibrium mixture therefore is determined by the slightly endothermic Claus reaction (Equation 22-7).

Fig. 22-2 is a representation of theoretical equilibrium conversion as a function of temperature for

- An acid gas from a wellhead-type treater, with about 3.5 mol % hydrocarbons (Curve 1)
- An acid gas from a refinery treater, with about 7 mol % hydrocarbons and 1 mol % mercaptans (Curve 2)
- Pure H_2S (Curve 3)

These curves indicate:

- Sulfur recovery would be expected to be lower for a feed gas from a refinery than for a wellhead treater because of higher hydrocarbon content
- The calculated equilibrium conversion for both acid gas feeds follows closely the idealized curve for pure H_2S
- Conversion of H_2S to elemental sulfur is favored in the reaction furnace by higher operating temperatures of

1800 °F and in the catalytic converters by lower operating temperatures of less than 700 °F

To attain an overall sulfur recovery level above about 70%, the thermal, or combustion, section of the plant is followed by one or more catalytic reaction stages. Sulfur is condensed and separated from the process gases after the combustion section and after each catalytic reaction stage in order to improve equilibrium conversion. Although Fig. 22-2 indicates that the Claus reaction is favored by lower temperatures, the process gases must be reheated prior to being fed to the catalytic reaction stage in order to maintain acceptable reaction rates and to ensure that the process gases remain above the sulfur dewpoint as additional sulfur is formed. Fig. 22-3 is the flow sheet of an example three-stage Claus sulfur recovery plant; Fig. 22-4 shows the mechanical arrangement of an example small, package-type, two-stage Claus plant.

Gases leaving the final sulfur condensation and separation stage may require further processing. These requirements are established by local, state, or national regulatory agencies. These requirements can be affected by the size of the sulfur recovery plant, the H_2S content of the plant feed gas, and the geographical location of the plant.

CLAUS PROCESS CONSIDERATIONS

The Claus sulfur recovery process includes the following process operations:

- Combustion — burn hydrocarbons and other combustibles and 1/3 of the H_2S in the feed
- Waste heat recovery — cool combustion products. Because most Claus plants produce 150–600 psig steam (365–490 °F), the temperature of the cooled process gas stream is usually about 600–700 °F
- Sulfur condensing — cool outlet streams from waste heat recovery unit and from catalytic converters. Low pressure steam at 50–70 psig is often produced and the temperature of the cooled gas stream is usually about 350 °F

FIG. 22-2
Theoretical Equilibrium Percent Conversion of Hydrogen Sulfide to Sulfur³

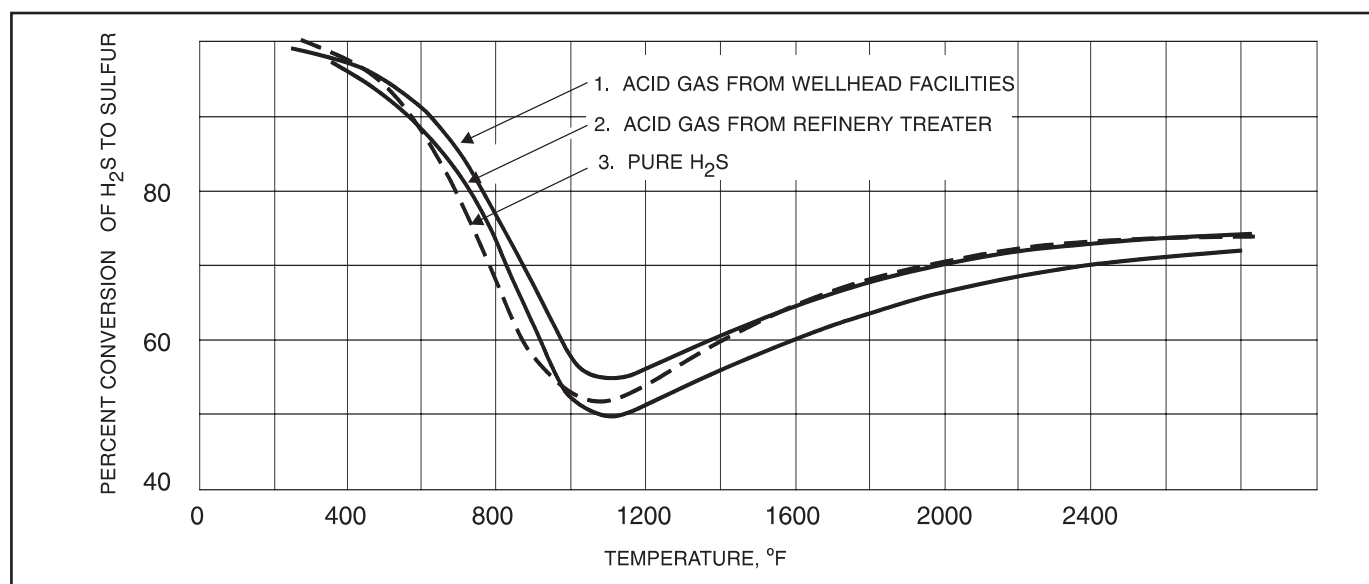


FIG. 22-3
Example Three-Stage Sulfur Plant
(Straight-Through Operating with Acid Gas-Fueled Inline Burners for Reheating)

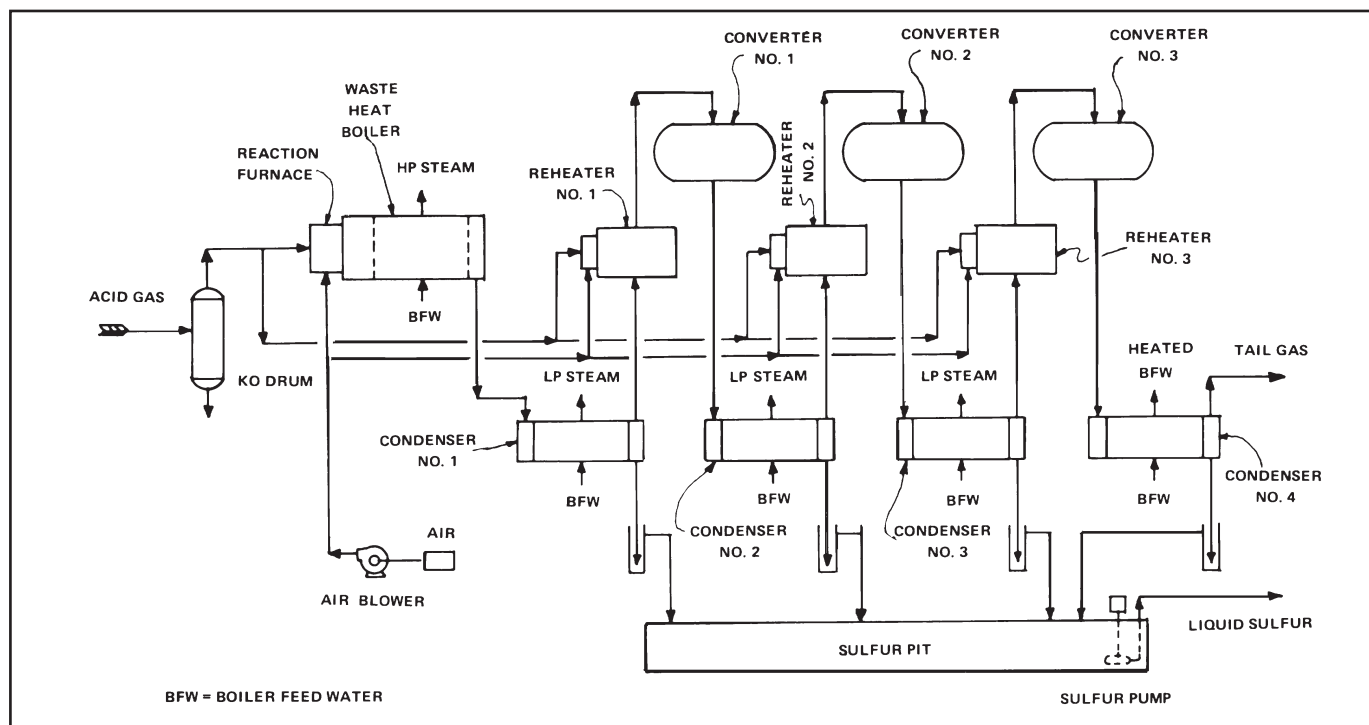
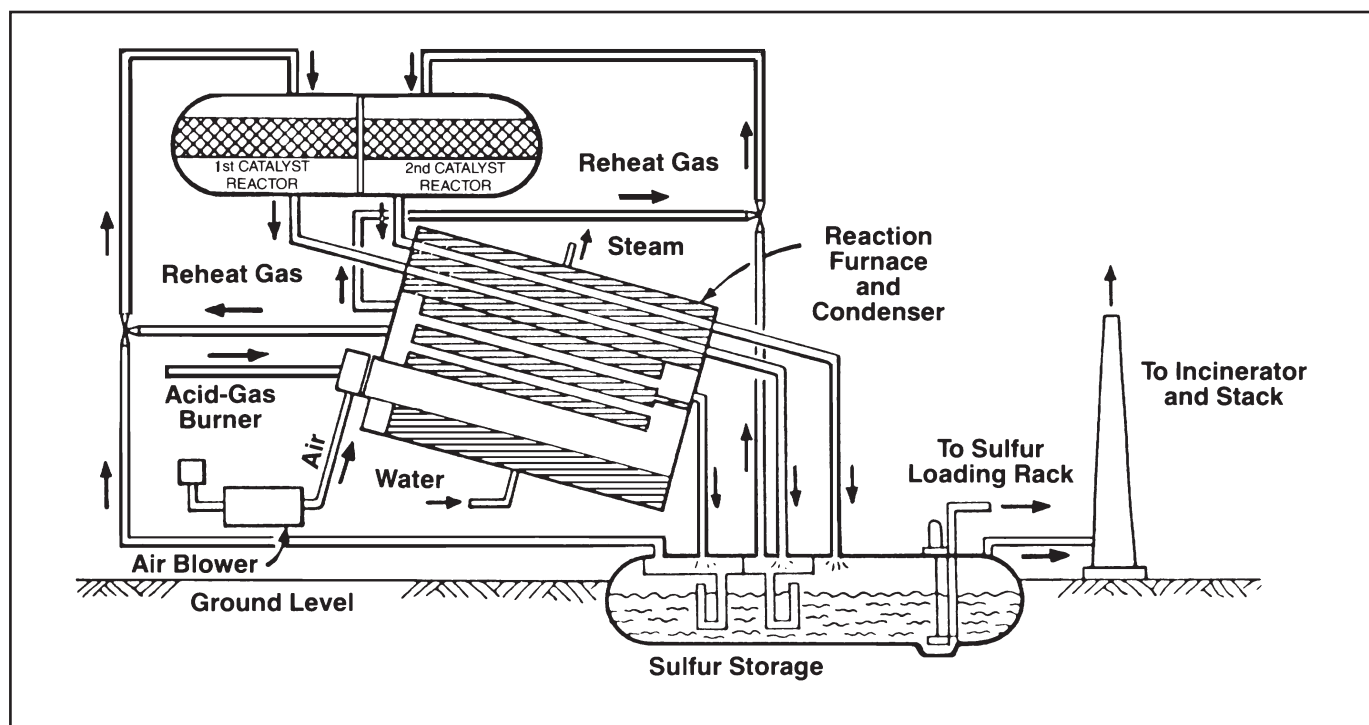


FIG. 22-4
Example Package-Type Sulfur Plant



or 260–300 °F for the last condenser, generating 15 psig steam or preheating boiler feed water

- Reheating — Reheat process stream, after sulfur condensation and separation, to a temperature high enough to remain sufficiently above the sulfur dewpoint, and generally, for the first converter, high enough to promote hydrolysis of COS and CS₂ to H₂S and CO₂



- Catalytic Conversion — Promote reaction of H₂S and SO₂ to form elemental sulfur (Equation 22-3)

Process Variations

Several variations of the basic Claus process have been developed to handle a wide range of feed gas compositions. Some of these are shown in Fig. 22-5. Straight-through operation results in the highest overall sulfur recovery efficiency and is chosen whenever feasible.

Fig. 22-6 can be used as a guide in Claus process selection.

Combustion Operation

Most Claus plants operate in the “straight-through” mode. The combustion is carried out in a reducing atmosphere with only enough air (1) to oxidize one-third of the H₂S to SO₂, (2) to burn hydrocarbons and mercaptans, and (3) for many refinery Claus units, to oxidize ammonia and cyanides. Air is supplied by a blower and the combustion is carried out at 3–14 psig, depending on the number of converters and whether a tail gas unit is installed downstream of the Claus plant.

Numerous side reactions can also take place during the combustion operation, resulting in such products as hydrogen (H₂), carbon monoxide (CO), carbonyl sulfide (COS), and carbon disulfide (CS₂). Thermal decomposition of H₂S appears to be the most likely source of hydrogen since the concentration of H₂ in the product gas is roughly proportional to the concentration of H₂S in the feed gas. Formation of CO, COS, and CS₂ is related to the amounts of CO₂ and/or hydrocarbons present in the feed gas. Plant tests indicate concentrations of H₂ and CO in the product gas to be approximately at equilibrium at reaction furnace temperatures; Fig. 22-7 indicates potential COS and CS₂ formation in the Claus furnace.

Heavy hydrocarbons, ammonia, and cyanides are difficult to burn completely in a reducing atmosphere. Heavy hydrocarbons may burn partially and form carbon which can cause deactivation of the Claus catalyst and the production of off-color sulfur. Ammonia and cyanides can burn to form nitric oxide (NO) which catalyzes the oxidation of sulfur dioxide (SO₂) to sulfur trioxide (SO₃). SO₃ causes sulfation of the catalyst and can also cause severe corrosion in cooler parts of the unit. Unburned ammonia may form ammonium salts which can plug the catalytic converters, sulfur condensers, liquid sulfur drain legs, etc. Feed streams containing ammonia and cyanides are sometimes handled in a special two-combustion stage burner or in a separate burner to ensure satisfactory combustion.

Flame stability can be a problem with low H₂S content feeds (a flame temperature of about 1800 °F appears to be the minimum for stable operation). The split flow, sulfur recycle, or direct oxidation process variations often are utilized to handle these H₂S-lean feeds; but in these process schemes, any hydrocarbons, ammonia, cyanides, etc. in all or part of the feed gas are fed unburned to the first catalytic converter. This can result

FIG. 22-5
Claus Process Variations

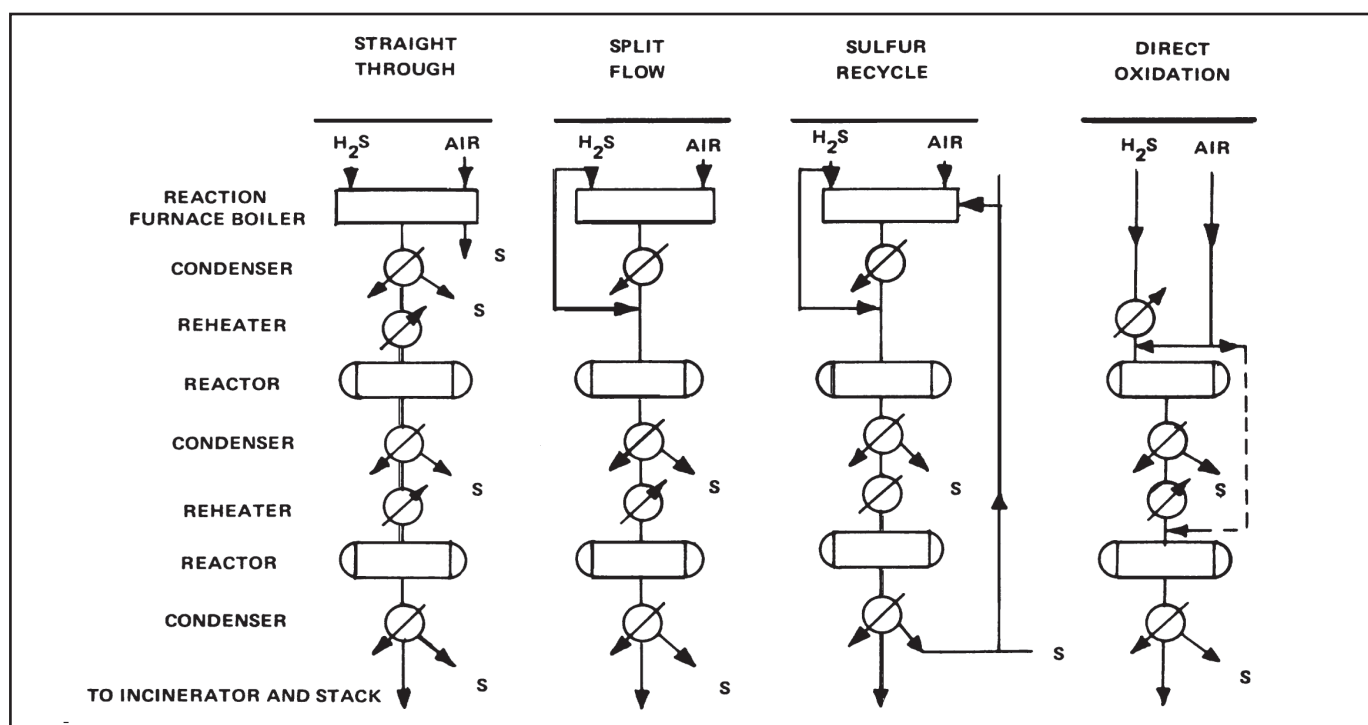


FIG. 22-6
Claus Plant Configurations

Feed H ₂ S Concentration, Mol%	Claus Variation Suggested
55 – 100	Straight-through
30 – 55	Straight-through or straight- through with acid gas and/or air preheat
15 – 30	Split-flow or straight-through with feed and/or air preheat
10 – 15	Split-flow with acid gas and/or air preheat
5 – 10	Split-flow with fuel added or with acid gas and air preheat., or direct oxidation or sulfur recycle
< 5	Sulfur recycle or variations of direct oxidation or other sulfur recovery processes.

in the cracking of heavy hydrocarbons to form carbon or carbonaceous deposits and the formation of ammonium salts, resulting in deactivation of the catalyst and/or plugging of equipment. A method of avoiding these problems while still improving flame stability is to preheat the combustion air and/or acid gas, and to operate “straight-through.” An example of such an arrangement is shown in Fig. 22-8. Steam-, hot oil-, or hot gas-heated exchangers and direct fired heaters have been used. The air and acid gas are usually heated to about 450–500 °F. Sometimes split flow is combined with acid-gas preheat. Other methods of improving flame stability are to use a high intensity burner, to add fuel gas to the feed gas, or to use oxygen or oxygen-enriched air for combustion.

Acid gas enrichment, using an absorber / regenerator pair is an alternative that concentrates the H₂S fed to the thermal reactor to stabilize the flame, increase thermal oxidation temperature and reduce the size of the Claus equipment. The major drawbacks are the increases in capital costs (may be balanced by reductions in the thermal reactor and Claus reaction train), operational complexity and the operational requirement for regeneration energy. A challenge with absorption systems is the absorption H₂S selectivity, which allows mercaptans, COS and CS₂ to pass through the absorber. These can be routed to the incinerator if the sulfur recovery target allows or can be routed to a COS hydrolysis reactor or upstream of the hydrogenation reactor, possibly through an in-line burner, to convert these sulfur species to H₂S at some cost in hydrogen.

Operation with significant amounts of BTEX in the feed is a significant hurdle because destruction of aromatics requires operation of the thermal reactor in excess of 2190 °F. Air and acid gas feed preheat, fuel enrichment of the acid gas stream and oxygen-enrichment of the air mentioned previously can be used to increase the thermal reactor temperature. Acid gas enrichment, an extra cycle of absorption/regeneration discussed above, can also be used to increase the acid gas H₂S concentration and hence thermal reactor temperature. Activated carbon bed regenerative absorption has also been used to remove aromatics from the acid gas feed. Xylene has roughly 13 times the deactivation effect on alumina as that of toluene, which has roughly 70 times the deactivation effect of benzene per reference 37. Activated carbon has the strongest affinity for the heavier aromatics.

FIG. 22-7
Potential COS and CS₂ Formation in Claus Furnaces¹⁹

Feed composition, mol%				COS, CS ₂ formation, % of sulfur in feed ^{a,b}
Hydrocarbon (as C ₃ H ₈)	Water	CO ₂	H ₂ S	
0	6	4	90	0.5
0	6	14	80	1.5
0	6	24	70	2.5
0	6	34	60	3.5
0	6	44	50	4.5
0	6	54	40	5.5
0	6	64	30	6.5
0	6	74	20	7.5
2	6	4	88	2.0
2	6	14	78	3.0
2	6	24	68	4.5
2	6	34	58	6.0
2	6	44	48	7.0
2	6	54	38	9.0
2	6	64	28	11.0
2	6	74	18	14.0
4	6	4	86	3.5
4	6	14	76	5.0
4	6	24	66	6.0
4	6	34	56	8.0
4	6	44	46	10.0
4	6	54	36	12.0
4	6	64	26	14.0
4	6	74	16	18.0

^a Maximum. Actual production varies with operating temperature and pressure, residence time, burner mixing and burner efficiency.

^b Units feeding <30% H₂S may operate other than “straight through,” causing reduced COS and CS₂ production proportional to amount fed to main burner.

Operation with significant amounts of ammonia present similar issues. If the ammonia is concentrated in one stream with less than 100 ppmw ammonia in the “clean stream,” a two stage thermal reactor design can be used where the ammonia stream is fed only to the first stage with some of the clean stream, and the balance of the clean stream is feed to the second stage of the thermal reactor. The first stage will require a minimum of 2250 °F oxidation temperature to destroy the ammonia.

Fig. 22-32 gives the theoretical flame temperature for a straight-through operation and for a split-flow operation with two-thirds of the acid gas bypassing the combustion section. For each operation there are isotherms, which represent the temperature of the acid gas feeding the combustion section. The isotherms for temperatures above 110 °F represent acid-gas preheat. For the split-flow operation, the part of the acid gas that bypasses the combustion section is not preheated. This figure can also be used for combinations of straight through and split flow. In this case, the split flow (i.e., the amount of acid-gas bypass) should be minimized, which will maximize the overall sulfur recovery and minimize the problems associated with acid-gas bypass that are mentioned in the foregoing paragraph. For acid-gas temperatures different than the isotherm values, and for acid-gas bypasses less than two thirds, corresponding flame temperatures can be estimated by linear extrapolation/interpolation of the curves.

Waste Heat Recovery Operation

Most Claus plants cool the process gases leaving the combustion section by generating steam in a fire-tube waste heat boiler. Steam pressures usually range between 150 psig and 600 psig. The waste heat boiler outlet temperature is therefore normally above the sulfur dewpoint of the process gases; however, some sulfur may condense, especially during partial loads, and provision should be made to drain this sulfur from the process stream (or the piping should be arranged so the sulfur will drain through downstream equipment).

Other methods of cooling the hot combustion gases include the use of glycol-water mixtures, amine solutions, circulating cooling water (no boiling), and oil baths. The utilization of one of these alternate cooling fluids can be especially advantageous at locations where good quality boiler feed water is not available, or where steam generation is not desired.

Some small Claus units use a closed steam system. Steam is generated at 20–30 psig, condensed with air in an elevated condenser, and the steam condensate returned by gravity to the boiler as feed water.

Sulfur Condenser Operation

Sulfur is condensed ahead of the first catalytic converter (except in the case of split-flow operation) and following each catalytic converter in order to promote the Claus reaction. These condensers (other than the one following the last catalytic converter) are typically designed for outlet temperatures of 330–360 °F which results in a condensed liquid sulfur of reasonably low viscosity and a metal skin temperature (on the process gas side) above the sulfurous/sulfuric acid dewpoint. The final sulfur con-

denser outlet temperature can be as low as 260 °F, depending on the cooling medium available. A large temperature difference between process gases and cooling medium should be avoided, however, because of the possible formation of sulfur fog; this is especially important for the final sulfur condenser.

Reheating Operation

The temperature of the process gas at the inlet of the catalytic converters should be such that the effluent gas temperature is:

- Higher (by 25–30 °F) than the expected outlet sulfur dewpoint
- As low as possible to maximize H_2S conversion but high enough to obtain a satisfactory Claus reaction rate
- High enough for hydrolysis of COS and CS_2 (for the first catalytic converter only)

Fig. 22-9 shows the methods of reheat commonly used.

- The hot gas bypass method takes a slip-stream of hot process gases from the waste heat recovery unit, usually at 900 °F to 1200 °F, and mixes this stream with the sulfur condenser outlet gases upstream of the catalytic converter.
- The direct fired method of reheating uses inline burners burning either fuel gas or acid gas, with the combustion products being mixed with the sulfur condenser outlet gases.
- The indirect reheat methods use direct fired heaters or heat exchangers to heat the sulfur condenser outlet gases; high pressure steam, hot oil, and hot process gases have been used. Electrical reheating has also been used.

FIG. 22-8
Sulfur Recovery Process with Acid Gas and Air Preheat

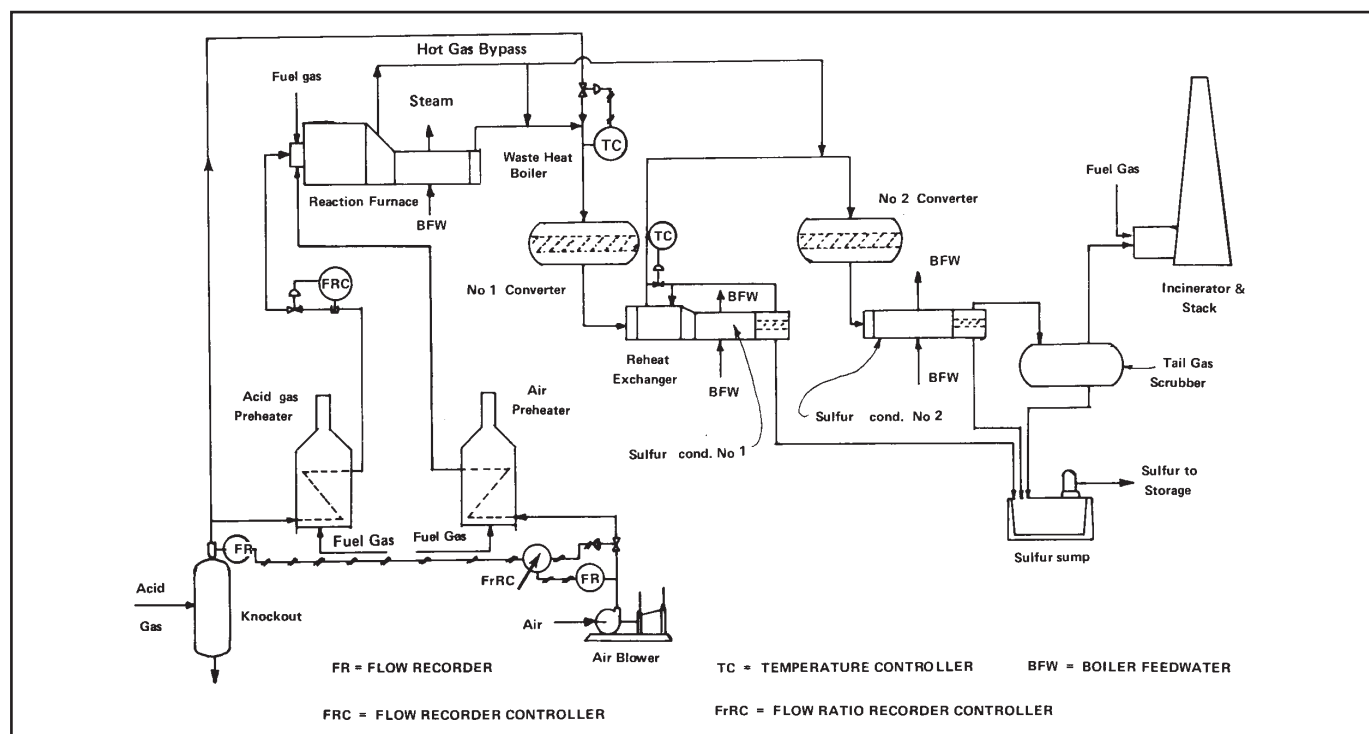
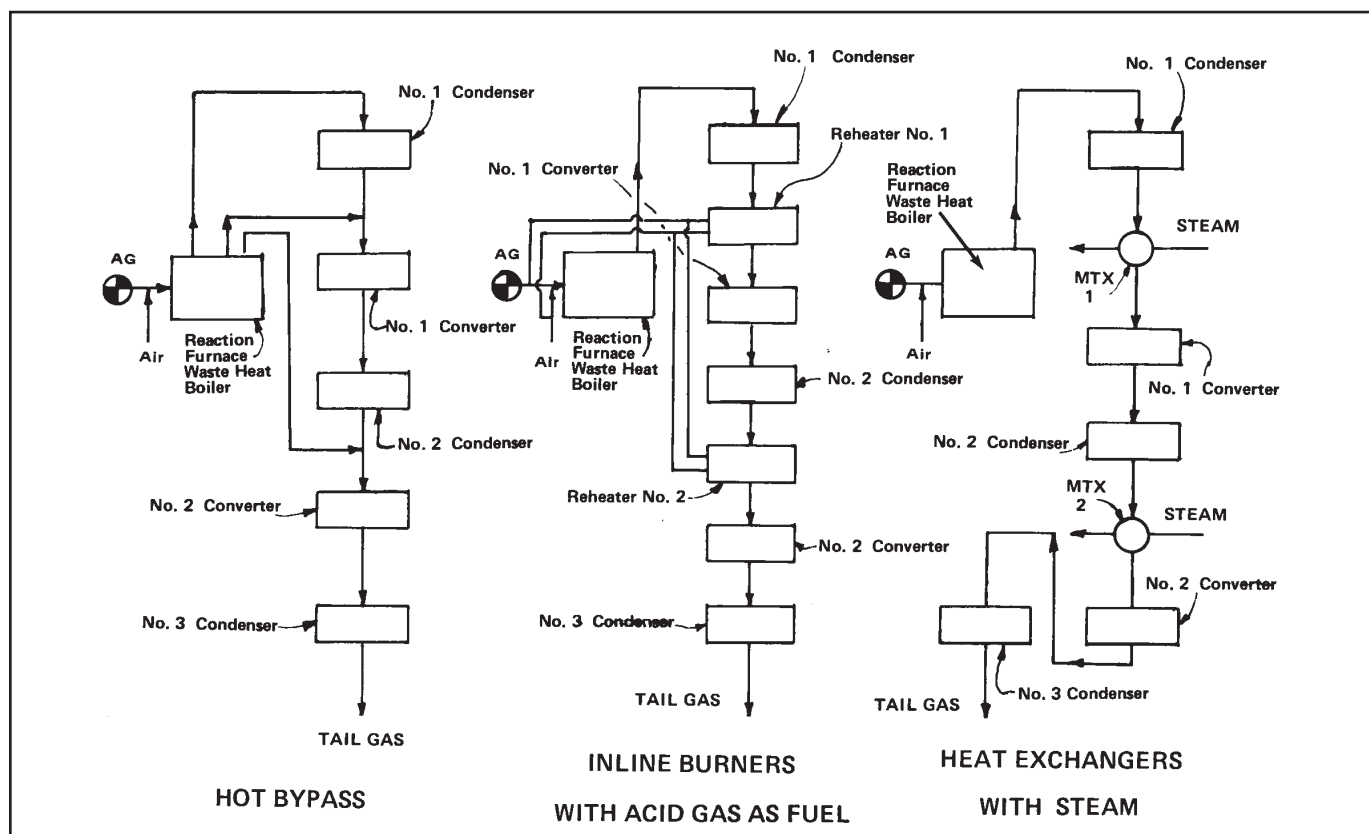


FIG. 22-9
Alternate Methods of Reheating³



Hot gas bypass reheating is normally the lowest cost alternative, is relatively simple to control, and results in low pressure drop. Its disadvantage is lower overall sulfur recovery, particularly at reduced throughput. The hot gas bypass method is sometimes used for the first two catalytic converters and an indirect method of reheat used for the third converter.

Direct fired reheating uses an inline burner which usually burns a portion of the Claus plant feed gas but which sometimes burns fuel gas. This reheating method can be designed to heat the process gases to any desired temperature level. Pressure drop is also relatively low. Potential disadvantages of inline burners are the possible formation of SO_3 , if acid gas is burned (sulfates deactivate the catalyst) and of soot, if fuel gas is burned (soot can plug and also deactivate the catalyst). A well-mixed, high-intensity burner capable of operating stoichiometrically without producing soot should be utilized for burning fuel gas. Burner requirements are less stringent for burning acid gas; the $\text{H}_2\text{S}:\text{SO}_2$ ratio in the inline burner outlet gases is usually maintained at about 1:2 to 1:3. Precautions must be taken, however, to avoid oxygen breakthrough from the inline burners. Oxygen in as low a concentration as 30 ppmv can rapidly sulfate the catalyst.

Indirect reheating, which involves a heat exchanger ahead of each catalytic converter, is the most expensive alternative and results in the highest pressure drop. In addition, converter inlet temperatures are limited by the temperature of the heating medium. For example, the use of 600 psig steam (489 °F) as the heat source would limit the converter inlet temperature to a maximum of about 470 °F. Thus, catalyst rejuvenation is usually not

possible and COS and CS_2 hydrolysis may be more difficult. However, indirect reheating usually results in the highest overall sulfur recovery, and deactivation of the catalyst (because of sulfation, carbon deposits, etc.) is less likely to occur.

Catalyst Converter Operation

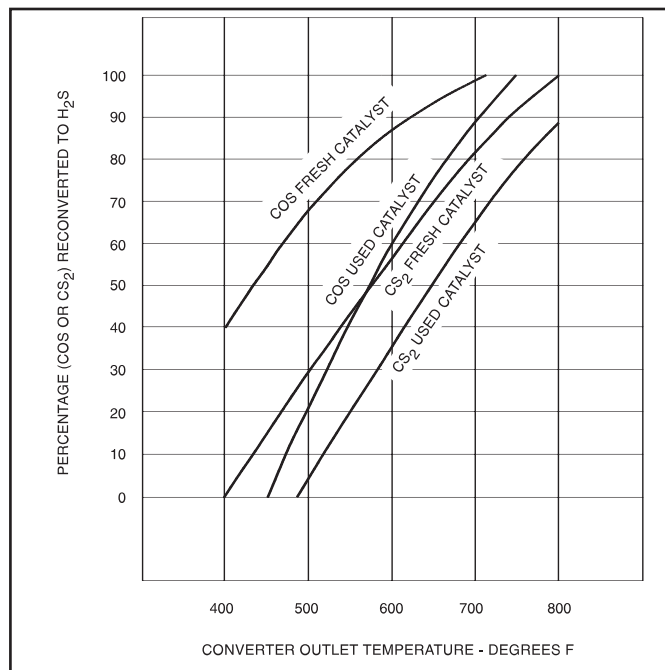
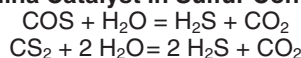
The Claus reaction is exothermic at converter temperatures, and the reaction equilibrium is favored by lower temperatures. However, carbonyl sulfide (COS) and carbon disulfide (CS_2) hydrolyze more completely at higher temperatures as shown by Fig. 22-10. The first catalytic converter is therefore frequently operated at temperatures high enough to promote the hydrolysis of COS and CS_2 ; the second and third catalytic converters are operated at temperatures only high enough to obtain acceptable reaction rates and to avoid liquid sulfur deposition and associated catalyst deactivation. A three converter Claus unit will utilize inlet temperatures in the following range: (1) first converter, 450–480 °F; (2) second converter, 390–430 °F; (3) third converter, 370–410 °F.

A temperature rise occurs across each catalytic converter because both the Claus and COS/ CS_2 hydrolysis reactions are exothermic. The temperature rise will generally be 80–180 °F for the first converter, 25–60 °F for the second converter, and 5–15 °F for the third converter. Because of heat losses, measured temperatures for the third converter will often show a small temperature drop.

The foregoing is based on using the regular Claus catalyst in all of the converters. Regular catalyst is made of activated

FIG. 22-10

Hydrolysis of COS and CS₂ with Activated Alumina Catalyst in Sulfur Converter



alumina (Al₂O₃). The primary function of activated alumina is to increase the rate of the Claus reaction (Equation 22-3) and ensure full equilibrium conversion to sulfur. It also helps hydrolyze the carbon sulfides, COS and CS₂, to H₂S and CO₂ in the first converter (Equation 22-8 and Equation 22-9); but it achieves reasonable hydrolysis only at high temperatures of 600 to 650 °F (Fig. 22-10), which reduces the equilibrium conversion to sulfur in the Claus reaction (Fig. 22-2). A catalyst made of activated titania (i.e., titanium dioxide TiO₂) can achieve greater than 90% hydrolysis of the carbon sulfides at temperatures of 600–650 °F, and reasonable hydrolysis at lower temperatures where Claus conversion is enhanced. Up to 50% of the sulfur in the plant tail gas can be in the form of carbon sulfides, and therefore titania in the first converter can be a way to achieve higher sulfur recovery. However, titania is very expensive, and can be 10–15 times the cost of activated alumina. Sometimes a combination such as 50–50% activated alumina and titania is used. When this is done, the titania should be placed in the bottom of the bed to protect it from contamination.

MECHANICAL CONSIDERATIONS

Combustion Operation

Combustion is carried out in the reaction furnace which may be either external (separate from waste heat recovery facility) or internal (combined with waste heat recovery facility). At the normal operating temperature of 1800–2500 °F, external furnaces require a refractory lining to protect the steel shell, but with internal furnaces, the burner is surrounded by the cooling medium and refractory is not required. For small Claus units, an internal furnace is less expensive. For units larger than about 30 LTD, an external furnace is usually more economical.

Reaction furnaces are designed for a residence time of at least 0.5 seconds; plant tests indicate this is adequate to reach equilibrium. Feed gases richer in H₂S generally require less residence time than leaner feeds. The thermal reactor should be purged with 5 volumes of nitrogen (over a span of 15 minutes to ensure displacement of the volume) before start-up.

The refractory in the external reaction furnace serves to resist the high flame temperatures and to protect the steel shell. Refractories capable of withstanding high temperatures normally have a high alumina content, e.g., 85–90% alumina. However, these refractories have relatively poor insulating properties and will not provide adequate protection for the steel shell. Therefore, an insulating refractory layer is normally placed against the steel shell, and a layer of high alumina refractory covers the insulating refractory. Occasionally, three different refractories have been used in reaction furnaces. (See Section 8 for additional information regarding refractories.)

Refractory selection and design is important because the steel shell can be overheated (above 650 °F) resulting in direct sulfide (H₂S) attack, or can be cooled below the dewpoint of SO₂ and SO₃, resulting in acid condensation and rapid corrosion. External insulation or shrouding for personal protection is often installed to allow metal temperatures above about 400 °F, which is generally safely above the acid dewpoint.

Interior refractory checker walls and matrix block are sometimes installed in external-type reaction furnaces to improve mixing, stabilize the flame and to serve as a heat buffer. This is of greater importance if ammonia or cyanides or high concentrations of hydrocarbons are present in the feed gas. Alternatively, choke rings can be used to promote mixing.

Reaction furnace burner types available are tangential and axial burners. Tangential burners tend to be low intensity, requiring significant thermal reactor volume to complete mixing of combustion products. Axial burners are often offered as a high intensity design maximizing mixing, allow full effectiveness of the residence time in the thermal reactor and aid flame stability.

Waste Heat Recovery Operation

For most internal reaction furnace-type waste heat recovery units, the acid gas burner is installed inside a single, large, first-pass firetube (radiant section) and the process gas then flows through one or more additional tube passes (convection section). The first pass firetube is cooled externally and therefore does not require refractory protection; however, pass plates and other uncooled metal surfaces exposed to the process gases at temperatures above about 650 °F should be protected with refractory. Tube sizes for the convection section passes range from 1" to 6" with a tube mass velocity of 2–5 lb/(sec · ft²).

To ensure a reasonable tube life, the inlet end of each tube is protected by inserting a ceramic ferrule that extends about 3"–6" beyond the inside of, and about 3" outside of the tube sheet. This prevents the hot gases from directly contacting the tube at the critical junction of tube and tubesheet. These ceramic ferrules should also be wrapped with a thin layer of insulation (1/8"–3/8" thick). The inlet tube sheet should be protected by a refractory overlay, usually about 3" thick.

A recent development has been the advent of two piece ferrules. These ferrules have hex heads designed to protect the tube sheet as well as the tube inlets. The tube sheet is covered with an insulating board perforated for the tubes and then hex head ferrules are inserted. The hex heads are sized to the tube

pitch to provide hexagonal tiling of the plane, therefore also protecting the tube sheet. These hex heads allow for thermal expansion, unlike the monolithic refractory overlay used with plain ferrules, and hence are less susceptible to thermally mediated cracking.

Waste heat recovery units are usually designed to meet pressure containment requirements according to Section I of the ASME Code rather than to TEMA standards. A two-pass tube welding procedure is normally used. Conventional practice is to apply the first-pass weld before tube rolling (or after a light rolling), which allows venting to eliminate gas traps. The first-pass weld is usually pressure tested to locate all weld pinholes for repairing prior to subsequent tube rolling and final welding. After final welding, the completed tube attachment is lightly rolled. During the final hydrotest, the tube weld surfaces should be inspected using a dye-penetrant test.

Tube rupture in the waste heat boiler is an important relief case if combined with tail gas diverter valves. This case can potentially be mitigated by blow through to the sulfur pit of the sulfur seal legs if these legs are designed for this contingency.

Tube sizes range between 2" and 6". Tube spacing is based on a minimum ligament (distance between outer edge of each tube) dimension of 0.75"–1.0". The design mass velocity in these tubes ranges between 1.0 lb/(sec · ft²) and 8.0 lb/(sec · ft²). For most installations, the tube mass velocity will be 2 to 5 lb/(sec · ft²). Allowable tube side pressure drop often determines tube velocity.

Both kettle-type and natural circulation-type waste heat boilers are used as horizontal units to ensure total submergence of the tubes.

The advantages of the natural circulation-type unit which has a separate elevated steam disengaging drum, include:

- Improved steam quality because of surface blowdown capability and more sophisticated steam/water separation devices
- More water holdup above the hot process tubes which provides additional time to react to emergency conditions and lessens the chance of tube failure from overheating
- Better steam/water circulation at the critical tube/tubesheet junction

The advantages of the kettle-type boilers include:

- Lower installed cost
- Ability to handle a much wider range of load conditions

Both kettle-and natural circulation-type waste heat boilers should be considered severe-service applications. Some early boilers were designed to TEMA standards and the resulting thick tubesheets combined with the high heat flux resulted in failures at the tube-tubesheet juncture.

The tubesheet design is based upon the thermal, mechanical stresses at the tube-tubesheet attachment. Tubesheets are usually thin (3/4" to 1-1/2") resulting in acceptable temperature profiles at the tube weld, the ligaments between tubes, and the portion of tubesheet not cooled by water. The deflection of these thin tubesheets during operation reduces the stress transmitted to the tube-tubesheet attachment. Natural circulation-type units have tube patterns arranged to accommodate the bending stress at the pattern's outer boundaries, while kettle-type units have stayrods to stiffen the portions of the tubesheet without

tubes. Waste heat boilers utilizing flexible, thin tubesheets have extremely good service histories.

Sulfur Condenser Operation

Sulfur condensers may be single pass or multi-pass units. Both natural circulation and kettle-type condensers are used; horizontal units are recommended. Condensers are designed with a minimum tube diameter of 1". Normally 12 BWG steel tubes are used, installed with a 1/2" to 3/4" ligament between tubes.

For Claus units smaller than about 100 long ton per day, the sulfur condensers are frequently installed in a single horizontal shell with internal full cross sectional baffles separating the condenser services.

Sulfur condensers operate at much lower heat fluxes than waste heat boilers and usually operate at lower shell side pressures. Both of these factors significantly reduce the mechanical design requirements for tubesheets and tube attachments. Sulfur condensers are designed to meet either ASME Section I or Section VIII Codes. Tubes are typically rolled, seal welded, and re-rolled.

The design mass velocity for the sulfur condenser tubes varies from 3.0 lb/(sec · ft²) to 8.0 lb/(sec · ft²) with a typical minimum mass velocity at design conditions of 5.0 lb/(sec · ft²). The design mass velocity should be sufficiently high to prevent sulfur fogging from occurring during turndown conditions.²¹ If sulfur fogging does occur, the liquid sulfur will not adequately separate from the process gas in the separator downstream of the condenser. The tube velocity is also limited by the allowable tube side pressure drop, which is usually about 0.3 to 0.5 psi.

Sulfur condensers are subject to plugging with solid sulfur. In the design of the plant piping system, the condensers should be the low points in the system and should also slope toward the sulfur drain end. This allows any liquid sulfur present upstream of the condenser, as well as that formed in the condenser, to drain into the liquid-vapor separator chamber and out through the sulfur drain.

To allow access to the tubes for cleaning and inspection, sulfur condensers should have inspection ports and manways at both ends. Additional access to the tubes should be provided by using bolted cover (end) plates.

Vapor-liquid separator chambers are installed downstream of the sulfur condensers to separate the liquid sulfur from the process gases and to allow the liquid sulfur to drain from the system. These separator chambers can be integral parts of the condenser or separate vessels and may be provided with wire-mesh type mist eliminators or impingement plates to reduce liquid sulfur entrainment. A superficial gas velocity of 20–30 ft/sec is commonly used as a basis for sizing the separator chambers.

Sulfur condensers are usually designed to generate low pressure (20–100 psig) steam on the shell side. The final sulfur condenser is often used to heat boiler feed water, but care must be taken not to over cool the stream and solidify sulfur. Sometimes 15 psig steam is generated, condensed and returned in a closed circuit.

Reheating Operation

Hot gas bypass method — Piping and valves are usually of stainless steel (although sometimes refractory-lined piping is used) in order to handle the hot (900–1200 °F) corrosive process gas. An additional valve is sometimes installed in the process

stream downstream of the hot gas bypass extraction point in order to improve turndown capability.

Direct (inline burner) method — Inline burners are usually designed to raise the temperature of the process gas at least 50 °F above the normal operating inlet temperature of the catalytic converter. This extra heat release capacity is useful during a “heat soak” or catalyst rejuvenation operation. Usually, a portion of the acid gas is burned in the inline burner; however, other fuels, such as natural gas, can be used. The burner is installed in a refractory lined combustion chamber and the hot combustion gases are mixed with the process gas to reach the reactor inlet temperature. The retention time in the mixing chamber is usually between 0.1 and 0.3 seconds.

Indirect (heating exchanger) method — Heat exchangers used for reheating are normally constructed to the same mechanical requirements as sulfur condensers. These exchangers should slope toward the inlet end so any liquid sulfur present can drain back into the liquid-vapor separator located downstream of the upstream sulfur condenser.

Catalyst Converter Operation

Catalytic converters are usually designed for a flow at operating conditions of 700 to 1400 standard ft³/hr of process gas per cu ft of catalyst bed. Because of pressure drop considerations, this usually results in a bed depth of 3–5 feet. The catalyst is activated alumina (Al₂O₃) or promoted activated alumina which is installed on top of a 3–6” thick layer of more dense support material. Catalyst bulk density is about 45–53 lb/ft³; the support medium, which usually has a bulk density of 84–100 lb/ft³, reduces migration of catalyst and/or catalyst fines from the reactor bed to the sulfur condenser downstream. These catalyst fines can plug the sulfur drain legs and condenser tubes. The catalyst and support material are installed on top of stainless steel wire screens which are tied to carbon steel grating. A minimum of 3” of the support material may be placed on top of the catalyst bed to serve as a gas flow distributor.

For Claus units smaller than about 100 LT/D, the catalyst beds are frequently installed in a single horizontal vessel, with internal partition plates. For larger units, individual catalyst bed vessels are used. Vertical (stacked) beds are sometimes used but this is usually not economical for units smaller than about 800 LT/D. Internal refractory lining of these vessels is not necessary unless it is planned to regenerate the catalyst in place; in this case the grating floor design must also be adequate for the expected elevated temperatures. If internal refractory is not used, a minimum of 3” external insulation is recommended. If a refractory lining is installed, the outside insulation thickness can be reduced to 1”–2”. Most converters have internal refractory from the bottom to about 6” above the top of the catalyst bed, which protects against high-temperature upsets.

Nozzles in the bottom of the catalyst bed vessels should be installed flush with the vessel interior.²⁹

Piping

The piping systems in Claus plants which require special attention are liquid sulfur lines and vapor process lines. Since sulfur freezes at about 245 °F, liquid sulfur lines must be adequately heated and insulated. Process lines are also insulated to prevent sulfur from condensing and/or desubliming to the solid form and to keep the metal temperature above the dew-points of sulfurous/sulfuric acids. Process lines operating at temperatures above 650 °F are often lined with refractory or,

especially in smaller units, are of stainless steel. Vapor process piping must also have proper allowance for thermal expansion. Either convoluted expansion joints or expansion “loops” are used. Convoluted joints should be constructed of series 300 stainless steel, and insulated to prevent either water and/or sulfur condensation. The expansion joints should be installed in vertical pipe runs so, if condensation does occur, the liquid can drain freely. If liquid sulfur does not drain, it could solidify, causing the convolutes to be inoperable. Undrained water results in corrosion because of the acids formed.

Carbon steel process piping is normally adequate. Because a Claus plant operates below 15 psig pressure, schedule 40 pipe is normally used for small lines. For 14” or larger lines, standard weight pipe is adequate. For process lines over 30” in diameter, the piping thickness can be the same as the catalyst bed vessel walls.

Valves should be steel and fully jacketed. Smaller valves usually have integral jackets; large valves may have fabricated jackets. Valves in liquid sulfur service should be full-opening gate or plug type to permit rodding out. Liquid sulfur normally drains by gravity from the condensers into a sulfur collection pit or storage vessel with a liquid sulfur seal on each drain line to prevent gases from escaping to atmosphere. Sulfur drain lines often include both horizontal and vertical sections of piping. Because of potential plugging of these lines, facilities should be installed to clean-out (usually by rodding) these lines to prevent a plugged sulfur drain from causing premature unit shutdown. As shown in Fig. 22-11, these “rodding-out” facilities usually include both horizontal and vertical crosses at each change in piping direction. The crosses are often equipped with external valves. Valves are also often placed in the horizontal sections of the sulfur drain lines to allow easy cleaning of these segments, either mechanically or with steam, while the unit continues to operate.

Each sulfur liquid/vapor separator should have a separate drain line and sulfur seal to facilitate detection of plugging. Each sulfur seal should be equipped with a sight port (oriented away from sidewalks, etc.) so the sulfur draining into the storage pit can be observed. When the flow of liquid sulfur stops, remedial action can be taken to eliminate the restriction or plug so as not to cause additional damage to the plant.

Steam-jacketing is the preferred method of heating liquid sulfur lines but ControTrace external formed tube jacketing is an economical alternative to traditional double pipe jacketing. Internal (gut) steam lines are sometimes used, especially for longer lines. Skin Effect Current Tracing (SECT) which utilizes the skin effect phenomenon exhibited when an alternating current passes through a steel pipe has also been used to heat long pipelines. For short lines, steam tracing may be satisfactory. Steam is the most common heating medium, but hot oil and hot water (under pressure) can also be used. Pressurized hot water has an advantage over hot oil in the higher heat capacity of water over organic hot oils. This advantage has been utilized in very long molten sulfur lines. Disadvantages of hot water are the higher vapor pressure and the need for corrosion inhibition. The liquid sulfur lines should be designed to maintain the sulfur at a minimum temperature of 280 °F which corresponds to a steam pressure of at least 50 psig. High pressure steam (above 100 psig) or superheated steam should normally not be used because of the possibility of heating the sulfur into the highly viscous region. (Fig. 22-16)

Since the liquid sulfur is used as a seal to prevent process vapors from being vented to the atmosphere, the “net” liquid

column head must be large enough to withstand the maximum expected operating pressure. For most plants this maximum operating pressure is the same as the air blower maximum discharge pressure. The density of liquid sulfur is about 112 lb/ft³, so for a 10 psi seal, the required “net” sulfur seal depth is 12.8 ft. Minimum safety factors would require at least a 13.0 ft. seal depth, and often an extra 6–12” is added to the calculated depth to allow for upsets, lower sulfur density, etc.

CLAUS UNIT TAIL GAS HANDLING

The tail gas from a Claus unit contains N₂, CO₂, H₂O, CO, H₂, unreacted H₂S and SO₂, COS, CS₂, sulfur vapor, and entrained liquid sulfur. Because of equilibrium limitations and other sulfur losses, overall sulfur recovery efficiency in a Claus unit usually does not exceed 96–97%. Venting of this tail gas stream without further processing is seldom permitted; the minimum requirement is normally incineration, the principal purposes of which are to reduce H₂S concentrations to a low level (which value will depend on the local regulations) and to provide the thermal lift for dispersion of SO₂ upon release to atmosphere through a stack. Depending upon the size of the Claus unit, the H₂S content of the feed gas, and the geographical location, a tail gas cleanup process may be required in order to reduce emissions to the atmosphere.

Incineration

Incineration of the H₂S (as well as the other forms of sulfur) in the Claus plant tail gas to SO₂ can be done thermally or catalytically. Thermal oxidation normally is carried out at temperatures between 900 °F and 1500 °F in the presence of excess oxygen. Most thermal incinerators are natural draft operating at sub-atmospheric pressure with air flow controlled with dampeners; the excess oxygen level varies between 20% and 100%. A typical concentration of oxygen in the stack effluent is 2.0%. Although the Claus unit tail gas contains some combustibles—for example, H₂S, COS, CO, CS₂, H₂, and elemental sulfur (in the case of “split-flow” plants, some hydrocarbons)—these combustibles are at too low a concentration to support combustion because they generally amount to less than 3% of the total tail gas stream. The entire tail gas stream must therefore be incinerated at a high enough temperature for oxidation of sulfur and sulfur compounds to SO₂.

Incinerator fuel consumption can be reduced significantly by utilizing catalytic incineration. This involves heating the tail gas stream to about 600–800 °F with fuel gas and then passing the heated gas along with a controlled amount of air through a catalyst bed. Catalytic incinerators are normally forced draft, operating at a positive pressure in order to maintain closer control of excess air. Catalytic incineration is a proprietary process which should be considered where fuel costs for conventional (thermal) incineration are high.

Another method of improving overall fuel economy involves recovering heat from the incinerator outlet gases. Saturated steam at pressures ranging between 50 psig and 600 psig has been produced, and saturated steam has been superheated, using waste heat from the incinerator outlet gases. The effect of lower emission temperature upon dispersion of the outlet stream, and therefore upon the required stack height, must be considered in evaluating this alternative. Incinerators with waste heat recovery are normally forced draft operating at a positive pressure.

Fuel required for thermal incineration is determined by the amount of heat needed to heat the Claus tail gas, air, and fuel

to the required temperature. Normally the incinerator is sized for at least 0.5 second residence time, and sometimes for as much as 1.5 seconds residence time. Generally, the longer the residence time, the lower the incinerator temperature needed to meet the environmental requirements. This is illustrated by Fig. 22-12 which shows the relationship between residence time and temperature for a typical installation to meet a maximum H₂S requirement of 10 ppmv.

The incinerator and stack can sometimes be combined into a single vessel. The incinerator is the enlarged base, and the smaller diameter stack is mounted on top of the incinerator. The burner is normally mounted horizontally in the side of the incinerator. The tail gas is sometimes fed through the burner, but it can also be fed into the incinerator adjacent to the burner.

Both the incinerator and stack are refractory lined to protect the steel from the high temperatures. This refractory is not as elaborate as that used for the reaction furnace at the front of the Claus unit, because of lower operating temperatures. The incinerator is normally designed for a maximum operating temperature of 2000 °F. Refractories rated as low as 2200 °F have been used in incinerator-stack installations; one layer of refractory is generally sufficient. The refractory is usually an insulating castable rated for service conditions of 2200 °F or above, except where flame impingement is anticipated. A high alumina castable (above 60% alumina) is used in the area of flame impingement.

For vertical incinerators installed at the base of the stack, protection for the incinerator steel floor is important. The best method to protect the floor is to allow for ambient (cooling) air circulation below the floor even though the floor is refractory lined. If there is no cooling below the floor, or if the space is too restricted (too close to grade), the floor refractory usually will not provide adequate protection.

The steel components (floor, walls, stack shell) should be kept below 650–700 °F and above 300 °F to remain above the acid gas-dewpoint. This requires careful design of both the inside refractory lining and outside insulation. Normally the refractory thickness to protect the incinerator shell (either vertical or horizontal type) will be between 2” and 4”, with an average of about 3”. The incinerator floor on the vertical style units normally has refractory thicknesses ranging between 4” and 6”.

FIG. 22-11
Typical Relationship of Sulfur Seal and Drain

