

SULFUR RECOVERY UNITS

Dennis H. Martens
Black & Veatch Pritchard, Inc.
10950 Grandview Drive
Overland Park, Kansas 66210

Joe Livesay
AMOCO Exploration & Production
P.O. Box 800
Denver Colorado 80201

Mark Tonjes
Black & Veatch Pritchard, Inc.
10950 Grandview Drive
Overland Park, Kansas 66210

ABSTRACT

This paper reviews the fundamental corrosion issues encountered in Sulfur Recovery Units. The information presented addresses the most common process applications, materials of construction and corrosion mechanisms. The units included are; Claus, Cold Bed Adsorption (CBA), tail gas treating and incineration. These units remove sulfur compounds from the acid gas process streams before they are vented to the atmosphere.

INTRODUCTION

Sulfur Recovery Units (SRU) are used to remove sulfur compounds (mainly hydrogen sulfide) from gases produced by sweetening of refinery gases or sour field production gases. The SRU converts the sulfur compounds to elemental sulfur and condenses the sulfur to a liquid state for removal. The sulfur compounds remaining in the stream are oxidized in the incinerator to sulfur dioxide before release to the atmosphere. The type of SRU units used depends on the acid gas feed composition and the necessary sulfur removal before the gases are vented to the atmosphere. For this review the feed gas is considered to contain mainly hydrogen sulfide (H_2S), with limited carbon dioxide (CO_2) and cyanide (HCN).

The feed gas to these units is considered an acid gas as the components will form acids when in the presence of liquid water. The feed gas most commonly comes from amine regenerators and sour water strippers located in various refinery units and gas processing plants. It should be noted that SRU's have very complicated sulfur chemical reactions resulting in many sulfur species existing at any one condition or process step. The overall combustion reactions taking place in the reaction furnace is the typical Claus reaction where one-third of the H_2S is converted to SO_2 . The catalyst beds convert most of the remaining H_2S and the SO_2 to elemental sulfur. For the discussion in this paper the most common sulfur species will be addressed as this is considered adequate for considering the corrosion aspects of the units.

Please refer to the simplified process scheme for a typical Claus unit, Tail Gas unit and Incinerator in the appendix for the balance of this introduction.

The acid gas enters the unit at low pressure (usually less than 15 psig) and a knock out vessel is utilized to remove condensed and entrained liquids which are mostly water, with some hydrocarbons (and amine if from an amine stripper). The acid gas is carefully combusted with air in a reducing atmosphere in the reaction furnace. Temperatures in the reaction furnace range from 1800 to 2800 °F depending on the composition of the specific acid gas feed. The combustion gases typically pass through steam generating shell and tube exchangers being cooled to about 400 to 450 °F. Most of the elemental sulfur formed during combustion is condensed, separated and drained to storage. The process stream is reheated (hot gas bypass system is indicated in the appendix) and passed through the

first catalyst bed where additional sulfur is formed. The process gas is again cooled and sulfur condensed, separated and forwarded to storage. Typically two or three catalyst beds, with condensation after the beds, are utilized in the Claus unit. To remove as much sulfur as possible from the process gas the final condenser outlet temperature is typically less than 300 °F.

Typically the remaining sulfur compounds in the process gas leaving the Claus unit must be reduced further before venting the stream to the environment. There are several types of tail gas unit process designs. A typical unit is indicated in the appendix. This tail gas unit uses a combustion burner, operating in a reducing atmosphere, with a mixing chamber to reheat the process gas to conditions suitable for the catalyst bed reaction. Some other designs use a heat exchanger and a hydrogen stream instead of the burner and mixing chamber. The tail gas catalyst bed converts the remaining sulfur compounds to H₂S. The process gas is then cooled in an exchanger and water quenched in a direct contact tower. The H₂S is then removed from the process gas using an Amine adsorption system and recycled to the front of the Claus unit. The remaining process gas is then forwarded to the incinerator.

The incinerator typically heats the process gas to 1200 to 1500 °F using a fuel fired burner in an oxidizing atmosphere. The small amount of remaining H₂S is converted to sulfur dioxide and released to the environment. In some incinerator applications a waste heat recovery boiler is utilized. In these applications the process gas is typically cooled to 500 °F to recover heat. The process gas is not allowed to reach the condensing temperature for water mixed with sulfur oxides to avoid sulfur acid formation.

CBA units have greater sulfur removal efficiency than a Claus unit. In some instances a CBA unit combined with an incinerator provides adequate sulfur removal. The CBA process uses the same reaction furnace and first catalyst bed as a typical Claus unit (in some CBA designs two Claus catalyst beds are utilized). The CBA catalyst bed is operated at the dew point for sulfur and the sulfur is adsorbed into the catalyst bed. The reaction in a CBA catalyst bed is essentially the same as in a Claus catalyst bed but the recovery is enhanced at the lower operating temperature. Two CBA catalyst beds are typically utilized with one in removal service and one in regeneration service. When the in-service bed has accumulated significant sulfur it is removed from service and regenerated. The regenerating bed is then heated from the typical 260 °F adsorption temperature (during accumulation of sulfur) to over 600 °F to remove the sulfur from the bed. The sulfur is removed from the bed in liquid and vapor states. The sulfur vapor is condensed in an exchanger and the liquid sulfur is forwarded to storage. The total cycle time for a CBA reactor typically ranges from 24 to 48 hours.

CORROSION MECHANISMS IN SRU's

The three most prevalent corrosion problems in an SRU are:

- Sulfidation of carbon steels due to high temperature exposure to H₂S
- Sour environment corrosion resulting in Wet H₂S Cracking
- Weak acids corrosion due to acids formed from water condensation with sulfur compounds

Hydrogen sulfide will react directly with iron (Fe) at moderate and elevated temperatures. This corrosion mechanism for carbon steels at elevated temperatures is documented in American Society of Metals (ASM) Metals Handbook Ninth Edition Volume 13⁽¹⁾. In the process atmosphere of a typical SRU, sulfidation (direct reaction of H₂S with iron (Fe)), forms an iron sulfide (FeS) scale. The scale is semi-permeable, is often flaky and offers only minimal resistance to additional scale formation. The sulfidation reaction is dependent on H₂S concentration and temperature. Typical SRU piping and equipment operate at metal temperatures up to 650 °F. At temperatures up to 650 °F the sulfidation corrosion rate for carbon steels can be accommodated by a 1/8" corrosion allowance (for a 20 year design life). It should be noted that the Couper-Gorman curves presented in the ASM reference⁽¹⁾ are for pressures considerably higher than the operating pressure of a SRU. Little information is published for near atmospheric pressure conditions and the authors suggest that, based on their experience, the curves are 50 to 100 °F conservative when applied to the typical SRU process conditions. In critical areas, such as the tube sheet of the waste heat exchanger after the Claus reaction furnace, the authors recommend that the metal temperature be limited to approximately 600 °F.

The FeS scale will be pyrophoric when exposed to air. The reader is referred to the reference paper by Robert Walker et al, American Chemical Society, 1996⁽²⁾. The FeS scale, when exposed to temperature changes in the order of 200 °F, or areas of high stress/strain nearing or exceeding yield of the material, will be subject to cracking and flaking, which increases the apparent corrosion rate.

The presence of H₂S and water is considered a SOUR ENVIRONMENT and associated Wet H₂S corrosion damage can be expected to occur. The SOUR ENVIRONMENT corrosion mechanism produces hydrogen charging of carbon steel with associated Hydrogen Induced Cracking (HIC) damage. The reader is referred to ASM Volume 13⁽¹⁾ and NACE publication 8X294⁽³⁾ for additional information on HIC. The corrosion of carbon steels by a sour environment can result in damage mechanisms of hydrogen blistering, sulfide stress cracking (SSC), Hydrogen Induced Cracking (HIC) and Stress Orientated Hydrogen Induced Cracking (SOHIC). The reader is referred to NACE publications MR-0175⁽⁴⁾, 8X194⁽⁵⁾, 8X294⁽³⁾ and RP 0472-95⁽⁶⁾ for further discussion of the various mechanisms.

In a typical SRU, the inlet acid gas line and associated knock out drum are the only areas that are normally considered at risk for Sour Environment damage during normal operation. The application of NACE MR 0175 is not strictly required based on the H₂S partial pressure and total operating pressure. Many users consider that 50 PPM(weight) H₂S concentration in a water phase will create a significant potential for HIC and apply this document even though it is a Production or Upstream document. The reader is referred to NACE publication 8X194⁽⁵⁾ for additional discussion.

The absorption of sulfur compounds (H₂S, SO₂, SO₃) into a condensed water phase forms a sour environment of sulfur acid. Operating pressures (generally less than 15 psig) and resulting constituent partial pressure in a SRU facility are low enough that only weak acids are produced. Strong acids can be produced under certain oxygen containing atmospheres and condensation conditions. Metal surfaces that are allowed to cool near the condensation temperature during normal operation, shutdown or startup operations will produce these acids and it is necessary to limit the time that the acids may exist. For further discussion on the formation of sulfur related acids and the ability of a less than 1% sulfuric acid vapor condition to produce an 85% sulfuric acid in the water phase, the reader is referred to an article by Robert W. Pierce, Chemical Engineering April 11, 1977⁽⁷⁾. It should be noted that even weak acids are significantly corrosive to the carbon steel materials typically used in a SRU.

The corrosion of austenitic stainless steels by these same acids is generally not significant unless the material is sensitized. Sensitization of austenitic stainless steel materials may occur in the 600 to 1200 °F range when there is sufficient carbon migration to the grain boundaries resulting in the carbon combining with chrome which reduces the chrome content at the grain boundary. The reader is referred to works by R. L. Piehl, such as "Stress Corrosion Cracking by Sulfur Acids" API 1964⁽⁸⁾ for further discussion on sensitization. The concern and mitigation for polythionic acid corrosion of sensitized austenitic materials is addressed in NACE RP0170⁽⁹⁾. Typically areas of an SRU will have operating temperatures within the sensitization range for 300 series austenitic stainless steels.

In certain areas of an SRU the operating temperatures will be high enough to cause the austenitic and high nickel alloy materials to develop significantly reduced ductility at ambient temperatures which will exist during shutdowns. This reduction in ambient temperature ductility may be attributed to mechanisms that effect grain structure and phase, such as Sigma Phase development in some austenitic materials. The reader may refer to any metallurgy text book for a basic understanding of this subject. However specific ductility reduction information for many higher alloys may only be available from the manufacturer. The designer must consider this reduction in ductility when selecting materials that may be stressed or subjected to impacts at ambient conditions.

CORROSION REVIEW OF CLAUS UNIT BY SYSTEM

Feed Gas System

System Description. The acid gas piping into the unit and the associated knock out drum used to remove most of the free liquids composes this system. The most common material of construction is carbon steel. The valves are usually specified as cast steel bodies with stainless steel trim and Teflon or Butyl seal materials.

Corrosion Concerns. The feed gas is normally rich in H₂S and is saturated with water vapor resulting in formation of a weak acid. The feed gas may contain entrained hydrocarbons and amines. The corrosion activity from this service will produce hydrogen charging and is considered a risk for HIC (including hydrogen blistering) and SSC. It should be noted that a refinery feed gas may contain ammonia resulting in the consideration for alkaline related stress cracking. A refinery feed gas may also contain cyanide which interacts with the sour environment to

increase the corrosion rate and resulting hydrogen charging. Feed gas resulting from production operations typically do not contain ammonia or cyanide.

Mitigation of Corrosion. The gas piping design should avoid accumulation of liquids as the piping will be exposed to entrained and condensed waters that will produce weak acid. The piping for amine stripper acid gas is usually not insulated unless the climate is extremely cold. The piping for sour water stripper gas is usually insulated and traced in all climates if the gas contains appreciable amounts of ammonia which will form ammonia salts at low temperatures. Small diameter piping is usually seamless while large diameter pipe is made from plate materials. As there should not be an accumulation of liquids in the gas piping concerns for hydrogen blistering and stress orientated cracking are usually minimal for seamless piping materials. Piping made from plate materials may increase the risk for damage from these mechanisms and the application of additional material and fabrication controls as discussed in NACE RP 0472-95⁽⁶⁾ and 8X194⁽⁵⁾ may be considered. Mitigation of Stress Corrosion Cracking (SSC) is the prime consideration for the piping and mitigation is accomplished by utilizing the recommendations of NACE RP 0472-95⁽⁶⁾ to control the hardness of welds. The use of carbon equivalent controlled steel and Post Weld Heat Treatment (PWHT) of welds or special weld procedures is a reasonable approach to mitigation of SSC in the piping system.

The knock out vessel is usually carbon steel with a maintained liquid level. The maintained liquid level gives concern for hydrogen charging with risk of Sour Environment damage developing. The most common mitigation is the use of PWHT to reduce the risk of SSC and Clean Steel Technology (HIC resistance steels) to control hydrogen blistering. The reader is referred to NACE publication 8X194⁽⁵⁾ for further discussion on the use of Clean Steel Technology.

Inspections. The fabrication of piping is usually monitored by standard procedures with the addition of hardness verification of production welds.

Piping weld hardness control can be provided by utilizing a one sided manual metal arc welding procedure with out the use of post weld heat treatment as indicated in NACE RP 0472-95⁽⁶⁾. For the use of other welding processes, the authors recommend the weld procedure qualification record (WPQR) include a Vickers micro hardness verification with value requirements per the recommendations of NACE RR 0472-95⁽⁶⁾. The inspection and quality assurance of production welding utilizing such a procedure should include additional effort to assure compliance with the WPQR weld variables (essential and non-essential).

The vessel fabrication is monitored as any typical vessel.. The WPQR should include adequate hardness controls and typically will include PWHT. Commonly the interior of the vessel is given a Wet Magnetic Particle examination (WMP) with acceptance criteria per the ASME Boiler and Pressure Vessel Code criteria for dry magnetic particle examination. The WMP is usually documented to provide flaw reference for future inspections as noted in NACE 8X194⁽⁵⁾.

The in-service inspections are usually conducted per standard procedures with additional attention to water accumulation and gas liquid interface areas. The reader is referred to NACE RP 0296⁽¹⁰⁾ for further discussion relative to inspection for wet H₂S related damage.

Reaction Furnace and Waste Heat Exchanger System

System Description. The reaction furnace system includes the burner assembly and reaction furnace chamber. The burner air plenum and mounting is typically carbon steel with stainless steel and refractory materials utilized in flame and radiation exposure areas. The acid gas is usually considered dry at the entrance to the burner due to heating from the burner. The reaction furnace chamber usually is a carbon steel vessel with refractory lining. The waste heat exchanger is usually a carbon steel fire tube steam generating design with a refractory covered tube sheet utilizing ceramic or alumina ferrules

Corrosion Concerns. The corrosion concerns are sulfidation of the steel and alloys due to high temperature exposure to H₂S and weak acid corrosion where acids may condense during normal operation or shutdowns.

Mitigation of Corrosion. The parts of the burner that operate less than 600 °F are carbon steel. For the higher temperature parts the use of type 316 stainless steel is most common with some usage of type 316 and higher nickel

alloys. It must be noted that some higher nickel alloys are not resistant to sulfidation. Some burners utilize refractory or ceramic parts in the higher temperature locations.

The operating temperature in the furnace chamber is usually in the range of 1800 to 2800 °F and utilizes a carbon steel shell with a refractory lining system. The refractory lining system is designed to maintain the carbon steel shell above the weak acid condensing temperature of approximately 250 °F and below the steel sulfidation temperature of approximately 650 °F. An external shroud is often used for additional shell temperature control. For castable refractory installations the use of type 310 stainless steel refractory anchors is most common. The refractory selected for the high temperature lining service is usually a high alumina type. The percentage of alumina increases with increasing furnace operating temperature. It is customary to require the refractory to be free of elemental phosphorus and to be a low iron content type as these materials may react with the process environment.

It should be noted that it is customary for refinery operations to require the sulfur units be started up before there is an acid gas feed and operated in a hot standby condition for considerable time. As oxygen (from excess air) can not be allowed to enter the catalyst bed and the production of free carbon (from incomplete combustion) must be avoided it is necessary to operate the burner in a stoichiometric fuel gas combustion condition. The stoichiometric flame temperature is above the maximum operating temperature of refractory systems. Consideration should be given to the flame stability to prevent flame impingement on the refractory and the use of steam to temper the flame temperature to avoid excessive temperature refractory damage.

The exchanger is carbon steel on the process and on the steam side. The steam pressure may vary from 50 to 700 psi depending on the process design details such as type of re-heating and utility requirements. The refractory utilized on the tube sheet is similar to that used in the furnace chamber. The ferrules are usually zirconium silicate or high alumina materials. It should be noted that the use of sodium silicate (commonly called water glass) should be avoided in the ferrule installation as it may be a fluxing agent for some ferrule materials. The design of the tube sheet refractory and ferrule system is critical to protecting the exchanger tubesheet and tube inlet from damage. The design must address limiting the heat flux and metal temperature sufficiently to prevent sulfidation. The reader is referred to a technical paper on this subject presented by D. H. Martens et al, at the American Society of Mechanical Engineers Pressure Vessel and Piping Conference 1996⁽¹¹⁾. The balance of the system that operates above 650 °F is usually carbon steel with refractory lining protection against sulfidation. It is not customary to use post weld heat treatment in this area, except that required by the governing fabrication code, as the normal operation is considered dry acid gas service with only occasional exposure to weak acids.

Inspections. The inspections for the carbon steel fabrication are usually limited to those that are required by the governing fabrication code or agency. The use of extensive hardness or flaw detection is not commonly recommended or required. The inspections for the refractory installation should be conducted per the refractory suppliers' recommendations. The authors recommend that refractory installation inspection procedures be very thorough including verification of such things as the material quality prior to installation and refractory installers work processes such as those required for "gunned" refractory installations.

The in-service inspections for the carbon steel are usually conducted per standard procedures with consideration for any areas that may be operating cold enough to be susceptible to continuous weak acid corrosion. On line ultrasonic thickness monitoring can be utilized in suspect areas. On line refractory condition can be monitored utilizing thermography.

During unit shutdown it is customary to inspect refractory systems for degradation. Damage to refractory systems may be due to many factors including operational conditions. It is not uncommon for changes in operating practices, such as hot standby conditions and rate of heating on startup to have a significant impact on refractory life. It should be noted that minor cracking observed in refractory during inspections should be considered normal depending on the type of refractory installation. It is common to find minor cracking in ferrules utilized in the waste heat exchanger tube sheet and such cracks should not be a concern for continued operation. Major cracks, spalling or damage to the refractory or ferrules should be repaired in accordance with manufactures' instructions.

Claus Reactors, Condensers And Reheat System

System Description. The CLAUS reactor, condenser and reheat system is composed of two or more catalyst beds with associated sulfur condensers and various type reheaters. The reactor vessels are commonly carbon steel

horizontal vessels with austenitic stainless steel catalyst support systems and carbon steel support beams. The condensers are usually carbon steel with cooling provided by generation of steam on the shell side of the exchanger. The final condenser in the train will operate the coldest to remove the most sulfur from the process steam. The reheating types range from hot gas bypass, steam heated shell and tube exchanges, direct and indirect fired types. The usual materials of construction are carbon steel with the use of some alloys in some of the fired reheaters.

The use of refractory linings in the reactor vessels is typical due to the concern for sulfur fires in the reactors if oxygen enters a hot catalyst bed (beds usually contain appreciable amounts of liquid sulfur and sulfur in the catalyst pores). The refractory lining of the piping to the condensers and the inlet channel is dependent on the operating conditions.

Corrosion Concerns. The reactor outlet and condenser inlet carbon steel may be subjected to temperatures that are near the sulfidation range during normal operation. There is a risk of continuous exposure to weak acid if the condenser is operated in the acid condensation range. The concern for sensitization and polythionic acid stress corrosion cracking of austenitic stainless steels must be addressed for any such materials used in the system.

Mitigation Discussion. It is not customary to use post weld heat treatment for carbon steel materials in this area for the process service reasons, except that required by the governing fabrication code, as the normal operation is considered dry acid gas service with only occasional exposure to weak acids.

The exposure to temperatures high enough to cause sulfidation of carbon steels is usually avoided in normal operation. Some operations fire the reaction furnace burner on fuel gas with a small amount of excess oxygen during plant shut down to remove sulfur from the catalyst bed. This procedure can increase the operating temperature significantly resulting in concerns for sulfidation of the steel parts. The use of refractory is common to protect the steel parts, including in the catalyst bed vessels. Where refractory is used it may be necessary to use an external shroud or insulation system to maintain the metal above the acid condensation temperature. The catalyst support system will also be subjected to process gas temperatures and requires the same consideration. Commonly, refractory covering of the carbon steel support beams, similar to fireproofing installations, is provided for short term sulfur fire protection but this approach will also provide some limited protection for the support beams during the use of oxygen in the catalyst beds during shutdown.

It should be noted that the introduction of oxygen into a hot (or warm) unit will result in a sulfur fire as liquid sulfur is retained in the catalyst bed and in the pores of the catalyst. The introduction of oxygen (or air) into a cold unit, such as could occur during a shutdown or inspection activity, can result in a pyrophoric reaction with the FeS scale that will exist through out the unit. Similarly, atmospheric air has enough moisture content to cause polythionic acid corrosion attack on sensitized austenitic stainless steels. If oxygen is allowed to enter a cold plant during startup, it is possible to produce SO_3 with results in strong acid (sulfuric acid) corrosion.

Inspection. The inspections commonly utilized in this service are the same as stated in previous sections. The outlet channel of condensers, and particularly the final condenser, are the areas that may be subjected to increased weak acid corrosion on startup, shutdown and normal operation. These areas should be inspected for corrosion of the channel and tube wall thinning. If the catalyst bed outlet temperature exceeded 650 °F inspection for sulfidization of the carbon steel materials should be considered.

Liquid Sulfur Rundown Lines and Storage System

System Description. The sulfur rundown lines are customarily carbon steel with external steam jacketing to maintain the sulfur in a molten state. The sulfur storage system considered for this paper is a concrete pit. The concrete pit is fully enclosed and has steam coils to maintain the sulfur temperature. Pumps are utilized for transferring the sulfur from the pit. The pumps are usually of the sump pump type with carbon steel construction.

Corrosion Concerns. The corrosion concerns result from low concentrations of H_2S contained in the molten sulfur. The temperatures are not high enough to cause carbon steel sulfidization but the formation of weak acid is of concern. The formation of FeS can occur where H_2S is exposed to carbon steel.

Mitigation of Corrosion. The run down lines and the sulfur seals will not be subjected to weak acid corrosion unless water vapor enters the system and condenses. The entrance or air into the system through sight ports and

look boxes can provide water vapor for formation of acids. The volume of air ingress is low and a normal corrosion allowance of 1/8" for the general weak acid corrosion is customary.

It is customary to provide positive air venting to prevent an explosive mixture of H₂S from building up in the pit. The sulfur pit is usually purged with atmospheric air or in some cases an inert gas such as nitrogen. The pit concrete is usually specified as acid-resistant type IV concrete. The pit cover may be concrete or aluminum construction. Aluminum has a good resistance to the corrosion effects of the weak acid that is formed in this area and will not sulfide like carbon steel. The steam coils placed in the pit may be carbon steel in the liquid sulfur area but the carbon steel will be subjected to considerable weak acid corrosion at the sulfur liquid and air interface. The use of type 316 stainless steel to extend the coils from the minimum liquid level through the pit top is suitable for most services. Where the type 316 materials have proven unsuitable, the use of materials such as Alloy 20 has been effective. The sulfur pump materials are customarily carbon steel with ductile iron impeller with austenitic shaft and carbon shaft bushings. The pump column is steam jacketed and is subjected to weak acid corrosion. The carbon steel materials have proven suitable for most services and the use of type 316 usually is specified only for severe services where carbon steel has proven unsatisfactory.

It should be noted that formation of weak acids is much greater if the sulfur pit is allowed to operate with steam leaks (as these saturate the pit vapor space with water), the atmospheric conditions are extremely humid or if rainwater is allowed to penetrate the pit roof.

Inspection. The inspections commonly utilized in this service are the same as stated in previous sections. The inspection of the pit is difficult as the pit must be emptied to accommodate access. Partial inspections can be accomplished with specialized remote viewing equipment. The deterioration of the pit concrete is usually most prevalent in the vapor space and this area should be inspected on a routine basis.

CORROSION REVIEW OF CBA UNIT BY SYSTEM

CBA Reactors, Condensers And Piping

System Description. The CBA system is similar to the discussions above, including materials of construction, except that two reactors and associated condensers and piping are operated in a temperature cycle. The temperature cycle is usually 24 to 48 hours in duration. During regeneration about 1/3 of the time is in heating mode, 1/3 in bed hold time and 1/3 in cooling mode.

Corrosion Concerns. The same sulfidation and weak acid corrosion considerations apply to this type of unit as stated above. In addition there are cyclic temperature considerations for the CBA reactors, condensers and associated piping. The FeS scale that is formed during normal operation of a SRU will crack when subjected to temperature changes in excess of approximately 200 °F (which occur during the CBA bed operation and regeneration cycle). The cracking of the FeS scale is not severe and the scale will re-establish with each cycle. The apparent corrosion rate increase due to the cracking and re-establishing of the FeS scale is estimated to be 150% of a non-cyclic equivalent temperature application. The apparent corrosion rate may be increased significantly if the carbon steel base materials are cyclic stressed near the yield due to the corresponding material strain. The weld areas of mitered fittings and other stress concentrating contours can develop stresses in the yield range or greater.

Mitigation of Corrosion. The use of aluminization to reduce the FeS scale formation is typical in the reactor vessels and exchanger channels that are subject to the CBA cycle temperature change. The piping may be aluminized depending on the maintenance and capital cost criteria

For all large equipment surfaces exposed to the process stream the aluminization is usually accomplished by thermal spray coating techniques. The use of a diffusion coating technique is practical for smaller items and is preferred for items that are difficult to apply a thermal spray coating to, such as small equipment and piping nozzles. The thermal spray aluminization coating has similar considerations as any coating system. The preparation of the surface, removal of sharp edges and the application techniques are critical for the coating to remain serviceable. The reader is referred to publication by Richard P. Krepski titled "Thermal Spray Coating Applications in the Chemical Process Industries Published by NACE⁽¹²⁾ and American Welding Society publication C2.18-93⁽¹³⁾.

The repair and renewal of the thermal spray aluminization coating may be necessary during the life of the unit. Areas of high stress/strain such as mitered piping elbows can be expected to cause additional damage to the FeS layer with each temperature cycle. These areas may display coating damage or increased apparent corrosion rates of bare carbon steel materials with failures reported in as short as 3 to 5 years of operation. The designer is cautioned to maintain localized stresses to well less than yield of the material. It is possible to utilize austenitic stainless steel materials, with proper consideration for sensitization, where bare and coated materials prove unsatisfactory.

Inspection. The fabrication inspection is similar to that described above. The application inspection for the thermal spray applied coating is important. The authors recommend that considerable attention be given to establishing the applicators' ability to apply the coating under the actual conditions and assuring that this technique is continued throughout the application. The references noted above include relative inspection information. The control of atmospheric conditions such as humidity, dew point and temperatures is necessary for successful coating application.

Aluminization by diffusion is conducted in high temperature retorts. Inspection for diffusion depth and dimensional changes to the base materials is considered necessary.

In-service inspections are similar to those noted above. The inspection of the aluminization coating requires internal access and visual observation. The coating is usually considered to be fully serviceable unless flaking or complete loss of the coating is visually observed. Destructive testing of the coating is not considered necessary or practical.

CORROSION REVIEW OF TAIL GAS TREATING UNIT BY SYSTEM

Burner And Mixing Chamber

System Description. The tail gas unit shown in the appendix uses a burner and mixing chamber to heat the Claus tail gas before entering the hydrogenation reactor catalyst bed.

Corrosion Concerns. This system has very similar materials of construction, corrosion concerns and inspection requirements as the Claus Burner and Reaction Furnace. The process gas enters the mixing chamber and combines with the flue gases from the burner. The temperature range of the process gas leaving the mixing chamber is approximately 550 to 725 °F and the piping to the reactor vessel is customarily refractory lined carbon steel.

It should be noted that it is customary to operate the burner in a sub-stoichiometric fuel gas combustion condition, as oxygen (from excess air) can not be allowed to enter the catalyst bed. It is also necessary to operate the burner flame temperature at slightly less than stoichiometric conditions to control flame temperatures, as the stoichiometric flame temperature of methane is above the maximum operating temperature of refractory systems. Consideration of the burner chamber configuration is necessary as cooling of the combustion flame by radiation to the mixing chamber is necessary to prevent refractory damage. The production of free carbon (from incomplete combustion) must be avoided as it will collect on the catalyst bed. The addition of steam to the burner flame may be necessary if free carbon production occurs. The addition of steam to the burner flame will also reduce the flame temperature. It should be noted that due to the slightly higher operating temperature in the tail gas treating unit the approach to external heat conservation is extremely critical. This will be discussed further in the Reactor mitigation section.

For this area, including the refractory lined piping, the mitigation and inspection descriptions are very similar to that in the Claus unit and will not be discussed further.

Tail Gas Reactor And Waste Heat Exchanger

System Description. The hydrogenation catalyst bed reactor is customarily a carbon steel vessel with a refractory lining. The reactor vessel is similar to the Claus reactor vessel but the consideration for sulfur fires is not necessary. The waste heat exchanger has the same considerations as described for the Claus unit.

Corrosion Concerns. The corrosion concerns are essentially the same as described for the comparable portion of the Claus unit.

Mitigation of Corrosion. The mitigation discussion is similar to the comparable section of the Claus unit. It should be noted that due to the slightly higher operating temperature in the tail gas unit the approach to external heat conservation is extremely critical. The reactor carbon steel shell temperature must be maintained above the acid condensation temperature while not allowing the carbon steel to reach a temperature high enough to develop sulfidation. It is customary to utilize an internal refractory lining and a very thin layer of insulation or special lagging on the external surfaces to accommodate the two conditions. The catalyst support is usually an austenitic stainless steel. The support beams may be carbon steel with a large corrosion allowance or austenitic stainless steel as determined by the criteria pertaining to maintenance and capital expenditures. The catalyst bed is in a reduced state and will react with any entering oxygen. It is customary to use a controlled amount of oxygen in the circulating gas stream to oxidize the catalyst prior to any opening of the system for maintenance or inspection

Inspection. For inspection discussion and requirements refer to the Claus descriptions.

Water Quench and Re-circulation Blower System

System Description. The water quench system consists of a direct contact tower, a water pump around loop and a cooler. Most systems utilize a re-circulation blower to recycle quenched process gas to the mixing chamber during unit startup. In some units the blower will operate continuously during normal or turndown operations. The materials of construction are typically carbon steel.

Corrosion Concerns. The direct contact cooling of the process gas with water produces a weak acid. The circulating water must be pH controlled to avoid a low pH corrosion condition from developing. The use of caustic for buffering is common. The use of a 1/8" corrosion allowance is typical for carbon steel materials in the pump around loop. The entrance of oxygen into the circulating water system will lower the system pH and induce oxygen related corrosion mechanisms.

The re-circulation blower that is used for startup service only is customarily cast iron or steel with an internal coating and an aluminum impeller. A continuously operating blower will usually be constructed of austenitic stainless steels.

Mitigation of Corrosion. The carbon steel materials will be subjected to weak acid corrosion if the pH of the circulating water is not controlled in the proper range. The use of on-stream pH monitoring and control to 6.5 to 7.0 is customary. One of the most aggressive conditions that can develop in this system is the entrance of oxygen. This can occur if care is not taken during the oxidation of the hydrogenation catalyst bed from service. This condition will result in a lowering of the pH and if not compensated by pH adjustment the circulating water can develop extreme corrosion rates. The circulation of water with oxygen present even with reasonable pH conditions can be corrosive. The low pH conditions will cause removal of the FeS layer quickly and direct attack on the exposed surface will occur. This type of corrosion can be damaging in just a few hours of operation. The reader is referred to additional information related to this corrosion mechanism in THE CORROSION HANDBOOK BY HERBERT H, UHLEG⁽¹⁴⁾ and technical paper by Martin et al Materials Protection and Performance Vol. 10 No. 12, 1971⁽¹⁵⁾.

Blowers utilized only for startup service need to be fully isolated from the process stream, completely purged and provided with a continuous purge of an inert gas such as nitrogen.

Inspection. The inspection discussion in the Claus section is applicable for the water quench area. The inspections can be expected to find the most corrosion in areas that are exposed to the highest velocity. Areas such as pump discharge piping can be expected to display the greatest effects of velocity assisted corrosion.

H₂S Adsorption System

System Description. The adsorption of H₂S customarily uses an amine system with the H₂S recycled to the acid gas feed to the Claus unit. As amine systems are fully discussed in other reference information on further discussion will be included here. The reader is referred to a technical paper on AMINE TREATING by L. R. White and D. Street, NACE, 1997⁽¹⁶⁾ for considerations for the amine area.

Non Amine related Corrosion Concerns and Mitigation. The overhead gas from the Amine contactor tower flows to the incinerator and contains CO_s with low concentrations of H₂S saturated with water vapor. The line is typically

carbon steel and should be designed to be self-draining. Material provisions indicated for carbon steel materials in the Acid Gas Feed section may be applied to this line. The addition of heat tracing may be considered to avoid condensed liquid increasing corrosion and to prevent liquid from entering the incinerator burner.

The overhead gas from the Amine stripper tower flows to the front of the Claus unit and contains CO_s with high concentrations of H₂S saturated with water vapor. The line is typically carbon steel and should be designed to be self draining. Material provisions indicated for carbon steel materials in the Acid Gas Feed section should be applied to this line. The addition of heat tracing may be considered if corrosion is excessive (to avoid condensed liquid increasing apparent corrosion rates).

Inspection. The typical inspection techniques utilized in industry and addressed in previous sections may be applied in this area.

CORROSION REVIEW OF INCINERATOR SYSTEM

Burner, Retention Chamber And Stack System

System Description. The incinerator system customarily use a fuel gas fired burner to heat the waste gas stream to approximately 1200 to 1500 °F to oxidize any remaining H₂S to SO₂ prior to exiting to the environment. The burner is usually a naturally aspirated type utilizing stack draft. Some incinerator applications use a waste heat boiler to recover energy, which will require an air blower to provide combustion air at sufficient pressure to overcome the additional pressure drop of the boiler.

Corrosion Concerns. The burner, mixing chamber, waste heat boiler and stack are customarily carbon steel. The corrosion concerns are similar to those for the Claus unit. It should be noted that the excess oxygen used in the burner allows some SO₃ to be formed. This allows the condensation of sulfuric acid if the temperature is allowed to drop to below 250 to 300 °F. The reader is referred to an article by Robert W. Pierce, Chemical Engineering April 11, 1977⁽⁷⁾ for further discussion on acid dewpoints.

Mitigation of Corrosion. The use of refractory, insulation and shroud designs need to accommodate protection from sulfidization and acid condensation. The 1200 °F operating temperature requires the use of refractory to protect the carbon steel materials. The use of external insulation is usually limited to applications where a waste heat boiler reduces the 1200 °F operating temperature to less than 600 °F. It should be noted that the steam generation temperature should be above the acid condensation temperature. It is common to utilize a shroud or special stack design to control metal temperatures for units with out a waste heat boiler.

Inspection. The inspection techniques are similar to those for the Claus units. It is common to utilize Thermography to evaluate the internal refractory lining of the stack during operation.

REFERENCES

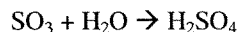
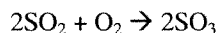
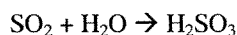
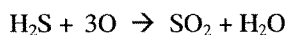
1. American Society of Metals, Metals Handbook Ninth Edition, Corrosion Volume. Gulf Publishing Co.
2. Robert Walker et al, Pyrophoric Nature of Iron Sulfides, American Chemical Society, 1996
3. NACE Publication 8X294, Review of Published Literature on Wet H₂S Cracking of Steels Through 1989
4. NACE Publication MR 0175-98, Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment
5. NACE Publication 8X194, Materials and Fabrication Practices for New Pressure Vessels to be Used in Wet H₂S Refinery Environments
6. NACE Publication RP 0472-95, Methods and Controls to Prevent In-Service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments
7. Robert W. Pierce, Estimating Dewpoints in Stack Gases, Chemical Engineering, April 11, 1977
8. R. L. Piehl, Stress Corrosion Cracking by Sulfur Acids, API proceeding, 1964
9. NACE Publication RP 0170-97, Protection of Austenitic Stainless Steels and Other Austenitic Alloys from Polythionic Acid Stress Corrosion Cracking During Shutdown of Refinery Equipment
10. NACE Publication RP 0296-96, Guidelines for Detection, Repair, and Mitigation of Cracking of Existing Petroleum Refinery Presssure Vessels in Wet H₂S Environments
11. Dennis H. Martens et al, Analysis Of Tubesheet Stresses In A Sulfur Recovery Unit, ASME Pressure Vessel and Piping Conference Proceeding 1996

12. Richard P. Krepski, Thermal Spray Coating Applications in the Process Industries, Published for the Materials Technology Institute of the Chemical Process Industries, inc. by NACE, 1993
13. American Welding Society publication C 2.18-93, Guide for the Protection of Steel With Thermal Sprayed Coatings of Aluminum and Zinc and Their Alloys and Composites
14. Herbert H. Uhlig, The Corrosion Handbook, sponsored by The Electrochemical Society, Inc., John Wiley & Sons, Inc.
15. R. L. Martin et al, Inhibitor Control of Oxygen Corrosion: Application to a Sour Gas Gathering System, Materials Protection and Performance, Vol. 10, No. 12, 1971
16. L. R. White et al, Amine Treating, NACE Corrosion '97 conference proceeding, 1997

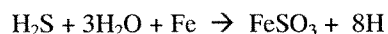
TABLE 1

SOME CORROSION REACTIONS RELATED TO SRU UNITS

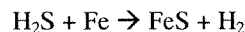
Acid Formation



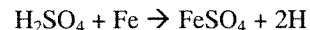
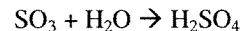
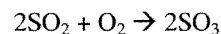
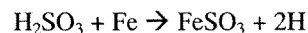
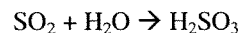
Iron Corrosion With H₂S Absorbing Into Water



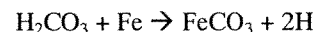
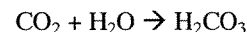
Iron Scale Formation With Temperature



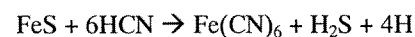
Sulfur Oxides



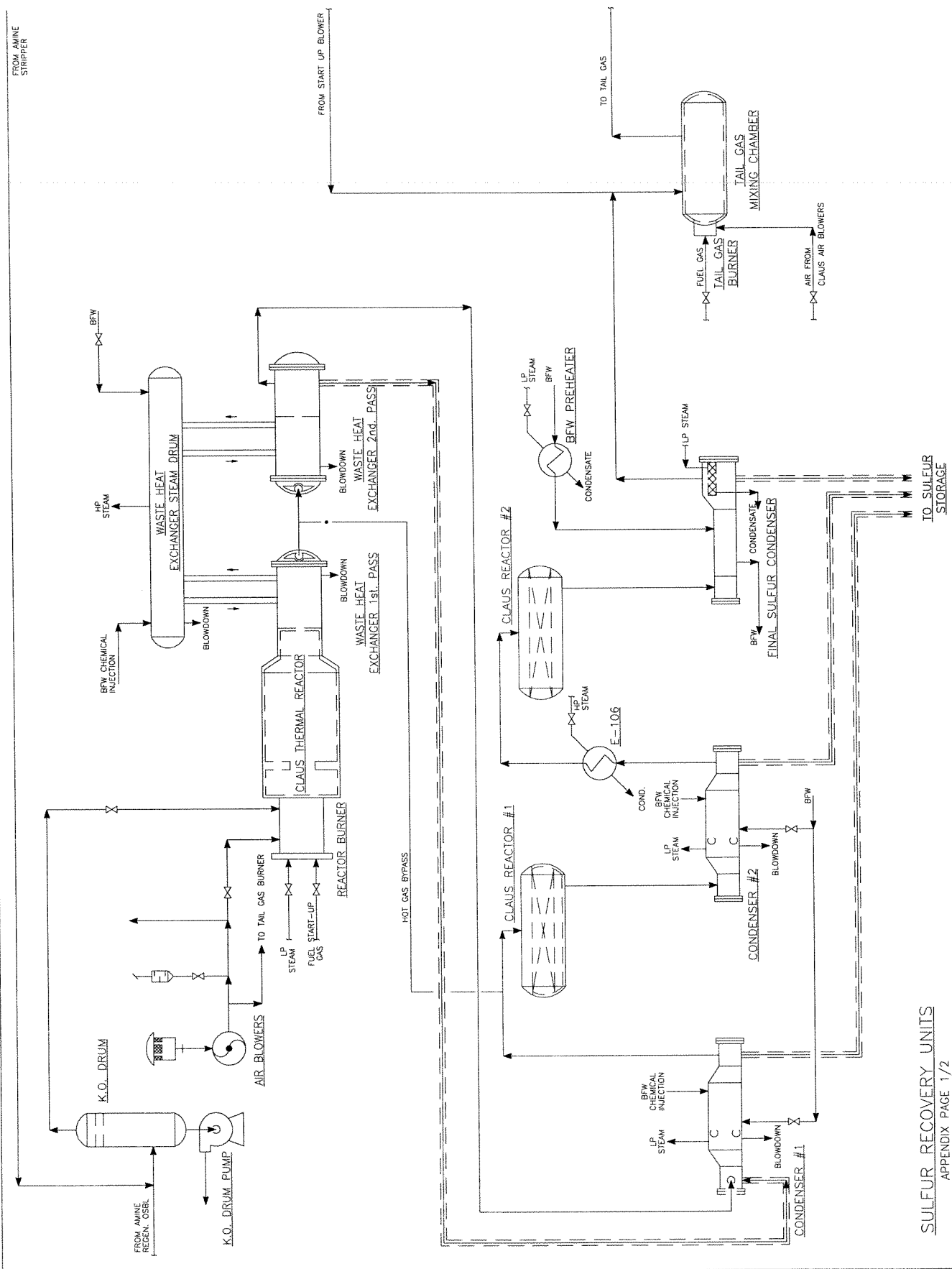
Carbon Dioxide Related



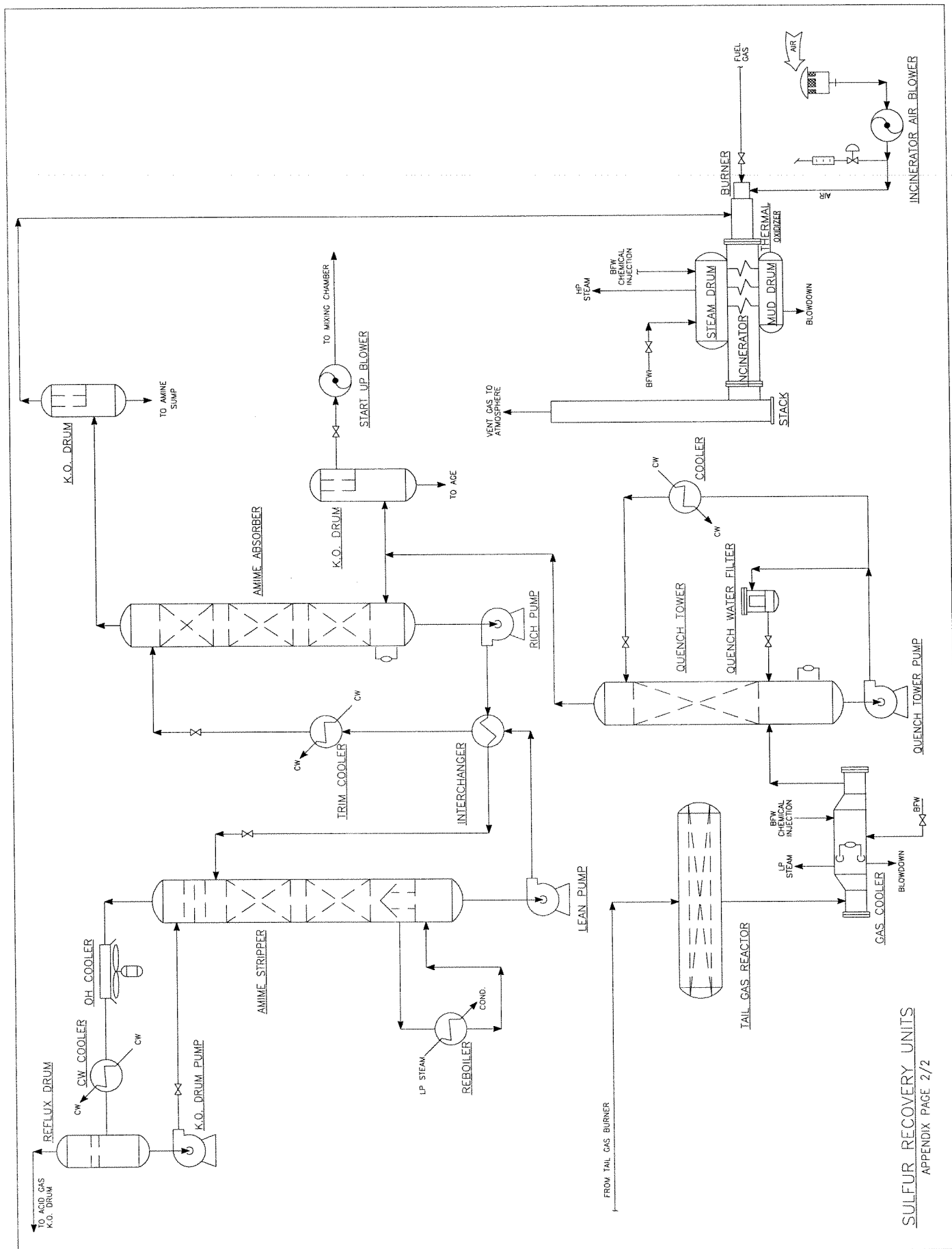
Hydrogen Cyanide

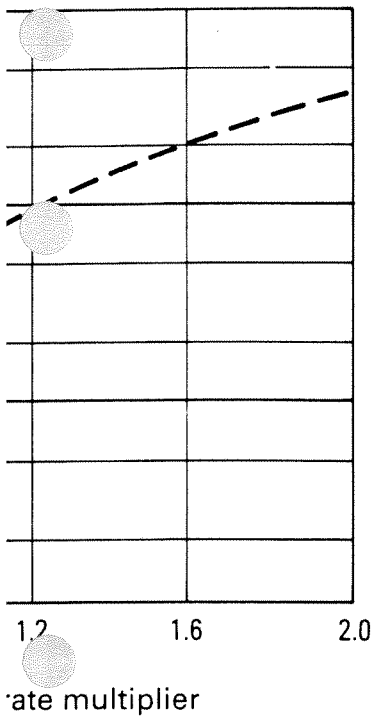


FROM AMINE
STRIPPER



SULFUR RECOVERY UNITS
APPENDIX PAGE 1/2





content on corrosion rates
modified McConey curves in
(10-°F) temperature range.

rnal refractory lining.
er type 321 (S32100)

ected corrosion rates,
erating above approxi-
is made of type 321
minized low-alloy
el, or carbon steel with
nces. When selecting
the recommendations
Institute (API) should
e with high-temper-
98). The same consid-
separator drums and
erating at temperatures
pe 321 (S32100) stain-
ed for heat-exchanger

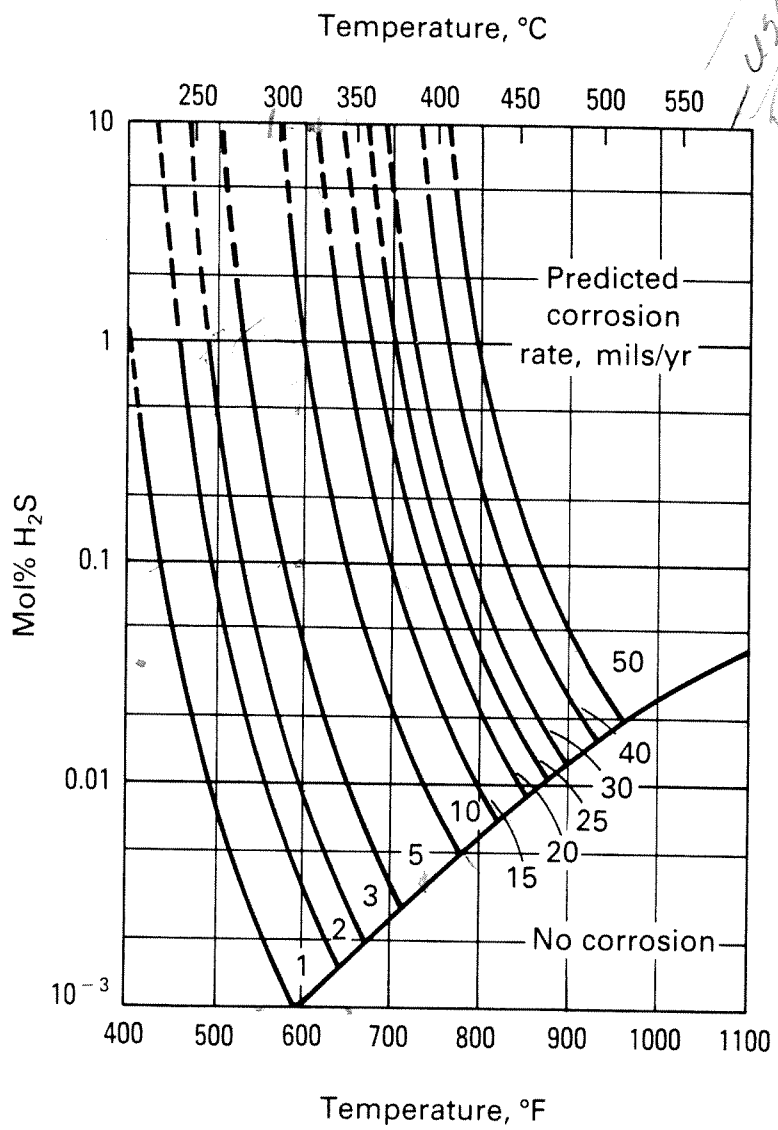


Fig. 4 Effect of temperature and hydrogen sulfide content on high-temperature H_2S/H_2 corrosion of carbon steel (naphtha desulfurizers). 1 mil/yr = 0.025 mm/yr. Source: Ref 96

the absence of hydrogen, there is often no real improvement in corrosion resistance unless chromium content exceeds 5%. Therefore, the curves for 5Cr-0.5Mo steel also apply to carbon steel and low-alloy steels containing less than 5% Cr. Stainless steels containing at least 18% Cr are often required for essentially complete immunity to corrosion. Because the Couper-Gorman curves