

“Ultra Capacity with Ultra Low Emissions- Thiopaq O&G Tail Gas Treating of Oxygen-Enriched Claus SRUs”

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**Presented at the 30th Annual Brimstone Sulfur Recovery Symposium
Vail Colorado September 11, 2023**

ABSTRACT:

As environmental SO₂ emission regulations become more stringent, Tail Gas Treating options become limited while solely catalyst-based TGT options are eliminated. To potentially achieve lower OPEX and improved plot plan, utilizing a biological desulfurization process as an alternative to a conventional amine-based TGT unit is becoming of increased interest in the Oil & Gas Industry during this energy transition era. At the same time, demands for increased SRU capacity and reliability favor the use of medium and high-level oxygen enrichment.

Fluor recently evaluated revamp options for an existing Refinery with Air Operated 3 x 100 metric tons per day SRUs. Fluor's COPE®II Oxygen Enrichment technology was selected to increase each train capacity to 150 TPD, essentially providing the equivalent redundancy of a spare train. The existing trains have insufficient tail gas treating to achieve an environmental emission specification below 300 mg SO₂ /Nm³. Thiopaq O&G (TOG) and Thiopaq O&G ULTRA (TOG ULTRA), bio-desulfurization technologies developed by Paqell, can comfortably achieve an H₂S treated gas specification of <25 ppmv in low pressure units.

A Case Study is presented comparing the use of TOG (ULTRA) in lieu of a conventional amine-TGT.

1.0 PROJECT INTRODUCTION

Fluor recently evaluated revamp options for an existing Refinery with Air Operated 3 x 100 metric tons per day (TPD) SRUs. The primary project objectives include:

- Achieve an environmental emission specification below 300 mg SO₂/Nm³ (thermal oxidizer stack SO₂ emissions limit of 100 ppmv, dry at 2% excess O₂)
- Increase each train capacity to 150 TPD Sulfur
- Optimize CAPEX and OPEX
- Optimize plot space
- Optimize flexibility in operating window
- Enhance Sulfur recovery efficiency and on-stream time
- Enhance Client Image as an Environmentally Friendly Company
- Reduce carbon footprint by mitigating the need for building new SRU units

- Handle some sour gas streams with unfavourable H₂S/CO₂ ratios

Fluor's COPE®II Oxygen Enrichment technology was selected to increase each train capacity to 150 TPD, essentially providing the equivalent redundancy of a spare train.

The existing site uses SUPERCLAUS® Tail Gas Treating (TGT). As with many sites using a solely catalyst-based method for Sulfur recovery (SUPERCLAUS®, EUROCLAUS®, or simply three stage Claus configuration), the existing system can no longer meet the increasingly-stringent environmental SO₂ emission regulations.

Two tail gas treating options proven for high Sulfur removal efficiency (SRE) are being considered:

- Hydrogenation followed by Amine treatment using a specialty MDEA
- Hydrogenation followed by the biological desulfurization process Thiopaq O&G (TOG)

The Amine TGT process is well known, capable of achieving high SRE and flexible to capacity variations between air-based and oxygen-enrichment operation. However, the Client wished to search for alternative systems, considering that Amine TGT systems have relatively high CAPEX, plot space requirements and high steam consumption. With the goal to achieve lower OPEX and smaller plot space, an option utilizing a biological desulfurization process as an alternative to a conventional amine-based TGT unit is becoming of increased interest in the Oil & Gas Industry during this energy transition era.

Thiopaq O&G (TOG) and Thiopaq O&G ULTRA (TOG ULTRA), bio-desulfurization technologies developed by Paqell, can comfortably achieve an H₂S treated gas specification of <25 ppmv in low pressure units.

The following sections describe these two TGT technologies and compare relative CAPEX, OPEX and advantages.

1.1 INTRODUCTION THIOPAQ O&G TECHNOLOGY

The Thiopaq O&G (TOG) Process is an environmentally friendly biological process to remove H_2S from sour gas streams and recover it as elemental Sulfur (S). The most unique aspect of the process is that it utilizes a living biocatalyst to oxidize H_2S to elemental S. The process consists of three sections: (i) an absorber column, (ii) a bioreactor and (iii) a sulfur separation section, see Figure 1.1-1.

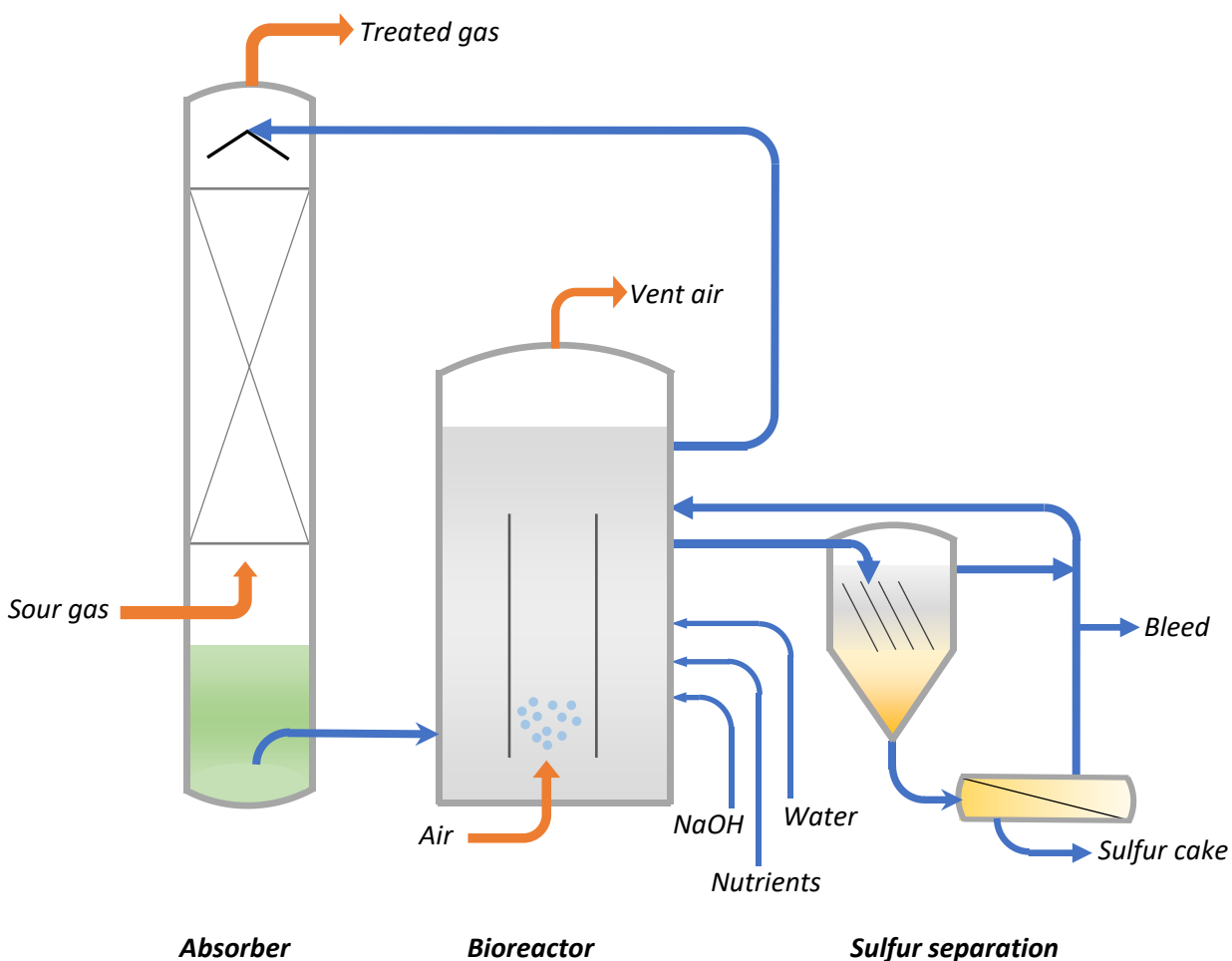


Figure 1.1-1 Process Diagram of Thiopaq O&G (TOG) System

In the absorber, sour gas is counter-currently contacted with lean process solution. Lean process solution coming from the bioreactor is fed to the top of the absorber. The mildly alkaline solution (pH 8 - 9.5, project depending) removes practically all H_2S . Due to the alkalinity of the process solution, H_2S is converted into soluble bisulfide (HS^-). The treated gas exits the absorber from the top of the column. The sulfide rich solution is collected in the sump of the absorber, from where it is routed to the bioreactor.

In the bioreactor the biocatalyst converts the dissolved sulfide into elemental Sulfur (S) using oxygen, thereby regenerating the process solution. Air is sparged into the bioreactor for the supply of oxygen. The biocatalyst consists of naturally occurring haloalkaliphilic Sulfur oxidizing bacteria. These organisms are not genetically manipulated or modified. The bacteria gain metabolic energy for growth (i.e. reproduction) from the oxidation of H_2S and use CO_2 as their sole carbon source. The biocatalyst is fast growing and highly resistant and adaptive to varying process conditions. The regenerated solvent is recycled from the bioreactor back to the absorber.

The formed hydrophilic elemental Sulfur particles are suspended in the process solution. These are removed from the circulating solution in the sulfur separation section, which typically consist of a settler and/or decanter-centrifuge.

Refer to Section 2.1 for a more detailed description of the TOG process and major equipment.

The TOG Process has the following performance features:

- Applicable to sour feed gases with H_2S concentrations ranging from 50 ppmv to 100 vol%
- H_2S removal efficiencies of >99.9%
- Suitable for high range of $H_2S:CO_2$ ratios (down to 1:100)
- Simple process configuration and control with stable operation
- Low operating and chemical costs.
- No use of environmentally unfriendly chemicals—No hazardous waste streams
- Attractive CAPEX
- Wide and flexible operating range
- Bacteria produces hydrophilic non-sticky Sulfur - prevents plugging
- Environmentally friendly process based on a naturally occurring biocatalyst
- Biocatalyst reproduces by itself; after initial fill, no refills are needed
- Inherently safe operation – no concentrated H_2S stream created

Bio-sulfur can be readily used in the agricultural industry.

Engineering and construction for licensed TOG systems can be provided by several sub-Licensing engineering companies, including Fluor.

1.2 INTRODUCTION AMINE TECHNOLOGY

Figure 1.2-1 below shows both the Hydrogenation Section, which is common for both Amine and TOG systems and the Amine TGT section. The common hydrogenation section is discussed under Section 1.4. Process Gas leaving the common hydrogenation section has nearly all the Sulfur species converted to H_2S (with zero SO_2 content), suitable for treatment in either the TOG or Amine TGT. This process stream has also been cooled and excess water has been removed (i.e., the process gas leaving the hydrogenation section is water-saturated).

The Amine TGT section consists of the Amine Contactor (Amine Absorber), amine regeneration system, and amine filtration section as described further in Section 2.2. The Amine Contactor is the key equipment item for meeting the stack emissions; any untreated H_2S in the overhead from

the Amine Contactor will be converted to SO_2 in the Thermal Oxidizer stack, along with any COS and CS_2 that passes through the hydrogenation section. Sour Gas enters near the bottom of the Amine Contactor and is contacted counter-currently with lean amine solution. H_2S is preferentially absorbed into the lean amine solution, with un-desired co-absorption of some CO_2 .

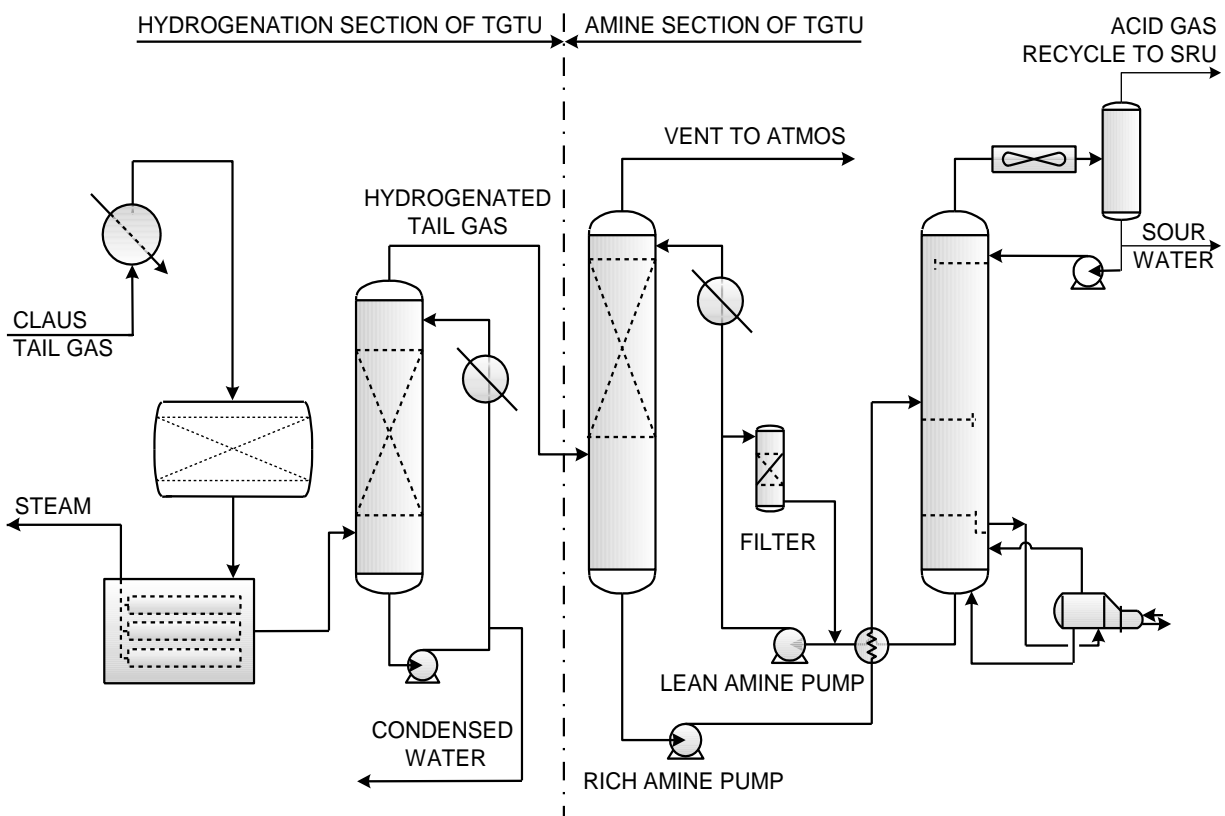


Figure 1.2-1: Common Hydrogenation and Amine TGT Schematic

Generic MDEA is the most widely used, inexpensive chemical solvent suitable for selective H_2S removal at low pressure. MDEA has become more widely used than DIPA for refinery and gas plant amine treatment units and for SRU tail gas treating. MDEA provides lower operational costs than DIPA, MEA or DEA, because MDEA requires lower stripping duty per unit of circulation. Lower stripping duty also decreases Regenerator overhead condenser duty.

Most specialty solvents are MDEA based, with additives to increase H_2S selectivity (decreased CO_2 co-absorption). Common proprietary solvents for selective H_2S removal are listed below:

- BASF OASE Yellow
- DOW HS-101 and HS-103.
- INEOS GAS SPEC TG-10.
- EXXON-MOBIL/BASF FLEXSORB SE Plus. This is used for sites with tight H_2S removal specifications where the Absorber operating temperature is high

- EXXON-MOBIL/BASF OASE SULFEXX. This is used for sites with tight H₂S removal specifications where the Absorber operating temperature is high

The selectivity of the solvent is important because any CO₂ co-absorbed into the rich amine solution will pass into the Regenerator overhead and into the TGT acid gas recycle and be routed to the front of the SRU for further processing. This recycling allows increased conversion of Sulfur than can be achieved in the Claus Section. However, the TGT acid gas recycle stream increases the volumetric throughput across all the Claus, common, and TGT equipment (entire process gas path). Thus, solvents with higher selectivity for H₂S decrease the TGT acid gas recycle stream, improving the hydraulic profile through the entire process gas path (Claus SRU, common hydrogenation section and amine TGT section equipment).

Specialty solvent has higher fill and makeup costs compared to generic MDEA, but generic MDEA typically requires higher circulation rate, and often cannot achieve the desired Contactor overhead H₂S specification. As overall stack SO₂ emission specifications become increasing stringent, higher removal of H₂S in the amine contactor is required, especially when considering that essentially all of any COS and CS₂ present will pass through the contactor untreated.

Amine based TGT treating is a well known method for achieving higher Sulfur recovery efficiency than can be achieved with a 3-stage Claus SRU or other solely catalyst-based system.

Refer to Section 2.2 for further information on the Amine TGT system.

1.3 INTRODUCTION OXYGEN-ENRICHMENT TECHNOLOGY

Fluor's COPE®II Oxygen Enrichment technology was selected to increase each SRU train capacity to 150 TPD, essentially providing the equivalent redundancy of a spare train. Capacity refers to the nominal Sulfur content in the combined acid gases. For the purposes of this paper, the produced Sulfur (Claus SRE) is fixed at 95% of the Sulfur contained in the feed acid gases. Figure 1.3-1 depicts the COPE®II process schematic and the principles of oxygen enrichment are described below. Oxygen enrichment provides the following major advantages:

- Increases Amine Acid Gas and Sour Water Stripper Acid Gas processing capability in each train. This could be used for increasing the overall Plant processing capability to handle future expansions in upstream Refinery units. For this project, pre-investment for future expansions was considered, but not implemented. The overall SRU capacity is fixed at 300 TPD, either by operating three trains at 100 TPD each using only combustion air, or by operating two trains at 150 TPD each using oxygen enrichment. In this manner, the oxygen-enrichment design provides spare capacity while avoiding the need for constructing a fourth SRU train.
- Achieves a Higher Temperature in the Thermal Reaction Furnace, which enhances destruction of ammonia, hydrocarbons and BTEX in the feed gases. Higher temperature in the Thermal Reaction Furnace also could allow processing of weaker acid gases with higher CO₂ content such as is required for many Gas Plants and Gasification system acid

gases. For this project, ammonia is present in the SWS off-gas, which has a typical composition with about 35 to 40 mole percent for each of H_2S and NH_3 . The Amine Acid Gas contains about 90 to 93 mole percent H_2S , which is within a typical range for refinery amine acid gas streams.

- In addition, many sites report smoother, more reliable and flexible operation when using oxygen enrichment as well as slightly enhanced Claus Sulfur recovery efficiency.

For Oxygen Enrichment, the total O_2 required for combustion is supplied by a combination of high-purity oxygen (at least 90 vol% O_2 content) and air from the combustion air blower. Variation in the relative amounts of these sources provides enriched air to the burner, which contains from ~21 vol% (no enrichment or air-only operation) up to 100 vol% O_2 blown systems. For H_2S -rich refinery acid gas streams, it is not necessary to use high-level oxygen enrichment that might be considered for treating weak acid gases from gas plants or gasification plants.

In COPE®II operation, high-purity oxygen is introduced to the burner separately, partially substituting for air to provide O_2 for combustion. This can produce a significant decrease in downstream flow rate. The decrease in downstream flow is mostly due to the reduction in nitrogen associated with the combustion air flow that is replaced by the high-purity O_2 stream. Reducing the flow rate of nitrogen lowers the pressure drop through the SRU. Consequently, this allows for an increase in the acid gas flow rate processed, with resultant increased produced Sulfur capacity.

Combustion with oxygen-enriched air increases the flame temperature in the Thermal Reaction Furnace compared with air-only combustion. If not tempered, the combustion temperature resulting from high oxygen enrichment levels can exceed the limits of the standard refractory lining that protects the carbon steel shell of the Main Burner (combustion chamber area) and of the Thermal Reaction Furnace.

COPE®II operation allows for higher levels of oxygen enrichment, even for rich acid gases, without exceeding the temperature limits of the standard refractory linings by recycling process gas from the outlet of the 1st Sulfur Condenser, through the COPE® Ejector, to the COPE® Burner. The recycle gas flow rate is controlled to moderate the Thermal Reaction Furnace operating temperature. The COPE® Ejector uses motive steam; this steam enters the process, also contributing to the attemperation.

For this project, the normal oxygen enrichment level at expanded 150 MTPD Sulfur capacity per train can be achieved using medium level oxygen enrichment at about 50 mole% percent oxygen enrichment.

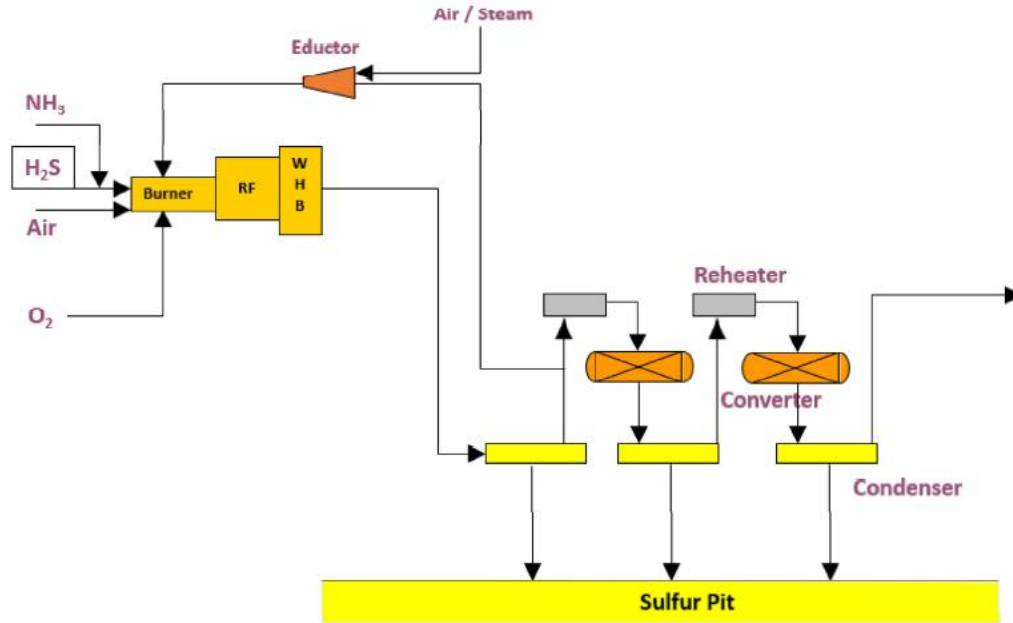


Figure 1.3-1 COPE® II Process Schematic

1.4 COMMON HYDROGENATION SECTION AND CONFIGURATION

Figure 1.4-1 shows the major equipment items in the common hydrogenation section; this part of the design is identical for either TOG or Amine TGT options. For this project tail gas leaving each SRU Claus train is routed to a dedicated tail gas heater; there are three trains of the common hydrogenation equipment. Tail gas enters with an $\text{H}_2\text{S}/\text{SO}_2$ ratio of between 2 to 4; for optimal Claus Sulfur recovery efficiency this ratio is controlled at 2 in the upstream Claus train.

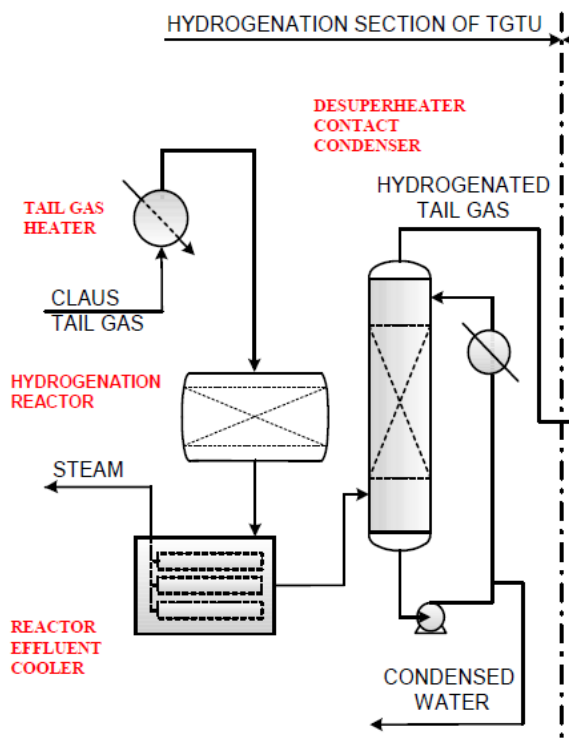
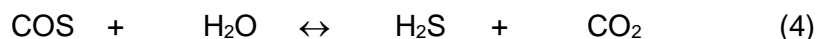
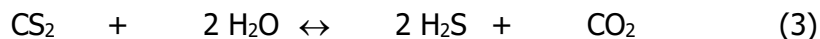
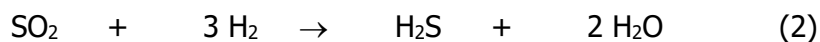
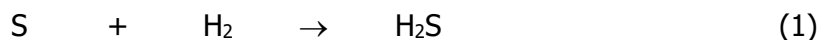


Figure 1.4-1: Simplified Schematic for Common Hydrogenation Section

Hydrogenation Reactor with associated exchangers

The hydrogenation process catalytically reduces Sulfur compounds and elemental Sulfur vapor in the Claus tail gas to H_2S , which is subsequently removed in the downstream TOG Absorber for Option 1 or Amine Contactor for Option 2.

Hydrogenation and hydrolysis reactions for the four primary Sulfur constituents are as follows:



Process gas is heated in an indirect Tail Gas Heater using HP Steam, prior to introduction into the Hydrogenation Reactor. Carbon monoxide in the Claus tail gas reacts with water in the Hydrogenation reactor to make hydrogen and CO_2 . Often, the Claus tail gas has sufficient H_2 and CO for hydrogenation of the Sulfur compounds in the tail gas for normal operation with no consumption or a small consumption of externally-supplied hydrogen.

There is a temperature rise across the Hydrogenation Reactor due to the exothermic reactions. A Reactor Effluent Cooler removes some heat from the reactor effluent by generating LP Steam on the shell-side. The process gas leaving the reactor effluent cooler is still superheated.

Desuperheater Contact Condenser

The reactor effluent will be further cooled to a temperature suitable for amine or TOG performance (about 35°C) in a Desuperheater Contact Condenser (DCC) column. The process gas has less capacity to retain water as it is cooled, so the excess water will be removed. This has the benefit of reducing the volumetric flow rate of the cooled process gas.

In a single bed design, the reactor cooler enters the bottom of a packed bed, where it is cooled and water vapor is condensed by counter-current direct contact with cooled circulating water in a bed of random packing. Water is circulated with the Contact Condenser Pump, which draws liquid from the chimney tray below the top packed section. The circulating water is cooled in the forced draft Contact Condenser Air Cooler (not pictured in Figure 1.4-1) and Contact Condenser Trim Cooler (by heat exchanger against Plant cooling water) and returned to the column above the packed bed on flow control.

A single bed DCC design requires stainless steel material to reduce corrosion rates, in case of condensing sulfuric acid, which may occur especially during a major SO₂ breakthrough event. Also facilities for either ammonia or caustic injection are required in case of undesired SO₂ breakthrough from the upstream Hydrogenation Reactor.

If SO₂ breakthrough is un-mitigated in the DCC, SO₂ will enter the downstream Amine TGT system for Option 2, where degradation of the circulating amine solvent may occur. There have been incidents where the entire inventory of circulating amine solvent needs to be replaced because the degraded solution can no longer perform sufficiently. Poor H₂S removal in the Amine Contactor leads to inability to meet the stack SO₂ emission specifications.

In Fluor's proprietary two-bed DCC design, the upper bed serves the same function, namely contact condensing. However, there is also a lower bed, where the superheated reactor effluent enters and is contacted counter-currently against a circulating buffered weak caustic solution. In this manner, some caustic is available at all times to mitigate against SO₂ breakthrough.

Some systems implement ammonia injection based on pH after an SO₂ breakthrough event has occurred to reduce corrosion, but in these ammonia-injection systems, some SO₂ may have already slipped to the downstream amine system. Caustic systems that only inject caustic based on pH similarly have this issue, namely that some SO₂ may have already slipped to the downstream amine system.

Configuration

For this project, separate trains are included through the hydrogenation section for greater reliability. With the use of Fluor's proprietary two-bed DCC design, the risk of SO₂ breakthrough

slipping into the downstream amine system is mitigated. However, per the Client's decision, because of the remote possibility of a major SO₂ breakthrough event degrading the entire inventory, or a significant portion of the circulating amine solvent, there are also three separate Amine Contactors for Option 2, the Amine TGT.

The TOG system is robust against SO₂ breakthrough incidents. Due to the buffering capacity of the solution, the pH will remain relatively stable, mitigation can be done by temporarily dosing more caustic. Due to this robustness of TOG, only a single Absorber is required. When the Claus unit is operated on air, the combined Tail gas from the three Tail Gas Treating DCC columns enter the TOG absorber. When the Claus unit is operated with enriched air, the combined tail gas from two Tail Gas Treating DCC columns enter the TOG absorber. The flow rates and compositions of the total feed to the absorber differ for both cases, however the total design Sulfur load is identical (15 metric tons S/day).

Process Gas Leaving the Common Hydrogenation Section

In summary, process gas leaving the hydrogenation section has nearly all the Sulfur species converted to H₂S (with zero SO₂ content), suitable for treatment in either the TOG or Amine TGT. This process stream has also been cooled and excess water has been removed (the process gas leaving the hydrogenation section is water-saturated).

Although the SRU tail gas leaving the final Sulfur condenser has nearly equal volumetric flow rate for the SRU Air Case as for the SRU Oxygen Enrichment Case, there is more water contained in the tail gas for the SRU Oxygen Enrichment Case. This is because water is a by-product of the Claus reaction, and in the SRU Oxygen Enrichment Case, a higher flow rate of acid gases is processed, producing more water. Downstream of the DCC after removal of excess water, the Air Case process gas has a higher volumetric flow rate.

Revamp of the Common Hydrogenation Section

As part of the revamp for this project, the existing third SUPERCLAUS stage will be converted into the tail gas heater, hydrogenation reactor and reactor effluent cooler. Some modifications are required to accommodate these changes in service, such as sealing the unnecessary liquid Sulfur outlet on the converted reactor effluent cooler and modifications to the reactor bed support internals.

Note that new and/or modified equipment common for both TGT system options is not included in either system cost estimate.

1.5 THERMAL OXIDIZER SECTION

The Thermal Oxidizer Section is the same process scheme for both Option 1 and Option 2.

Treated process gas from either the TOG Absorber for Option 1, or from the Amine Contactor overhead for Option 2, is routed to the Thermal Oxidizers, where essentially all Sulfur species are

incinerated to SO_2 at 649°C with 2 mole percent excess oxygen prior to release from the stack at safe location.

In the existing facilities, each of the existing SRU trains has a dedicated natural-draft Thermal Oxidizer. As part of the upgrade, these must be converted to forced-draft Thermal Oxidizers with low NO_x burners. Due to plot limitations, the new Thermal Oxidizers, associated stacks and associated new air blowers will be located on an adjacent plot area.

2.0 PROCESS DESCRIPTION

The following sections describe TOG, Amine Tail Gas Treating, and Fluor's COPE[®]II Oxygen Enrichment technology.

2.1 PROCESS DESCRIPTION TOG SECTION

The TOG Process consists of three integrated process sections: (i) an absorber to remove H_2S from sour gas, (ii) an aerated bioreactor where bacteria convert dissolved sulfide to elemental Sulfur using oxygen, and (iii) a Sulfur separation section to recover the elemental sulfur from the process solution.

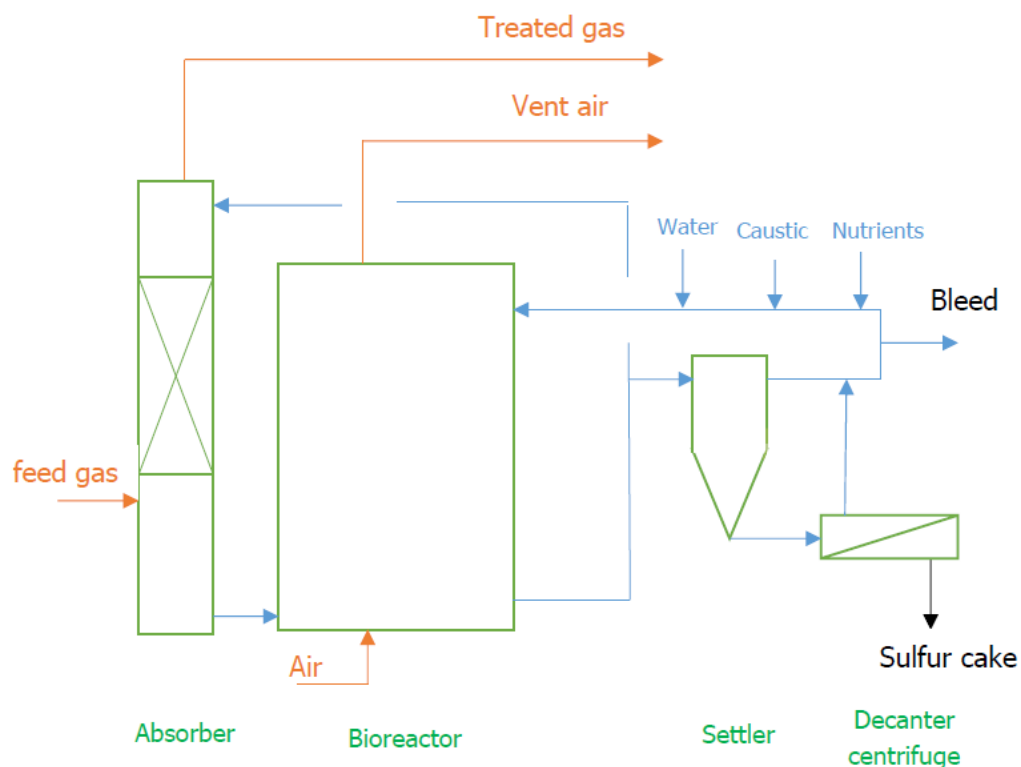


Figure 2.1-1: Process Schematic of TOG System

The major equipment items in the TOG System are described below.

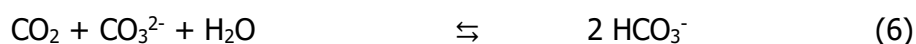
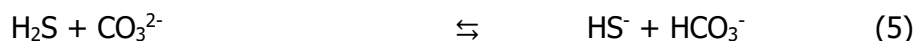
Absorber

The absorber column is a pressure vessel constructed out of stainless steel. In the absorber, the sour feed gas is injected near the bottom of the absorber column and counter-currently contacted with lean process solution making use of random packing. The packing material is polypropylene, internals are made of SS. The TOG process solution is an aqueous sodium (bi)carbonate solution with a sodium concentration of approximately 1.5 Molar and a pH between 9 to 9.5 is expected for this project. The pH depends on the actual feed gas composition and flow rate; however pH variations are minimized due to the buffering capacity of the (bi)carbonate solution.

The mildly alkaline TOG process solution, is fed to the top of the absorber. H₂S is removed from the tail gas in the absorber by the TOG solution and some CO₂ is co-absorbed. Due to the alkalinity of the process solution, H₂S is converted into soluble bisulfide (HS⁻). The treated gas passes through a demister to minimize entrainment of solvent and exits the absorber. Any untreated H₂S in the overhead from the absorber will be converted to SO₂ in the stack, along with any COS and CS₂ that passes through the hydrogenation section. The sulfide rich solution is collected in the sump of the absorber, from where it is routed to the bioreactor.

For this project, the SRU air case controls the required solution circulation flow and the diameter of the absorber column in view of the higher volumetric flow and the lower H₂S concentration in the feed.

The overall reactions taking place in the absorber are as follows:



A slip stream of the lean solution is sprayed downwards to the sump of the absorber to control the froth layer. From the absorber bottoms, the HS⁻ rich solvent is routed to the bioreactor via a rich solution cooler. Heat exchange takes place with plant cooling water.

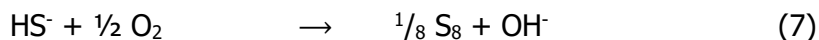
Bioreactor

The Bioreactor is an atmospheric tank constructed out of Glass Reinforced Plastic (GRP), typically referred to as Fibreglass (FRP) in the USA. The bioreactor is sparged with air to supply oxygen and to mix the bioreactor solution. The oxygen enables the biocatalyst to oxidize the dissolved sulfide into elemental Sulfur (S), thereby regenerating the process solution. The regenerated solvent is recycled from the bioreactor back to the absorber.

A small fraction of the sulfide is converted into the by-products sulfate (SO₄²⁻) and thiosulfate (S₂O₃²⁻). As these products do not regenerate the process solution, caustic soda (NaOH) is added at a small dosing rate to maintain the alkalinity of the process solution. Bioreactor solution, containing elemental Sulfur particles is circulated over the Sulfur recovery section.

The following reactions take place in the bioreactor:

The main reaction is the biological oxidation of dissolved sulfide to elemental sulfur:

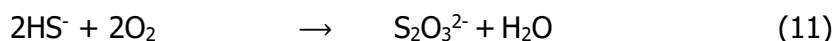


Through the buffer reaction, the pH of the solution will be recovered, excess CO_2 will be stripped out by the air:



The biomass covers the Sulfur particles with a hydrophilic layer making them non-sticky. Because of the hydrophilic nature of the biologically produced Sulfur, plugging problems that frequently occur in conventional caustic or liquid iron-based scrubbing systems are minimized in the TOG process. The biologically produced elemental S actually enhances the H_2S uptake in the absorber section.

The oxidation process in the bioreactor will also result in the formation of sulfate and thiosulfate as by-products (typically $\sim 5\%$). Sulfate formation is a biological process, which is enhanced at increased oxygen levels, whereas thiosulfate formation occurs due to a chemical reaction.



The formation of sulfate and thiosulfate does not regenerate the process liquid. The loss of OH^- ions due to the formation of sulfate and thiosulfate ions has to be compensated for by the addition of soda ash or caustic. A continuous bleed stream is required to avoid accumulation of sulfate and thiosulfate salts in the system.

Appropriate bioreactor internals are used to ensure complete mixing. The volume of the bioreactor is designed to achieve optimal activity of the biocatalyst. The exhaust air from the reactor can normally be emitted to the atmosphere without further treatment. The spent air contains less than 1 ppmv H_2S . The air supply to the bioreactor is automatically controlled based on the online measurement of the redox potential in the bioreactor. By proper control, the formation of sulfate and thiosulfate is minimized.

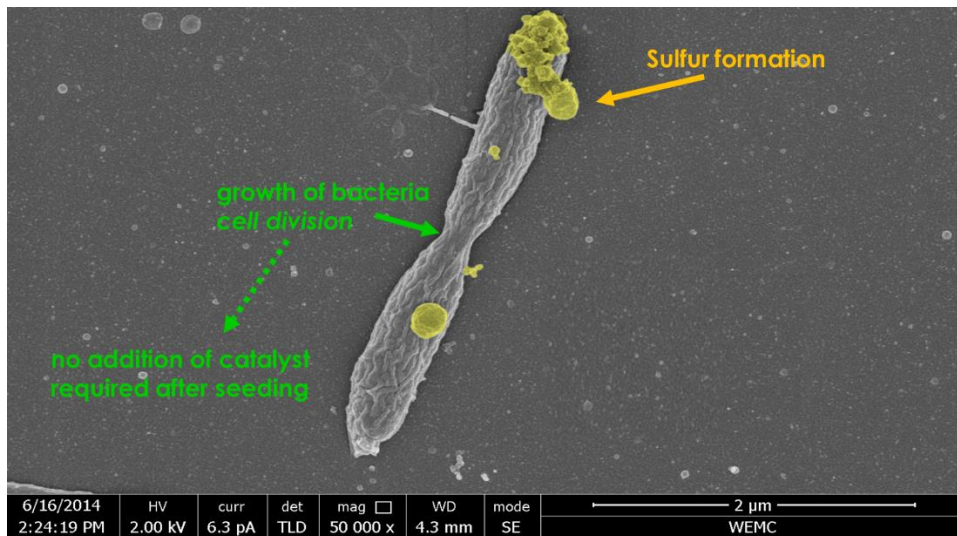


Figure 2.1-2: The workhorse

The optimum solution operating temperature is 35-40°C (95 -104°F).

The conversion of H_2S into elemental S is a biological process. The biocatalyst requires nutrients to maintain good performance. The nutrients include certain salts for their growth and maintenance. Extensive laboratory and field research have led to the optimization of the nutrient solution and dosing rate for this process. The nutrient solution is called THEO Powermix 5000 solution.

Automatic control is provided by a programmable logic controller (PLC) which monitors pH, conductivity, temperature, oxygen demand, and other parameters to keep the bacteria healthy. The biocatalyst is introduced once, at the initial start-up. Exposure to temperatures above 44°C (112°F) is fatal for the bacteria. At temperatures <15 °C, the biocatalyst becomes inactive, but activity is restored when temperature returns to normal operating temperatures.

Biocatalyst harvested from an existing operating plant is used for initial start up purposes.

TOG Sulfur Recovery

The elemental Sulfur forms hydrophilic solid particles, which are suspended in the process solution. These are removed from the circulating solution by application of a settler and/or decanter-centrifuge. For this project Sulfur load, both a settler and centrifuge are included.

A portion of the bioreactor contents is recycled over the settler where solids are concentrated by gravity settling. A decanter-centrifuge is included as a dewatering step downstream of the settler to reach approximately 65% dry matter. The elemental Sulfur typically has a purity of ~95-98% on dry basis. The process solution with the desired dry solid content is recycled to the bioreactor.

A small slipstream of solvent is typically bled from the system to prevent build-up of salts.



Figure 2.1-3: Decanter with installed spare



Figure 2.1-4: Sulfur product

TOG Sulfur applications

The produced Sulfur can be used as raw material for agricultural applications as fertilizer or fungicide. Produced Sulfur is considered as organic. Several brands of bio Sulfur-based suspension concentrates are marketed. Other options include melting the produced Sulfur to obtain the Claus Sulfur purity specification.

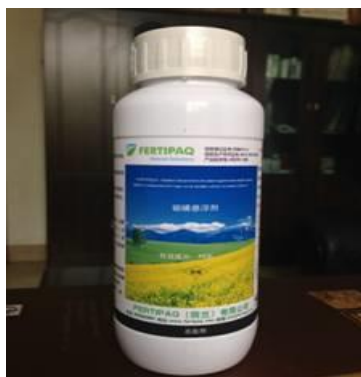


Figure 2.1-5: Sulfur application

Bleed water

The bleed water stream is water with sodium salts, biomass and elemental Sulfur. The pH of this stream is the same as the lean process solution (9 - 9.5). Depending on the location facilities this stream can be sent to the existing site waste water treatment; otherwise a separate (biological) water treatment unit needs to be installed or the bleed water needs to be sent offsite for disposal.

TOG Operating window

The flexibility of the TOG unit allows processing of tail gas resulting from either SRU case: the Claus enriched oxygen 15t/d case and the Claus air-only 15t/d case. During operation, the bioreactor can be running at Sulfur load turndown conditions even below 20-30% of the design Sulfur load by closing part of the air inlet lines to the bioreactor. This prevents low air velocities in the inlet lines and therefore prevents Sulfur settling issues in the air lines. The flexibility of the TOG absorber in terms of gas flow rate handling capability is high since random packing is used.

Following an extended period of turndown operation, gentle increase of the Sulfur load to the unit is required to allow the bacteria population to adjust.

2.2 PROCESS DESCRIPTION AMINE TGT

The main sections of the Amine Treatment unit are the Amine Contactor (Amine Absorber), amine regeneration, and amine filtration sections as depicted in Figure 2.2-1.

Amine Contactor

The Amine Contactor is the key equipment item for meeting the stack emissions; any untreated H_2S in the overhead from the Amine Contactor will be converted to SO_2 in the stack, along with any COS and CS_2 that passes through the hydrogenation section. Sour Gas enters near the bottom of the packed Amine Contactor (Amine Absorber) and is contacted counter-currently with lean amine solution. H_2S is preferentially absorbed into the lean amine solution, with un-desired co-absorption of some CO_2 . Packing is used instead of trays to minimize pressure losses. It is

desirable to minimize the pressure losses across the entire process gas path of the Claus SRU, common hydrogenation and TGT sections to allow maximum acid gas processing capacity.

A specialty MDEA-based solvent is selected for this project. Applicable specialty solvents have higher selectivity for H_2S and higher slip of CO_2 (less co-absorption of CO_2), resulting in a higher strength acid gas which is better for Claus SRU performance, as well as decreasing the volumetric flow rate of the TGT acid gas recycle.

The treated process gas from the Contactor packed bed passes through a packed water wash section to recover any volatilized solvent (wash bed and related wash water pumps are not depicted in Figure 2.2-1). Washed treated gas from the Contactor overhead is routed to the Thermal Oxidizer, where it is incinerated and the stack flue gas is released to atmosphere at safe location. Refer to Section 1.5 regarding the Thermal Oxidizer system.

For this project, the SRU Air Case controls sizing of the Amine Contactor diameter, because the Air Case has the higher volumetric sour gas flow rate (downstream of cooling and water removal).

Note that the Amine Contactor materials are carbon steel clad with 316L stainless steel. Internals and packing materials are 316/316L stainless steel.

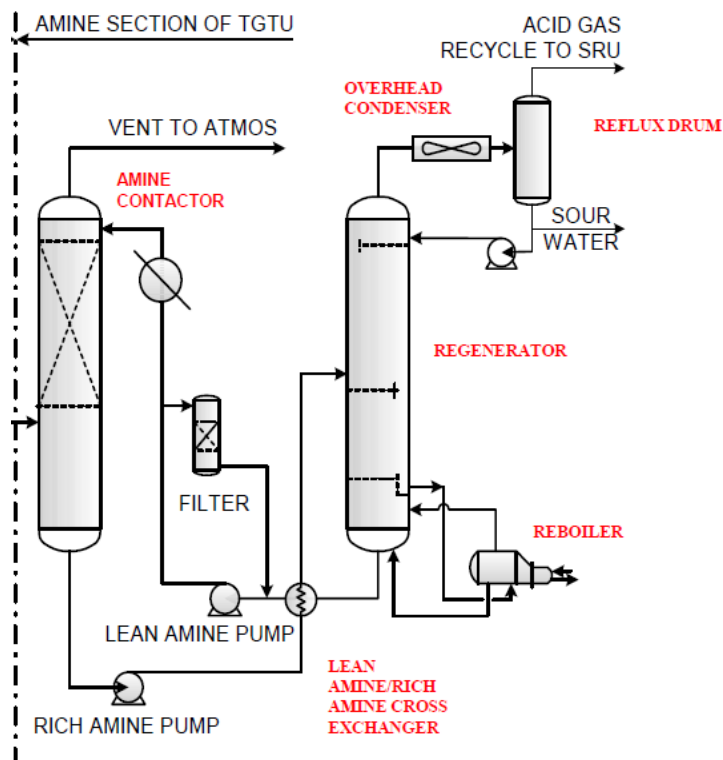


Figure 2.2-1: Simplified Amine TGT Process Schematic

Amine Regeneration System

Rich amine is pumped from the bottom of each absorber to the common regeneration system. Combined rich amine is heated in the Lean Amine/Rich Amine Cross Exchanger, while partially cooling the lean amine. Heated rich amine enters above the stripping section of the Regenerator column. The Regenerator strips H_2S and CO_2 out of solution to produce lean solvent and acid gas. The column has two sections: the stripping section below the feed with several packed beds separated by liquid redistributors, and a wash section above the feed with three moving valve trays. The H_2S and CO_2 are stripped from the rich solvent by countercurrent contacting with steam from the Regenerator Reboiler. As the stripping vapors heat the rich solvent, weak bonds between the solvent and $\text{H}_2\text{S}/\text{CO}_2$ are broken, releasing the H_2S and CO_2 . Solvent from the bottom chimney tray flows to the Regenerator Reboiler, where stripping vapor is generated and stripped lean solvent drains to the bottom of the Regenerator. The reboiler is heated using LP steam on feed flow ratio control reset by column overhead temperature.

Vapor from the stripping section is washed in the trayed reflux section to minimize solvent losses. The column overhead vapor flows to a forced draft air-cooled Overhead Condenser, where it is cooled and partially condensed. Vapor and liquid from the condenser flows to the Reflux Drum where the liquid is separated from the gas and returned to the column top reflux tray by the Reflux Pump.

Amine TGT acid gas is recycled to the front of each SRU train, joining with fresh Amine Acid Gas in the feed line upstream of the AAG KO Drum.

Hot lean solvent flows to the Lean Amine/Rich Amine Cross Exchanger on Regenerator bottom level control. Partially cooled lean solvent from the cross exchanger mixes with filtered solvent from the Lean Amine Tank and is pumped with the Lean Amine Pump through the forced draft Lean Solvent Air Cooler (not pictured in Figure 2.2-1). A 25% slipstream of cooled lean solvent is sent to the Amine Filter Package on flow control.

The circulating lean solvent is cooled further in the Lean Amine Trim Cooler, by heat exchange with Plant cooling water. The cooled lean solvent is routed to each of the Amine Contactors.

Note that the Amine Regenerator materials are carbon steel clad with 316L stainless steel. Internals and packing materials are 316/316L stainless steel. Similarly for other amine services, 316 stainless steel materials are typically used to reduce the rate of corrosion, extending equipment life. Piping materials for heated streams or for areas with velocity above about 1.8 m/sec (about 6 ft/sec) typically also require 316 stainless steel material, although velocity criteria may vary.

For this project, per Client instructions, no plate-and-frame exchangers are allowed in sour service. For the cost estimate, shell-and-tube exchangers are used in both amine and TOG systems for cross, trim and/or solution cooling. However, for TOG systems, plate and frame exchangers are typically used due to the lower H_2S concentration in the rich solution.

Amine Filtration System

A slipstream of lean amine is routed to the Amine Filtration Package on flow control to prevent the buildup of impurities in the circulating solvent. The filtration system has three filters, a pre-filter for particulate removal, an activated carbon filter and then a post-filter for removal of fines from the activated carbon filter. The particulate pre-filter removes any insoluble corrosion products and other suspended solids (i.e., pipe scale, iron sulfide, and iron oxide rust). The activated carbon filter removes hydrocarbons, excess antifoam, and surface-active contaminants. Filtered lean solvent then flows to the Lean Solvent Tank.

Amine Storage and Drainage System

A flow-through Lean Solvent Tank (not pictured in Figure 2.2-1) is provided to handle minor surge fluctuations between the three Amine Contactor columns and the common single Regeneration column. The Lean Solvent Tank is an atmospheric cone-roofed tank with a nitrogen blanket to prevent solvent degradation by air ingress. The Lean Amine Tank is sized to hold the entire system inventory of circulating amine solution (sum of each train amine absorption system amine volume and the common amine regeneration system amine volume).

A common Fresh Tank (not pictured in Figure 2.2-1) is provided to receive and store shipments of fresh concentrated amine, and is sized to hold the capacity of two ISO tanks (where one ISO tank ~ 20 metric tons). Fresh solvent pumps (not pictured in Figure 2.2-1) intermittently send fresh solvent into the Lean Solvent Tank when make-up solvent is required to compensate for any amine losses (i.e., increase solvent strength).

Several Amine Drain Drums (not pictured in Figure 2.2-1) are located in underground concrete sumps across the plot to collect amine drains from low-point drains associated with each of the three Amine Contactors, the common Regeneration column, and the common Amine Filtration System. Recovered amine is allowed to cool in these drums by heat loss to ambient. Recovered amine is periodically pumped through dedicated filters and returned into the circulating amine (pumps and filters are not pictured in Figure 2.2-1).

3.0 DISCUSSION OF COMPARATIVE ADVANTAGES

3.1 ADVANTAGES OF TOG PROCESS

TOG system advantages include:

- Simplicity of operation - PLC with minimal supervisory requirement (that is, low operator attention is needed).
- Low Opex
- Reduced plot space requirements, Lesser piperack infrastructure
- Flexible operation: covers Air case and Oxygen enrichment case operation and turndown

- Low caustic consumption compared to caustic scrubbing or other aqueous technologies. More than 95% savings on chemicals consumption expected compared to non-regenerative caustic scrubbers.
- Non-sticky (hydrophilic) Sulfur essentially eliminates plugging or fouling issues.
- Sulfur oxidizing bacteria, such as Thiobacillus, are naturally occurring, robust, self-sustaining, self-regulating, and self-reproducing.
- Product in either slurry or Sulfur cake form for agriculture, or for sulfuric acid production.
- Considered intrinsically safe and environmentally conscious process.
- No environmentally unfriendly spent caustic bleed stream is produced; typically bleed can be handled in waste water treatment system.
- No environmentally unfriendly chemicals are used.
- Large capability for buffering, which minimizes the impact of any upsets.
- Low number of equipment services- Although the equipment services count is similar between the options, TOG systems have slightly fewer equipment services to maintain and operate compared with conventional amine technology.
- Wide turndown capability in terms of gas flow and/or H₂S content.
- No TGT Recycle - TOG provides advantages in terms of debottlenecked SRU processing capacity which may be significant during future capacity expansions.
- Avoiding amine manufacturing provides a low carbon emission facility during this energy transition era—Reduced carbon footprint.
- Capable of treating streams with high CO₂ content and unfavorable H₂S to CO₂ ratio
- No steam consumption

In a conventional Claus/TGT system, the acid gas from the TGT amine system is recycled to the Claus burner system. This recycle gas stream is avoided when using a TOG unit in the TGT line up. This frees up space not only on the gas side of the Claus unit, but also on the liquid Sulfur side.

During oxygen enrichment, somewhat lower supply of high purity oxygen is required in the SRU if a TOG TGT is used, because there is no recycle flow.

Furthermore, there may be sour gas streams in the treating configuration upstream of the Claus unit, that have a H₂S/CO₂ ratio unfavorable for processing in the Claus unit. Such streams incur a relative high impact to the Claus unit in terms of gas flow rate, and potentially fuel gas used for co-firing and/or oxygen consumption. It can be considered to add an absorber (and flash vessel for HP applications) to the TOG unit for processing such undesirable streams. This debottlenecks the Claus unit, and may also lead to a lower requirement for fuel gas co-firing and/or oxygen enrichment level.

Using a TOG system in the tail gas treating line up will be especially attractive when there is a shortage of steam in the intended location of application.

The TOG process is approximately 95% efficient in regenerating the circulating aqueous soda solution containing the Sulfur Thiobacillus bacteria. No heating equipment is used for regeneration, there is no need to filter carbon or particulates. All bleed streams are environmentally friendly. The biocatalyst is self-sustaining, however the dosing of nutrients is required for their healthy growth.

Compared with typical caustic scrubber systems, only modest amounts of caustic addition are required to maintain system alkalinity and pH for absorption. The bacteria colony will expand or contract based on the amount of H₂S fed into the system. This supports significant process turndown (in terms of gas flow and/or H₂S content) if required. For this project basis, a turndown of 15% (both on flow and Sulfur load) is realistic.

The only bleed stream produced is environmentally friendly, a small amount, and typically routed to Waste Water Treatment.

TOG is considered intrinsically safe because the H₂S is not concentrated at any time during the process and because the H₂S is physically bound to the gas scrubbing solution. The TOG process is available with Environmental Technology Verification (ETV) produced in association with the US Environmental protection Agency (EPA). This may enable easier regulatory compliance and approval. Similar verification processes are available in Europe and other areas.

Differences between the TOG process, compared to the Amine TGT option are as follows.

- Handling of Sulfur product slurry or Sulfur cakes.
- Handling of caustic supply is required.
- Options have similar sampling requirements. TOG systems use automated monitoring, but samples need to be taken regularly to test for alkalinity for instance.

3.2 TOG OR TOG ULTRA AND OPTIMIZATION OPTIONS

There are several optimization options available for the TOG biological treating system.

OPEX reduction

At a Sulfur load of 15t/d as in this example, the addition of a sulfidic bioreactor called 'Selector' can be considered ('TOG ULTRA') that results in a significant reduction in the caustic consumption of the process. In the Selector, the sulfide oxidizing bacteria is exposed to high concentrations of sulfide. This promotes the growth of Sulfur producing micro-organisms that tolerate high sulfide concentration and suppresses the growth of Sulfate producing micro-organisms for which high sulfide concentrations are toxic.

Feed and Product Flexibility

Another additional process step that appears attractive to some locations is the conversion of the Thiopaq Sulfur product into a product that meets the Claus Sulfur purity requirements.

Vent gas stream co-processing can be easily handled in the TOG system despite unfavourable H₂S to CO₂ ratio.

Although not applicable for this project design basis, TOG systems could provide an advantage when Refineries convert to processing biofuels, which typically create sour gas streams with a very unfavourable H₂S to CO₂ ratio for SRU treatment. The biofuels sour gas stream can bypass the SRU and be directed to the TOG system for processing.

3.3 ADVANTAGES OF AMINE TGT

Advantages of the Amine TGT system include:

- Well-known system for achieving high Sulfur Recovery Efficiency
- Flexible operation: covers Air case and Oxygen enrichment case SRU operation
- Low Opex
- Simplicity of operation
- Only one type of Sulfur product is produced in the SRU followed by an Amine TGT

Differences between the Amine TGT option, compared to the TOG process, are as follows:

- Options have similar sampling requirements. Amine solution must be tested and analyzed regularly, for amine strength for instance
- Amine solution is subject to degradation by SO₂ breakthrough or by air/oxygen ingress
- Larger Infrastructure is required for collecting underground amine drains
- Amine poses risk to aquatic life if amine spill occurs
- Amine is corrosive and poses some risk for Operators while handling or if an amine spill occurs
- Amine Filtration System incurs higher maintenance requirements
- Uses Start-up/Turndown Ejector to keep minimum column vapor loading during start-up and turndown operation
- Incurs CO₂ emissions related to the manufacturing of the amine solvent

4.0 COMPARISON OF CAPEX AND OPEX

Fluor prepared an AACE Class 4 estimate (Equipment Factored) based on construction in the US Gulf Coast, 3rd Quarter 2023. Major assumptions include:

- Each Tail Gas Treating system is part of an existing larger Plant (Refinery).
- Equipment common for both TGT systems is not included in either cost estimate.
- Supply of power and utilities are available from the balance of Plant at the SRU/Tail Gas Treating Unit battery limit.

Total Installed Cost for the Case 1 Thiopaq O&G TGT is estimated as \$ 28.5 MM USD GC, 3rdQ2023. Total Installed Cost for the Case 2 Amine TGT is estimated as \$ 27.3 MM USD GC, 3rdQ2023.

The estimated annual OPEX for the Case 1 Thiopaq O&G TGT is estimated as \$ 1.39 MM USD GC, 3rdQ2023. The estimated annual OPEX for the Case 2 Amine TGT is estimated as \$ 1.58 MM USD GC, 3rdQ2023.

The two options are comparable in terms of both CAPEX and OPEX.

5.0 DISCUSSION AND CONCLUSIONS

Both TOG and Amine TGT processes are capable of achieving an environmental emission specification below 300 mg SO₂ /Nm³, emissions lower than the World Bank Standards for SRU facilities. The relative estimated CAPEX is comparable between the two options for this project basis. The relative OPEX is also comparable between the two options. The OPEX for TOG could be reduced if the TOG Ultra design is utilized.

Both options allow for flexible operation and can handle the range of operation between the SRU Air Case and SRU Oxygen Enrichment Case.

Both options provide safe and reliable tail gas treating. TOG provides better robustness against SO₂ breakthrough events.

Although the equipment count is similar between the options, TOG systems have slightly fewer equipment services to maintain and operate compared with conventional amine technology. The options are comparable in terms of simplicity of operation, with very few equipment items that require frequent maintenance. Comparable operator attention is required for monitoring operation of the two options.

The Amine TGT requires greater plot space and more infrastructure for pipe racks and underground drainage facilities.

TOG reduces the load on the Claus, both in terms of Sulfur load and gas load (due to absence of amine TGT recycle loop). During oxygen enrichment, somewhat lower supply of high purity oxygen is required in the SRU if a TOG TGT is used, because there is no recycle flow. During future capacity expansions, the advantage TOG provides in terms of debottlenecked SRU processing capacity may be significant.

Moreover, the TOG system can be designed to handle additional other refinery streams with unfavourable H_2S/CO_2 ratios, resulting in reduction of Claus load, reduction in fuel gas consumption from co-firing, and/or lowered oxygen enrichment level.

As another consideration, the Client's image can be enhanced by selecting Thiopaq O&G because it is an intrinsically safe and environmentally conscious process. Other intangibles, such as avoiding the carbon emissions associated with the manufacturing of amine solvent, may also influence the Client decision in favor of TOG.

In conclusion, using Thiopaq O&G for Tail Gas Treating provides a cost effective and attractive alternate to more traditional Amine TGT. This is especially true for this project, where the Client wishes to act as an Environmentally Friendly Company.