

Implementation of Caustic Scrubbing System and Sulphuric Acid as an Alternate Tail gas Treating Systems

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Emissions regulations are getting tighter and there is increasing demand to achieve higher sulphur removal and recovery efficiency.

The environmental regulatory agencies of many countries continue to promulgate more stringent standards for sulphur emissions from oil, gas, and chemical processing facilities. Typical sulphur recovery efficiencies for Claus plants are 90-96% for a two-stage, and 95-98% for a three-stage plant. Most countries require sulphur recovery efficiencies in the range of 98.5% to 99.9+% including typical tail gas treating units.

To comply with both progressively tighter product purity specifications and stricter environmental regulation agencies; the sulphur recovery efficiencies of near 100% is required by some locations such as California, USA to obtain the construction permit for new or modified sulphur plants.

There are many SCOTT type tail gas-amine units in operation and the standard allowable emissions has been 250 ppmv of SO₂ for many years. The improvement methods are available that could reduce SO₂ emission from 250 ppmv to 30-50 ppmv.

The World Bank regulation requires emissions of SO₂ less than 150 mg/Nm³ (~50 ppmv) to approve the loan. However any improvement will increase the capital and operating cost of the facility; the balance has to be kept.

The SCOTT type TGU Amine process for Claus tail gas treatment clearly represents Best Available Control Technology (BACT), potentially achieving 99.99+% overall sulphur recovery with emissions of < 10 ppmv H₂S and 30-50 ppmv total sulphur as SO₂ is achievable. When concentration of impurities in the acid gas such as COS and CS₂, H₂S content, and feed gas composition, and finally treated gas specifications are established, the overall SRU / TGU scheme including type of amine a generic or formulated for a particular application is specified.

Option 1- SRU/ TGU-Amine Design plus Forced Draft Incineration with Caustic Scrubber unit

The followings design-steps will be taken in summary to achieve the maximum possible overall recovery in the conventional SRU/TGU-amine type unit. The details of the limitations and how to overcome them are discussed

Design-Step 1 –the implementations of these features will reduce the emission of SO₂ from typical 250 ppmv to 30-50 ppm at the SOR (start-of-run) and EOR (end-of-run) respectively.

1. High Intensity SRU Burner for better destruction of ammonia, hydrocarbons and impurities
2. Use Titania catalyst at the bottom of the first SRU reactor bed and the alumina at the top. The volume of the Ti catalyst could be up to 50% of the total catalyst volume.
3. Using Titania catalyst on the second or third SRU reactor is not very effective due to lower operating temperature, but is evaluated case by case
4. Recycle the vent gas from the sulphur pit and the sulphur degassing to the front of SRU which traditionally were routed to the incinerator, it is very important the recycle gas to be routed to the proper location to prevent any cold spot or plugging as well as impact on the SRU recovery
5. The modern improvements of using TGU low temperature catalyst and steam reheaters instead of fired inline burner has significant impact on COS and CS₂ hydrolysis which the details are provided in this paper. To achieve 100% recovery, two options could be considered: 1) to use the conventional fired heater to make sure the operating temperature to the hydrogenation reactor is high enough or 2) to use dual steam reheaters instead of one by using superheated steam instead of saturated steam in the second reheater to achieve higher temperature to the hydrogenation reactor
6. Select the formulated amine solvent instead of Generic MDEA to achieve the 10 ppmv of H₂S from the absorber overhead, these amine solvents are described in detail in this paper such as HS-103, TG-10, MS-300 or Flexsorb SE plus

The above implementations will improve the performance of SRU/TGU unit to achieve higher recovery by lowering the SO₂ emission to 30-50 ppmv (SOR & EOR) of SO₂. It is also meets the World Bank Standards.

Design-Step 2- in this step the improvement will take place in the incinerator where we are able to reduce the SO₂ emission from 30-50 ppmv (SOR and EOR) to less than 5 ppmv.

Forced draft thermal design incinerator is employed where the tail gas absorber overhead enters the incinerator and is heated by burning fuel gas in a low or ultra NO_x incinerator burner to oxidize all the sulphur compounds to SO₂. The gas leaving the incinerator is cooled by recovering heat in the incinerator waste heat boiler and by producing saturated or superheated high pressure steam.

The outlet from the incinerator waste heat boiler enters the caustic scrubber to absorb the SO₂ from the gas. The gas leaving the caustic scrubber will contains less than 5 ppmv of SO₂ which is routed through a short stack to a safe location.

It may be required to heat the stack gas prior to emitting to the atmosphere to prevent condensation. In some cases gas/gas heat exchanger might be used to cool the gas entering the caustic system further and to heat the gas from the caustic scrubber. The spent caustic is sent to the water treatment system.

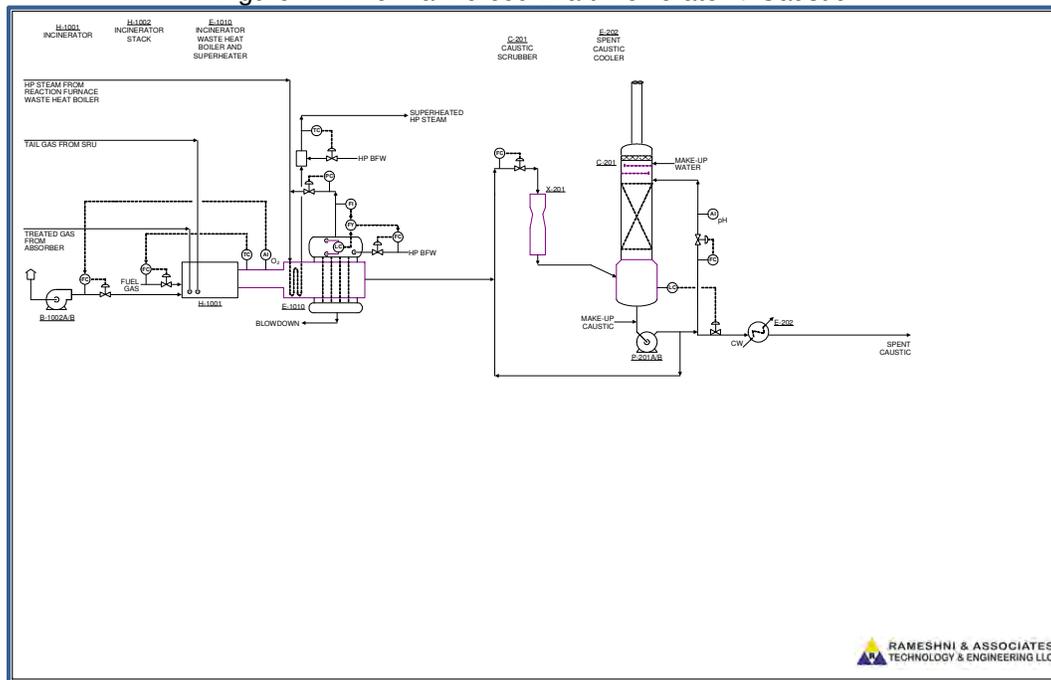
The effluent gas from the Incinerator Waste Heat Boiler is desuperheated in a venturi scrubber by intimate contact with a 10 wt % caustic solution. During the liquid vapor contact a portion of the SO₂ is removed from the vapor and the gas is cooled.

The liquid-vapor mixture then flows to the caustic scrubber. The vapor flows up through the packed bed of the caustic scrubber against a countercurrent stream of 10 wt % caustic solution to scrub the remaining SO₂ from the tail gas. The treated gas leaving the caustic scrubber will contain low ppm levels of SO₂.

Due to the temperature of the gas leaving the Incinerator Waste Heat Boiler there is a constant vaporization of water in the caustic scrubber which needs to be made up. This make up water is added to the column at the upper bubble trays to knock any remaining entrained caustic out of the vapor to minimize caustic loss. The caustic system uses a non-regenerable caustic (NaOH in water) to remove the SO₂ from the tail gas. The SO₂ that is removed slowly decreases the caustic strength of the solution so fresh caustic is added to replace this spent caustic. The spent caustic is purged on level control and cooled before being sent off-plot for disposal.

The following Figure No. 1 represents the caustic scrubbing system after the thermal forced draft incinerator. The stack located at the top of the caustic scrubber.

Figure 1 – Thermal Forced Draft Incinerator + Caustic



Caustic Scrubbing Systems – Tail Gas Alternate

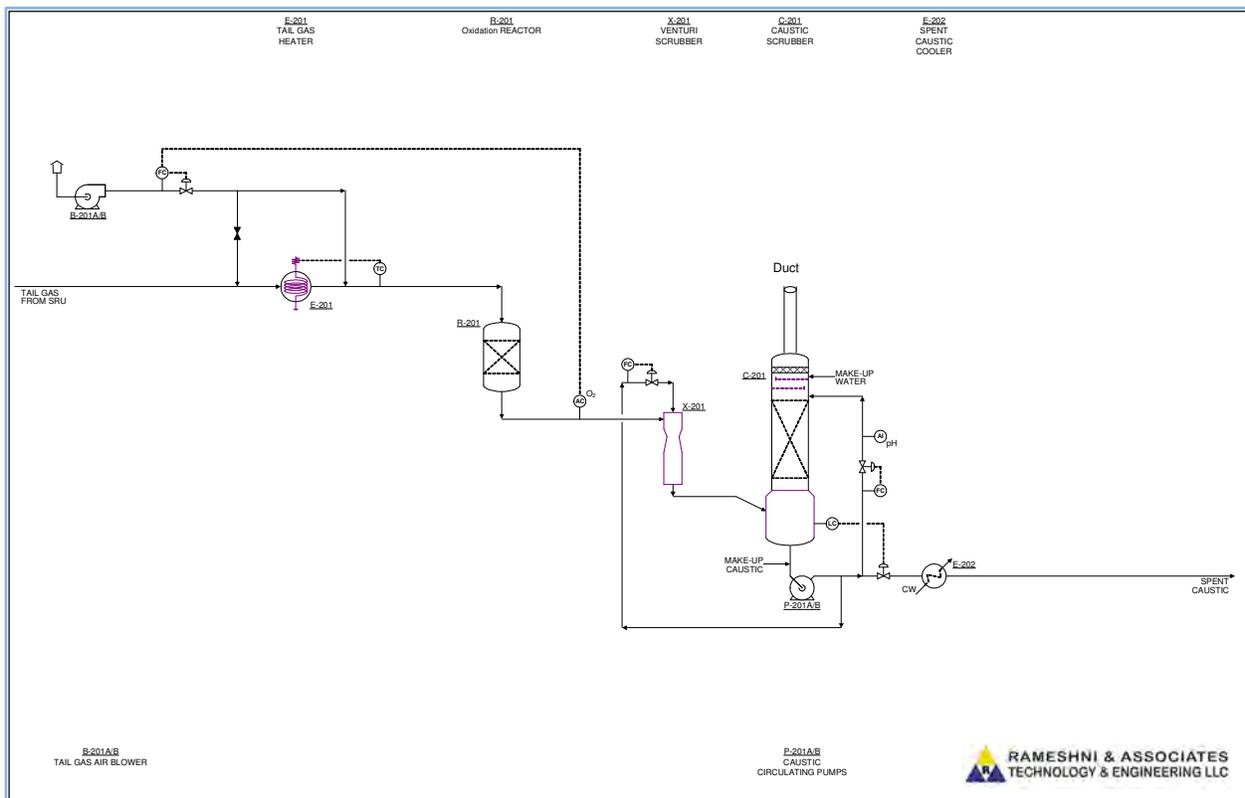
It is important to mention that in United States and many other locations small facilities such as gas plants or small refineries have adopted Caustic scrubber as their tail gas treating system, meaning the Tail gas Feed from the sulphur plants are routed directly to the incinerator followed by the caustic scrubber system. In addition in other processes such as sub dew point processes, or SuperClaus or similar where the sulphur recovery are higher than conventional Claus unit, adding Caustic scrubber after the incineration is a good option to increase the

recovery further. If the sulphur plants are large considering caustic scrubbing system alone is not economic and requires a very large volume of caustic to consume and processing high volume of the spent caustic or waste stream is not economical either. The configuration of using incineration-caustic as the stand alone tail gas unit is the same as shown above figure 1 except the gas comes directly from the Claus unit not the tail gas absorber.

Catalytic incinerator using oxidation catalyst followed by a caustic scrubber has also been used as a backup tail gas unit when the primary tail gas unit is down and there is no spare unit. Then catalytic incinerator and caustic scrubber has a lower capital cost but higher operating cost than a conventional tail gas treating unit, so it can be economical when only used occasionally. The COS and CS₂ hydrolysis needs to be evaluated case by case if regulation is tight.

A typical catalytic incineration and caustic scrubber is shown in Figure 2.

Figure 2- Stand Alone TGU-Catalytic Incinerator + Caustic



Option 1 -Detailed Description and Background

In a typical refinery sulphur plant the amine acid gas and the sour water stripper gas is processed in the SRU, Excessive HCs in the SRU acid gas feed will tend to increase the carbon-sulphur compounds in the effluent.

COS, and CS₂ are common byproducts from the reaction furnace as a results, it is recommended to have the Ti catalyst at the bottom of the first SRU reactor ranging from 6” to half the bed to promote the hydrolysis of COS and CS₂. If COS and CS₂ are not hydrolyzed in the SRU, there was one more chance in the conventional tail gas unit by operating the hydrogenation reactor using COMO catalyst at the high temperature using the Inline burner or RGG. Historically, Claus tail gas treating units (TGTU) have required reactor inlet temperatures of ~ 550°F for appreciable hydrolysis of COS, CS₂ and CO, typically requiring preheat by inline firing or heat exchange with hot oil or heat transfer fluid.

In the modern design a steam reheater is used instead of a inline burner / RGG with a low temperature hydrogenation catalyst which reduces COS/CS₂ hydrolysis since the hydrogenation reactor operates at the lower temperature.

The advisability of supplemental H₂ to the tail gas unit is also a source of controversy. Many clients consider the availability of import H₂ necessary to minimize the risk of SO₂ breakthroughs, whereas in reality it is as easy to reduce Claus combustion air (with the same effect) as increase H₂ addition. In the absence of supplemental H₂, the operator quickly learns the value of monitoring residual H₂ as a sensitive indicator of Claus tail gas ratio, and arguably is more likely to routinely optimize Claus air demand when constrained by a limited H₂ supply. Three-stage Claus units clearly do not need supplemental H₂, while residual H₂ may be marginal with 2-stage units, in which case supplemental H₂ may be advisable to ensure ability to optimize the Claus tail gas H₂S/SO₂ ratio. H₂ analyzers based on thermal conductivity measurement are very reliable, with minimal servicing. Where the TGU is coupled to a single Claus train, the H₂ analyzer can in fact supplant the Claus air demand analyzer. Where multiple Claus trains are coupled to a single TGU, combustion air to a Claus unit whose air demand analyzer is out of service can be temporarily adjusted based on TGU residual H₂.

Hydrogenation Reactor Performance

With good catalyst activity and no excessive HCs in the acid gas feed to the Reaction Furnace, organic residuals in the Absorber offgas should be as shown in Table 1:

Table 1 – Residual Sulphur with Fresh Catalyst

Contaminant	PPMV
Carbonyl sulfide (COS)	< 20
Carbon monoxide (CO)	< 200
Carbon disulfide (CS ₂)	0
Methyl mercaptan (CH ₃ SH)	0

With fresh conventional catalyst, temperatures of 400-450°F (204-232°C) are typically required to initiate the hydrogenation reactions, and 540-560°F (282-293°C) for hydrolysis. As the catalyst loses activity with age, progressively higher temperatures may be required. Typically, activity loss is first evidenced by (1) reduced COS, CS₂ and CO conversion, and (2) potential

methyl mercaptan formed by the reaction of CS₂ and H₂, while hydrogenation of SO₂ and S_x may still be complete because of the lower initiation temperatures required.

Low Temperature Hydrogenation Catalyst

Low temperature hydrogenation catalyst eliminates need for an inline burner /RGG and indirect heating system could be used instead. Low-temperature TGU catalysts reportedly capable of operating at inlet temperatures of 210-240 °C (410-464 °F), achievable with steam reheat, have become very popular over the past five years. The primary advantage (in a new unit) is elimination of the inline burner, translating to (1) lower capital cost, (2) operating simplicity, (3) improved turndown, (4) reduced TGU tail gas volume, (5) reduced CO₂ recycle to the SRU, and (6) elimination of risk of catalyst damage by inline burner mis-operation.

While reduced investment and complexity are a given, relative COS, CS₂ and CO conversion efficiencies need to be compared. It is not necessarily sufficient to achieve regulatory compliance.

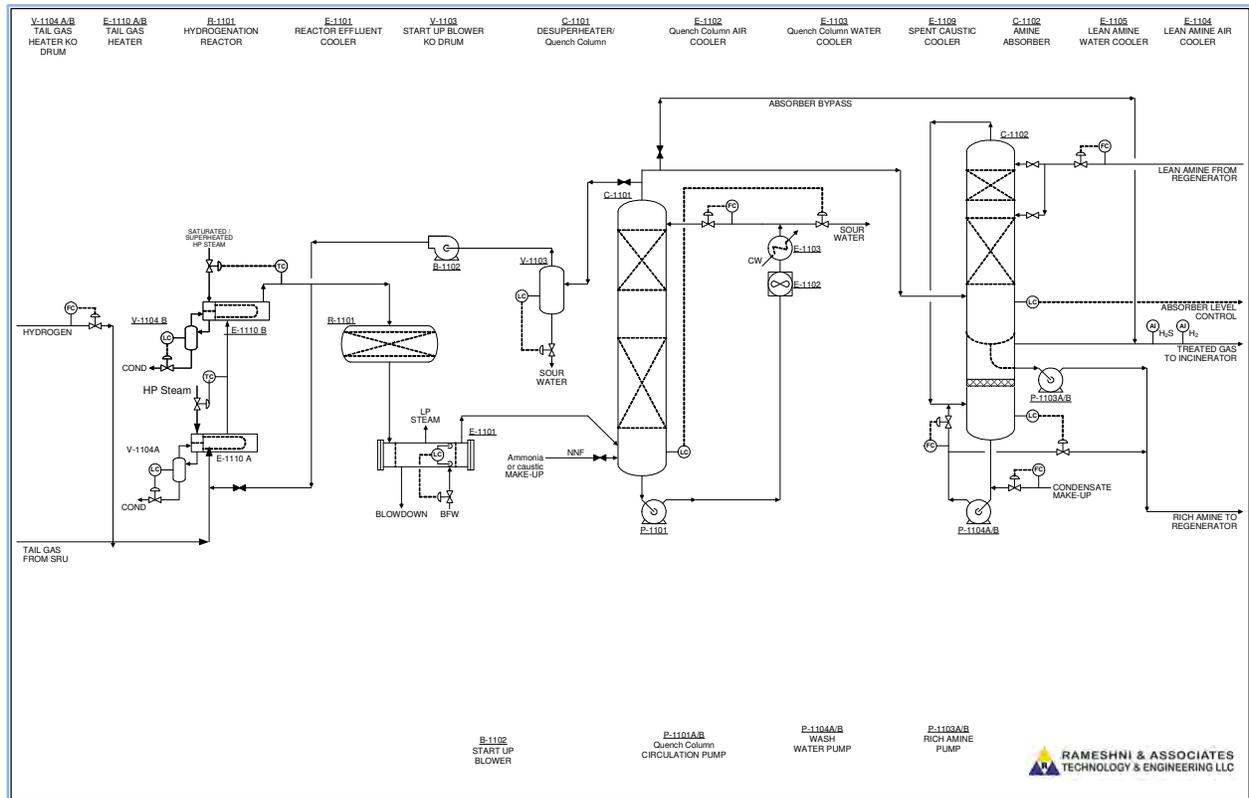
Hydrolysis of COS, CS₂ and CO typically requires higher temperatures than hydrogenation of SO₂ and S_x. Perhaps accordingly, COS, CS₂ and CO conversion efficiencies are the first to suffer as conventional catalysts lose activity with age. Higher reactor inlet temperatures will tend to compensate for deactivation, thus extending catalyst life considerably. Depending on the design limits, temperatures can generally be increased by 50-150 °F (28-83 °C).

Assuming the same holds true for the low temperature catalysts, a steam reheater will substantially limit the extent to which temperatures can be increased, in effect potentially shortening catalyst life. At 464 °F (240 °C) – generally the limit of a 600# steam reheater – hydrolysis of CO, COS and CS₂ approaches that of conventional high temperature catalysts.

Eliminating the inline burner has the benefit of reducing the TGTU tail gas volume (for the assumed basis with an inline burner). Assuming 85% CO₂ slip, the acid gas load on the TGTU amine is reduced significantly.

The following figure No. 3 represents the scheme for the dual steam reheaters configuration using low temperature hydrogenation catalyst in the tail gas unit to eliminate the limitation of adequate inlet temperature to the hydrogenation reactor. It is critical to confirm the availability of superheated high pressure steam at the facility.

Figure 3 – TGU Low Temperature Catalyst with Dual steam Reheater



Solvent Selection Criteria in the Tail Gas Unit

The most common solvent is 40-45 %-wt MDEA, (DOW HS-101, or similar) designed for a maximum rich loading of 0.1 mol acid gas (H₂S + CO₂) per mol amine with typical emission reduction to ~ 150 ppmv H₂S. Cooling of the lean amine to at least 100°F (38°C) is important for minimization of emissions and amine circulation rate. Specialty TGU amines are essentially pH-modified MDEA to facilitate stripping to lower residual acid gases for treatment to < 10 ppm H₂S, potentially obviating incineration. CO₂ slip is also improved. These products are variously marketed as

- ▶ Dow UCARSOL HS-103
- ▶ Ineos Gas/Spec TG-10
- ▶ Huntsman MS-300.
- ▶ FLEXSORB® SE Plus

In sulphur plant tail gas applications, FLEXSORB® SE solvents can use as little as one half of the circulation rate and regeneration energy typically required by MDEA based solvents. CO₂ Rejection in TGTU applications is very high, typically >90% rejection.

Option 2- SRU and Tail Gas Sulphuric Acid

Sulphuric acid plants are well known in industry mostly for the SO₂ conversion to acid in the following applications.

- Viscose fiber industry
- Petrochemical industry
- Sulphuric acid production & recycling
- Mining and roasting industry
- Tail Gas Treating Units (RECENTLY)

There are some refineries around the world that are able to produce sulphuric acid and to market that in addition to consume for in-house uses. The licensors of the sulphuric acid plants such as KVT Sulfox technology or Haldor Topsoe WSA technology use oxidation catalysts where all the sulphur compounds are oxidized to SO₂ to produce sulphuric acid.

The acid plant process is applied in all industries, such as processing of acid gases from amine regeneration units in hydrodesulphurization or treatment of tail gases from the Claus units.

According to the new regulations many refineries have to reduce the overall emissions by providing desulphurization units for their boilers and coking processes. Therefore, the technologies such as SNOX or similar are installed in many refineries. In existing refineries some of these units are designed larger to handle the SRU tail gas feed as a backup unit to meet the new requirements of redundancy therefore there is no need to install the additional tail gas units. In some of the new sulphur projects the tail gas units have been eliminated due to the high cost to achieve near 100% sulphur recovery and the sulphuric acid plant have been installed instead to eliminate SO₂ emissions to the atmosphere. In new refineries the concept of using a sulphuric acid plant as the tail gas allows any vent gas, or tail gas feed that contains sulphur compounds to be routed to the acid plant.

In this option, the SCOTT type TGU-Amine unit and the incineration system is completely eliminated and the tail gas from the SRU is routed to the sulphuric acid plant and the vent gas from the sulphur pit and the sulphur degassing could be routed to the front of the SRU or to the sulphuric acid plant directly. Overall sulphur recovery of nearly 100% can be achieved.

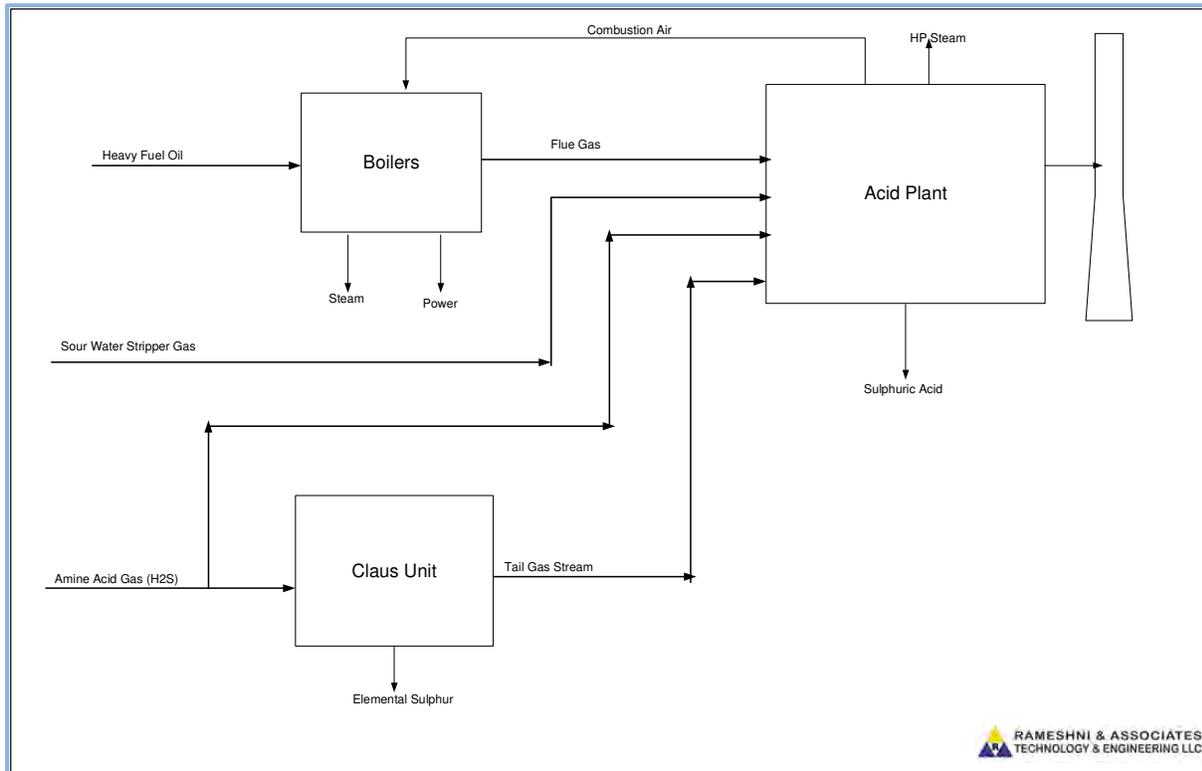
Another benefit of acid plant technology is if the refinery has to process a crude with a high nitrogen content, the sour water stripper ammonia gas may be beyond the capability of the sulphur plant. Ammonia could be processed in the acid plant.

Other options are processing the ammonia in the incinerator using John Zink or Duiker ammonia burning technology meeting NO_x emissions limits could be tight.

The following configuration is one of the common schemes where the design of the refinery is based on crude oils with high contents of both sulphur and nitrogen, it is obvious that the flue gas treatment technology should be well suited for this case. The SWS gas could not be processed in the SRU and could not be processed in the incinerator due to low NO_x emission level. The conventional tail gas unit similar to option 1 would be able to meet the emission

requirement but it would add additional cost having the extra units. Therefore it makes sense to have the sulphur plants without the TGU-MDEA type unit and instead installing an acid plant to serve as the tail gas unit, to process all the ammonia acid gas and to collect all the vent streams from other units that contain sulphur compounds and all will be processed in the sulphuric acid plant. The configuration presented in the Figure 4 will meet the emission requirements.

Figure 4- SRU and Sulphuric Acid Tail Gas



Cost Comparison -Option 1 versus Option

RATE was requested by one client to perform a study and cost estimate for a nominal 200 MTPD sulphur plant with the typical refinery applications. The following table represents the cost comparison between option 1 (TGU-Amine + Caustic Scrubber) versus option two (SRU + Sulphuric Acid TGU). The sulphuric acid technology selection is confidential.

Table 2- Cost comparison, Option 1 Versus Option 2

Item	Sulphur Recovery Unit, US \$	Tail Gas Treating Unit, US \$	Acid Plant, US \$	SRU+TGU, US \$	SRU+ Acid, US \$
Total	22,300,000	20,900,000	18,000,000	43,200,000	40,300,000

As noted above the cost of the SRU+ Acid is slightly lower than SRU+ TGU-Amine type unit but the cost is not the only factor for the technology selection, the following factors have to be evaluated.

- Overall refinery configuration
- Emission regulations from the SRU/TGU and overall allowable emission for entire facility
- Crude type, sulphur and nitrogen contents
- Market demand for selling acid
- Locations of the refinery
- Ease of transportation
- Availability of required utilities
- Sulphur contents from various boilers throughout the refinery
- Improve energy efficiency of boilers
- Reduce CO₂ emission

Conclusions

Higher sulphur recovery by reducing SO₂ emission is discussed. The nominal SO₂ emissions limit has been 250 ppmv for years, however, new regulations in some places requires below 100 ppmv, or below 50 ppmv or below 20 ppmv of SO₂.

It is possible to achieve nearly 100% recovery if necessary to comply with the new regulations, however, the design has to be optimized to reduce overall cost and to be economical for the refineries to process heavy crudes and meet the regulations and have a profitable business.

The alternative options for the tail gas treating unit are discussed to achieve 100% recovery. The caustic scrubbing system could be standalone tail gas treating or a polishing unit in the tail gas treating in the thermal incineration design while the sulphuric acid replaces the conventional tail gas unit. A detailed evaluations including the cost estimate, availability of the utility at the facility, location and market demand and overall allowable emission need to be performed before selecting any technology.