

TOP TREATMENT



Tofik K. Khanmamedov, TKK Company, USA, and Ralph H. Weiland, Optimized Gas Treating, Inc., USA, introduce new amine based desulfurisation strategies to enhance conventional tail gas treatment.

The Shell Claus offgas treating (SCOT) process, first utilised

commercially in California refineries in 1973, has become one of the standard treatments, allowing reduced sulfur emissions in the tail gas from Claus sulfur recovery units (SRUs). This technology has been applied extensively worldwide using a variety of solvents that selectively remove H_2S in the amine section of the tail gas treating unit (TGTU). Since its inception, the technology has remained relatively static in terms of the philosophy of designing TGTUs. However, there is demand for improvement of this process in terms of efficiency and reduction of operating cost. In this article, a new patented strategy is discussed for the amine section of TGTUs that is known in the market as the HIGHSULF process.¹⁻⁸

TGTU flowsheets

In a conventional TGTU (Figure 1) with reduction and amine sections, the tail gas from the SRU is heated by the combustion products generated by burning fuel gas under substoichiometric conditions to generate the reducing medium, hydrogen. The heated tail gas and reducing gas mixture is fed to a catalytic reactor containing an Al-Co-Mo type of catalyst. In the reactor all sulfur species (S_6 , S_8 , SO_2 , COS, CS_2) and partially CO are hydrogenated and converted to H_2S and CO_2 . Some of the COS and CS_2 is hydrolysed to H_2S and CO_2 . The effluent of this catalytic reactor has approximately 600 °F and is used to produce approximately 50 psig steam in a waste heat boiler (WHB). Gas then enters a water quench tower where it is cooled to 100 - 130 °F. Quench water goes to the refinery sour water stripping system (SWS). Cooled gas now enters the amine

section of the TGTU where H_2S is selectively removed by using a selective amine such as N-methyldiethanolamine (MDEA) or a hindered amine. High selectivity is paramount because ensuring a high level of CO_2 rejection is essential to minimise the flow rate of acid gas through the sulfur plant and to maximise its H_2S content. The acid gas from the regenerator is recycled back to the SRU. A conventional TGTU can be designed for a wide range of sulfur concentrations in the overhead from the absorber (an H_2S leak of up to 350 ppmv of H_2S). On the other hand, if the H_2S leak cannot be reduced by conventional means to a satisfactory level (as determined, for example, by local emission standards) other approaches such as amine stripping promoters or speciality amines can be used.

The main problem in many gas plants is a low concentration of H_2S and quite high concentration of CO_2 , i.e. raw gas with low H_2S to CO_2 ratio. This leads to extremely high CO_2 levels in SRU tail gases. And as a result, the gas from TGTU that is recycled and sent back to the SRU has high volume fraction of ballast CO_2 . This dilutes the fresh feed to the SRU, which is quite detrimental to sulfur

plant performance. Also, the high volume of CO₂ in the acid gas from the TGTU increases hydraulic load on the SRU. The quality of the acid gas from a TGTU is directly related to the H₂S to CO₂ ratio of the gas feeding it. If the H₂S:CO₂ ratio is low, the acid gas produced will also have a low H₂S:CO₂ ratio. If it is high in the feed gas it will also be high in the product. The new family of HIGHSULF strategies recognises this very important fact and takes steps to increase the H₂S:CO₂ ratio in the TGTU feed gas.

Figures 2 and 3 show two alternative flowsheets to conventional treating. Figure 2 shows HIGHSULF tail gas treating as it appears in the patent and technical literature. As can be seen, a HIGHSULF TGTU uses the same equipment as the conventional TGTU.

The SRU tail gas flows to the same heater, hydrogenation/hydrolysis reactor, produces steam in the same WHB, is cooled in the same quench tower and then feeds the amine section. H₂S is recovered in the amine section using the same MDEA solvent under identical operating conditions. Rich amine is sent from the absorber to the regenerator for reboiled stripping at the identical rate of energy consumption. The key element of HIGHSULF is that the acid gas to the absorber is enriched in H₂S by recycling a portion of the acid gas from the regenerator back to the front end of the absorber where it is mixed with the fresh tail gas coming from the quench tower. This so called HIGHSULF line automatically brings significant advantages to the process, similar to the acid gas enrichment cases described elsewhere.⁹⁻¹⁰

This new HIGHSULF strategy has inspired others to extend the use of this simple concept for amine units. For example, Palmer¹¹⁻¹² suggests introducing absorber feed gas and recycle gas at different

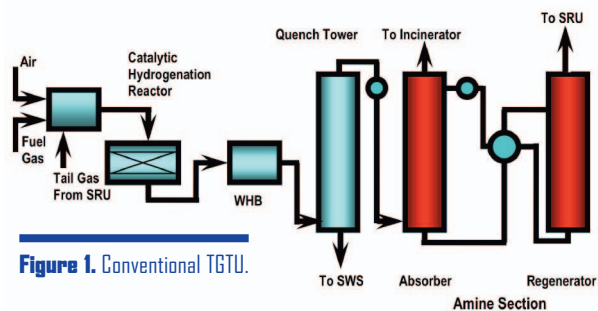


Figure 1. Conventional TGTU.

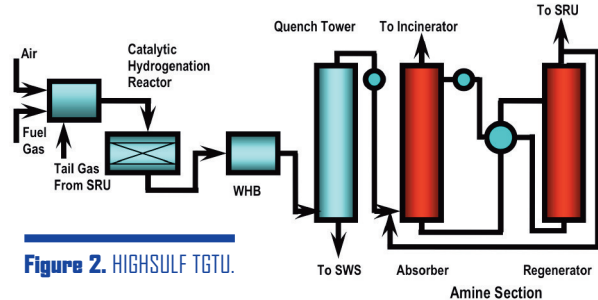


Figure 2. HIGHSULF TGTU.

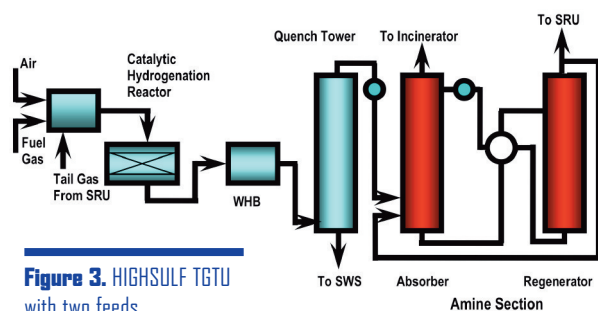


Figure 3. HIGHSULF TGTU with two feeds.

places in the common absorber instead of mixing the two gases together and introducing them as a single acid gas feed. The concept and strategy are very similar; the objective is to create absorber conditions such that the absorber is seeing a gas phase much richer in H₂S. This allows it to send a rich amine more heavily loaded in H₂S (and more lightly loaded in CO₂) to the regenerator, and the regenerator then produces an acid gas feed much richer in H₂S to the SRU at a lower total volume flow rate. This is considered as an extended use of HIGHSULF with two feeds to the absorber and its application for TGTU (Figure 3) will be discussed.

Comparing tail gas treating schemes

The schemes can be compared through accurate process simulation using a tool such as the ProTreat simulator. This tool uses a mass and heat transfer rate based column model that takes full account of the effect of column internals and hydraulics, vapour liquid equilibrium and chemical reaction kinetics on the actual performance of both absorbers and regenerators. It uses the actual number and design of trays and the actual depth of real packing (random and structured) in the columns as they are truly built. All calculations are done on real trays and packing, not theoretical stages.

In what follows, all comparisons are based on treating the same gas in identical equipment operated under identical conditions of amine type, strength and flow, and with the same reboiler duty. Pertinent parameters are listed in Table 1. Under these conditions in a conventionally configured amine unit with 10 trays in the absorber, the unit is simulated to produce a 55.7 mole% H₂S acid gas (wet basis) with 135 ppmv H₂S leak from the absorber. With only six trays the absorber is on the verge of breakthrough but the H₂S in the acid gas stream is predicted to be approximately 65%. One might build a 10 tray tower with solvent feed nozzles onto trays one, three and five to take possible advantage of better treating with fewer trays. However, one is unlikely to build a six tray tower so 10 trays are taken as the standard.

For the simple HIGHSULF flowsheet shown in Figure 2, the fraction of acid gas recycled from the regenerator condenser back to the absorber was varied from 50 - 85%. Figure 4a shows the effect of acid gas recycle on the H₂S in the SRU feed and Figure 4b shows how recycle affects the H₂S leak from the absorber itself.

With 75% acid gas recycle, ProTreat simulated that:

- ▶ H₂S in the SRU feed gas rises from 55% (conventional) to 80%.
- ▶ CO₂ drops from 37% to 13.6%.
- ▶ Acid gas flow to SRU drops from 1495 to 1033 m³/hr.
- ▶ H₂S to incineration rises only from 135 to 250 ppmv.

Figure 4a shows that the H₂S content of the SRU feed gas is almost a linear function of the percentage recycle. Figure 4b shows that although at 80% recycle the absorber is starting to exhibit breakthrough, the H₂S leak below this recycle level is smoothly responsive to recycle rate and can be readily controlled. As already noted, if 250 ppmv H₂S is too high, it can sometimes be significantly reduced by using a stripping promoter or one of several specialty amines developed by amine vendors specifically for this purpose. However, the efficacy of stripping promoters is very much dependent on the particulars of the specific case and sometimes they do not deliver as advertised. This is an area in which a good, reliable, soundly based in science process simulation tool such as ProTreat is essential to making the right decisions.

It should be mentioned that the HIGHSULF strategy works with any selective amine. This includes not just MDEA, but triethanolamine (TEA) and the hindered amines as well. All these amines can be made to perform with much higher apparent selectivity when a HIGHSULF line is in place. In addition, selectivity depends on the type of tower internals used, and packing often outperforms trays; hence, the results reported

here may be improved even further if the absorber is packed with the right packing.

When the simple HIGHSULF circuit having the HIGHSULF line and tail gas combined into a single feed is replaced with a two feed absorber setup as in Figure 3 (tail gas feed beneath tray seven), the results can be slightly improved. As Figure 5 shows, at approximately 80% recycle the H_2S leak has reached 280 ppm, and H_2S in the SRU feed is simulated to be nearly 85%. Bearing in mind that this absorber now has two rather large gas feed nozzles with an attendant potential problem with achieving good vapour distribution beneath a mid column tray, there is probably insufficient benefit to recommend this approach over the basic HIGHSULF scheme.

Conclusion

In a typical TGTU, ProTreat simulation shows that the use of HIGHSULF technology will bring benefits to SRU feed gas quality along with reduced gas loads on the sulfur plant. The capital cost of installing this technology amounts to low pressure piping and a flow controller, and there are no associated operating costs. Benefits include H_2S rising from concentrations in the 50% range to 80% and SRU gas volume loads decreased by at least 30%. [13](#)

References

1. KHANMAMEDOV, T. K., U.S. Patent Number 5,556,606, 17th September, 1996.
2. KHANMAMEDOV, T. K., U.S. Patent Number 5,718,872, 17th February, 1998a.
3. KHANMAMEDOV, T. K., U.S. Patent Number 5,716,587, 10th February, 1998b.
4. KHANMAMEDOV, T. K., NPRA Q&A Answer Book, V. Energy & Environmental Management, Atlanta, GA, p.14, 1998c.
5. KHANMAMEDOV, T. K., National Meeting of Am. Chem. Soc., San Diego, CA, 2000.
6. KHANMAMEDOV, T. K., U.S. Patent Number 6,506,349, 14th January, 2003.
7. KHANMAMEDOV, T. K., Canada Patent Number 2,204,351, 17th September, 2002.
8. KHANMAMEDOV, T. K., PCT/US1995/013768 26 October, 1995.
9. KHANMAMEDOV, T. K., WEILAND, R. H., 'Upgrading Acid Gas Streams', Hydrocarbon Engineering, November, 2008.
10. PALMER, G., Canada Patent Number 2461952, 25 September, 2005.
11. PALMER, G., U.S. Patent Number 7,147,691, 17th December, 2006.
12. WEILAND, R. H., KHANMAMEDOV, T.K. 'Selecting an Acid Gas Enrichment Flow Sheet', Sulphur, in press, 2010.

Note

ProTreat is a trademark of Optimized Gas Treating, Inc., HIGHSULF is a trademark of TKK Company.

Table 1. Parameter values used for ProTreat process simulation

Absorber	Solvent		
Tray type	Valve	Amine	MDEA
Number	10	Strength, wt%	45
Passes	2	Flow, m ³ /hr	340
Weir height, mm	50	Temperature, °C	40
Flood, %	70		
Pressure, kg/cm ² (g)	0.25	Gas	
		CO ₂ , mole%	22.602
Regenerator		H ₂ S, mole%	1.845
Tray type	Valve	N ₂ , mole%	68.650
Number	30	H ₂ , mole%	6.903
Passes	2	Water, % saturated	100
Weir height, mm	50	Flow, m ³ /hr	30 000
Flood, %	70	Temperature, °C	37.8
Pressure, kg/cm ² (g)	1.0		

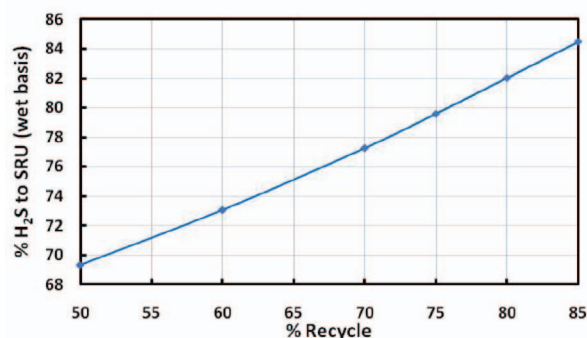


Figure 4a. Improving TGTU amine unit performance with basic HIGHSULF, SRU feed quality.

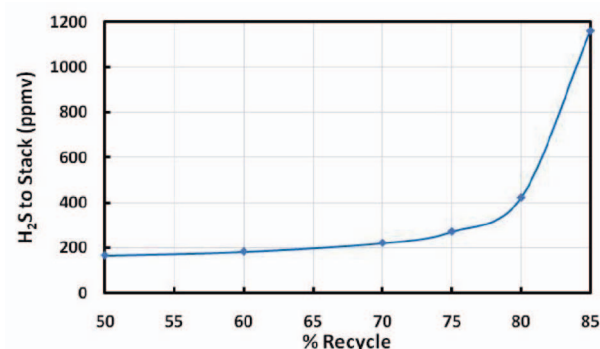


Figure 4b. Improving TGTU amine unit performance with basic HIGHSULF, H₂S leak to incineration.

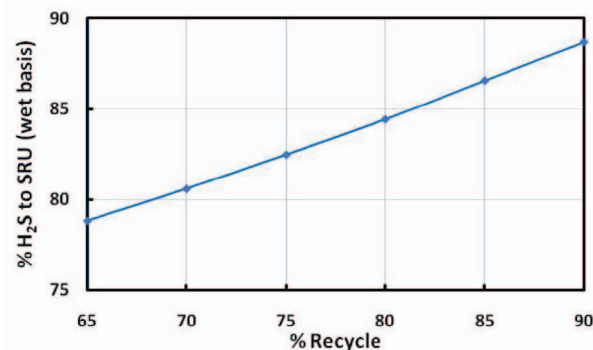


Figure 5a. HIGHSULF with two absorber column feeds, SRU feed quality.

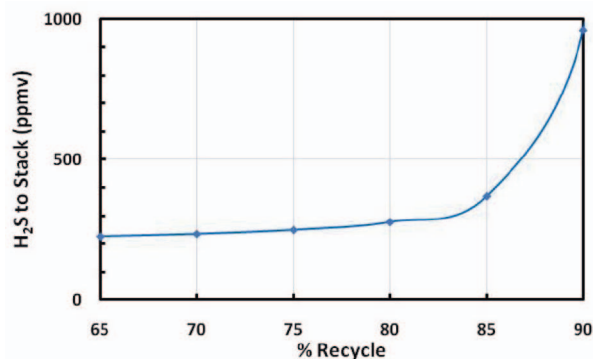


Figure 5b. HIGHSULF with two absorber column feeds, H₂S leak to incineration.