

THERE ARE MORE ROADS THAT LEAD TO ROME, WHICH IS THE BEST ROUTE FOR YOU?

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INTRODUCTION

In our modern society the need for energy is still increasing in a rapid pace, with expectations that hydrocarbon fuels production will have to almost double in the next thirty years. However, the easy to process sources are getting more and more depleted, whereas the new to develop fields are getting increasingly more sour and are going to be build on more and more remote locations.

On the other hand, the demand for clean technology with limited emission of sulfurous components is getting stronger and stronger, with new and very tight emission limits being forced by international organizations such as the Worldbank.

In this paper several examples will be shown, which combine state of the art acid gas removal techniques with minimal environmental impact. It will be shown that for the selection of the gas treating technology the removal of H₂S and CO₂ are only marginally determining the selected technology. More often the technology selection is determined by the requirement to remove trace components such as mercaptans and COS.

Once the acid components are removed from the main gas stream the processing of the acid gas is another challenge. The latest developments in acid gas processing with lean acid gasses and tight emission specs will be discussed. Often a treating solutions selected in an early stage might not be the best fit. Proper evaluation and screening of different options and technologies can decide on a case to case bases what the overall best solution is.

Finally, the synergies that can be found between acid gas removal and sulfur recovery will be stipulated, looking at options to integrate the two system such that both capital and operational cost will be minimized.

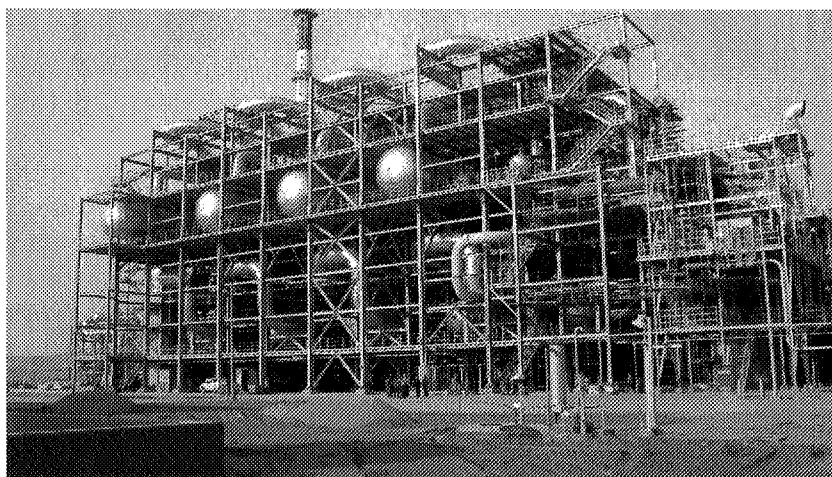
Examples that will be shown are the gas development in Turkmenistan using SUPERCLAUS[®] technology, and the latest development in the Middle East using Sulfinol Technology with a hot flash re-contacting step to enhance the Gas Feed to the Sulfur recovery unit.

Proper evaluation in the right stage of the project will decide success for the project or if additional cost need to be made to make up for not well considered decisions. This paper will try to highlight that it is worthwhile to invest money in proper studies in the feasibility stage of the project. This will be earned back many times in the other stages of the project e.g. when the hardware is being purchased.

CONVENTIONAL TREATING AND SULFUR RECOVERY

As stated in the introduction, trace components quite often determine the line-up of a gas treating facility. In case the contaminants in the raw gas are only H_2S and CO_2 , a conventional treater can be used, consisting of an absorber, a flash stage to recover the hydrocarbons in the rich solvent, and a regenerator to strip the acid components from the solvent. Depending on the volume of gas to be processed, the number of trains can be multiple. A good example of such a line-up is the new gas processing facility that is currently being built in Turkmenistan. The huge gas volume in combination with the transportation limitation made it necessary to install four parallel gas treating trains. However, thanks to clever logistics and smart engineering by the detailed contractor, the total acid gas of the four gas treating units can be processed in two parallel sulfur plants applying the SUPERCLAUS[®] process. These units are designed for a capacity of approx. 1200 tpd sulfur production per train. The expected acid gas composition varies between 37 and 45 % H_2S , and consequently between 50 to 58% CO_2 . With proper preheating a sufficient hot flame temperature is expected to convert most of the heavy hydrocarbons in the SRU.

The picture below gives a good impression of the typical line-up for such a unit. From right to left the thermal stage, the three Claus reactors and the SUPERCLAUS[®] reactor can be distinguished. In the very back, the incinerator and stack can also be seen.



Picture 1: Typical line-up

Case 1: An LNG plant in the Middle East

For one of the first LNG plants in the Middle East, the same strategy with a conventional treater and a SUPERCLAUS[®] was applied. However, since for LNG production there is a tight spec on CO₂ and organic sulfur (mercaptans, COS) in the treated gas the Sulfinol-D process was selected for the main treater.

Sulfinol-D is a mixture of sulfolane, di-iso-propanol (DIPA) and water. Due to its chemical composition it is capable of doing a deep CO₂, COS and H₂S removal (thanks to the amine component) as well as a substantial removal of mercaptans (thanks to the sulfolane). In combination with a molecular sieve unit, routing the regeneration gas of the mol sieves through a special mercaptans absorber, the Sulfinol solvent is capable of doing a one solvent fits all approach delivering on-spec, dehydrated gas to the liquefaction section and routing all sulfur species including the mercaptans to the SRU.

Since in this case the CO₂/ H₂S ratio was fairly high the acid gas to the SRU was of a rather poor quality, with following design composition:

Table 1: Design acid gas composition for case 1

	Vol. %
H ₂ S	23.0
COS	0.01
Mercaptans	0.9
CO ₂	67.0
HC's	4.8
H ₂ O	4.3
Total	100

The sulfur recovery unit was designed to handle this low H₂S containing gas, and considering the high amount of (especially heavy) hydrocarbons, a straight through process had to be selected, with special effort in preheating the air to meet the flame stability/flame temperature criteria.

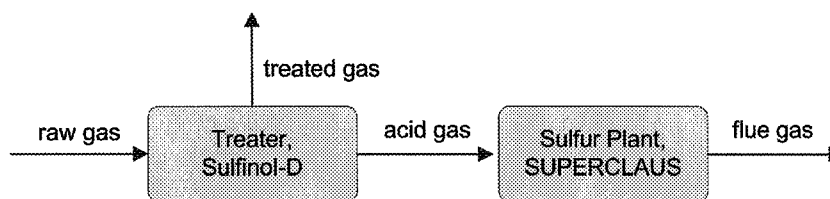


Figure 1: Case 1: Original Line-up

The design SRU recovery in those days was 96 %, which, despite the poor acid gas quality, could be met with a 2 + 1 reactor SUPERCLAUS[®] plant.

Fairly soon after start-up of the complex it became evident that the CO₂/H₂S ratio in the raw gas was even worse than designed for, resulting in the SRU feed gas as shown in Table 2 below.

Table 2: Actual acid gas composition from Sulfinol unit for case 1

	Vol. %
H ₂ S	17.0
COS	0.02
Mercaptans	0.32
CO ₂	76.5
HC's	1.9
H ₂ O	4.3
Total	100

Once it was recognized the acid gas was even leaner than expected, a project was started to add an acid gas enrichment unit in between the Sulfinol unit and the sulfur plant. The addition of this unit is shown in figure 2.

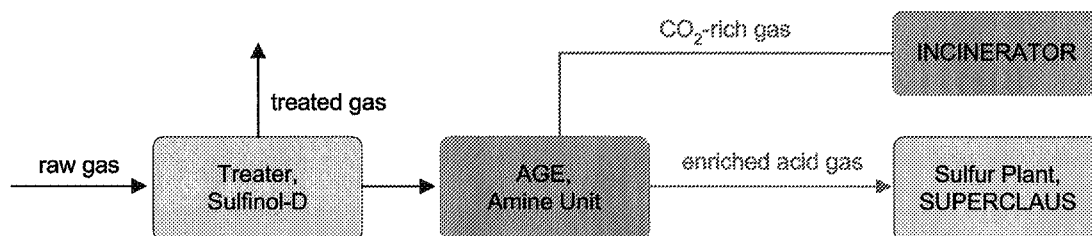


Figure 2: Case 1: Improved line-up with enrichment unit

The acid gas enrichment unit (AGE) uses an aqueous solution of a selective amine (selective meaning preferentially absorbing H₂S over CO₂). The AGE has a similar line-up to a conventional amine unit, and consists of a (low pressure) absorber and a regenerator with associated equipment such as heat exchangers, vessel and pumps. In the absorber virtually all H₂S is absorbed, whereas CO₂ is rejected as much as possible. The CO₂ reject gas still contains some traces of H₂S and will contain most of the mercaptans, since an aqueous solvent has little affinity for these species. The acid gas released from the AGE regenerator is now rich in H₂S and has following typical composition:

Table 3: Enriched acid gas and reject gas composition for AGE case 1

Vol. %	Enriched Gas	Reject Gas
H ₂ S	52.5	100 ppm
COS	0	300 ppm
Mercaptans	0.18	0.35
CO ₂	41.7	92.7
HC's	1.4	2.6
H ₂ O	4.3	4.3
Total	100	100

Since the reject gas still contains some H₂S and the majority of the mercaptans, this gas has to be routed to an incinerator to convert these species to SO₂. This SO₂ emission adds to the total emissions. However, since the acid gas to the SRU has now improved drastically, the recovery on the SRU itself increases from approx. 96 % to better than 99%. With this high recovery, this client was able to still meet the overall recovery requirements.

For this specific case the overall recovery could still be improved with relatively little extra effort. Since an AGE unit is already in place, an obvious improvement would be to convert the SUPERCLAUS[®] reactor to a hydrogenating reactor, and add the reject gas from the enrichment unit to the SRU tail gas. Upon passing the gas over the hydrogenating catalyst, most of the mercaptans will be converted to H₂S, which could subsequently be absorbed in an absorber using the same solvent as in the AGE; this processing scheme is visualized in figure 3.

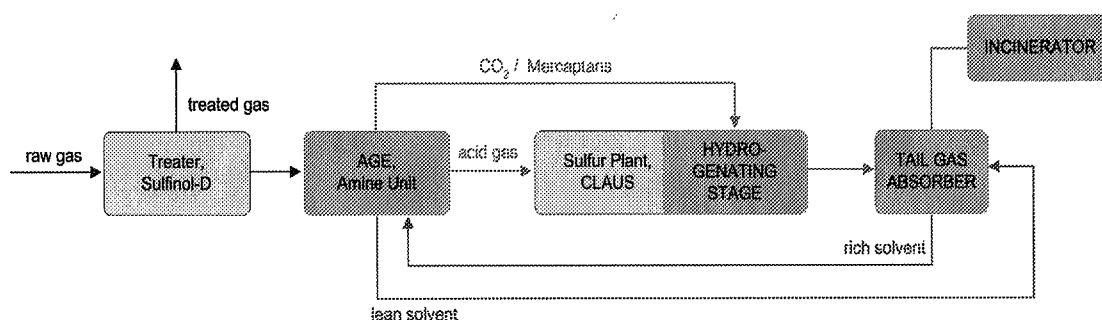


Figure 3: Case 1: Potential line-up for a recovery upgrade

By applying the above scheme, more than 80 percent of the mercaptans will be converted and recovered. Consequently, the overall recovery could be boosted from just above 95 % to better than 99 %.

Case 2: Investment cost reduction by integrated gas enrichment

On another location in the Middle East, a raw gas containing some 7.5 % CO₂ and 4.3% H₂S had to be treated to a pipeline spec of < 4 ppm H₂S and < 1000 ppm CO₂. Initially, a non selective aqueous amine solvent was considered for this plant. The consequence of such a processing scheme would have been a moderate size acid gas removal unit (AGRU), but since all the CO₂ would have ended up in the acid gas feed into the SRU this strategy would have increased the size of the already world scale units. This line-up of a conventional AGRU with a large SRU processing the lean acid gas is depicted in figure 4.

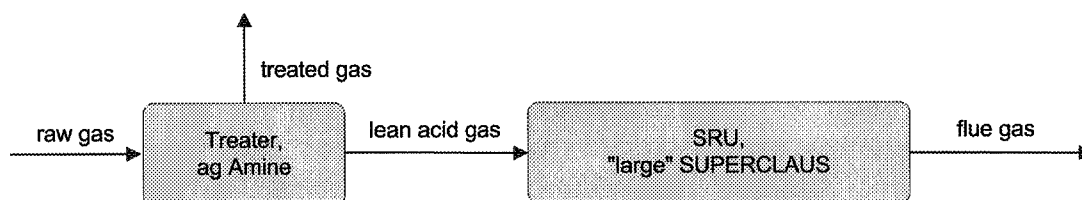


Figure 4: Case 2, Conventional line-up with large SRU

An alternative line-up for this client was to use Sulfinol-M in the main absorber. Similar to Sulfinol-D, Sulfinol-M is a blended solvent, but the amine used is methyl-di-ethanol-amine (MDEA) rather than DIPA. Since Sulfinol-M is basically a fairly selective solvent, the absorption of the CO₂ to meet the spec was quite a challenge, resulting in a tall absorber tower with many trays.

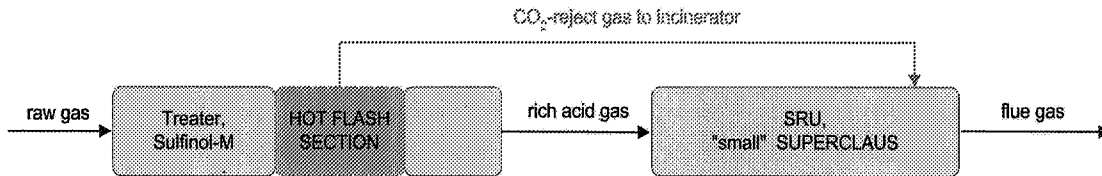


Figure 5: Case 2, Enrichment with hot flash

The acid gas enrichment in this line-up is achieved by heating and flashing loaded solvent from the main absorber. In this flash stage, substantial amounts of CO₂ are released from the solvent, together with some H₂S. By cooling the flash gas and re-contacting the gas at low temperature with cool lean Sulfinol-M the selectivity of the solvent can be used to its maximum, and a nearly pure CO₂ stream containing less than 100 ppm H₂S is obtained, that is routed to the incinerator to convert the H₂S.

Due to the flashing of the rich solvent, the ratio H₂S/CO₂ has improved substantially. As a consequence, the H₂S content in the acid gas to the SRU has now improved from 36% to better than 60%. As a consequence, the SRU can be much smaller, and will achieve a much better recovery. The relative cost saving on the SRU is about 30%, whereas the incremental cost for the AGRU is only about 10 to 15%. With the above line-up a total investment reduction for the combined AGRU/SRU of nearly 20% was achieved.

The better acid gas quality described above does however come at a certain cost. Due to the recontacting, the total solvent flow increased and consequently more heat (steam) was required for the regenerator reboiler. The increased reboiler duty however was only 15%, making this line-up an attractive alternative for this client.

CONCLUSION

Although in many cases the straight forward application of a treater for acid gas removal with a sulfur recovery unit to process the acid gas seems to be an evident choice it is shown in this paper that it often pays off to do a thorough feasibility study. In the study the basis of design shall be challenged, as well as several other parameters like total investment and utility cost, options for integration and overall recovery requirement to ensure the final design has sufficient flexibility. During such a study several ways that lead to Rome will be found, and the client can select the option that suits best his requirements.