Enhanced sulphur recovery from lean acid gases

A preferred acid gas enrichment scheme is combined with two gas-treating schemes to examine the lifecycle cost of a sour natural gas treatment facility

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The exploitation of increasingly difficult natural gas reserves has risen in recent years, requiring the removal of a number of harder to remove sulphur species, as well as H_2S, CO_2 and H_2O. In addition, maximum limits for sulphur content in pipeline gas continue to tighten. As a result, the treating requirements for gas field development projects have significantly increased in complexity, often requiring a combination of process steps and units. As the development of difficult sour gas fields is expected to further increase in the future, strategic integration of various gas-treating process units is necessary to achieve an overall optimised flow sheet with lowest lifecycle cost. The ability to combine technologies and process units in the optimum configuration results in a competitive advantage for addressing challenges and opportunities posed by undeveloped sour gas fields.

In 2010, a study by Black & Veatch compared several alternative Claus sulphur recovery unit (SRU)/tail gas-treating unit (TGTU) configurations for achieving high sulphur recovery and reliable operation from lean acid gas containing high concentrations of carbonyl sulphide (COS) and mercaptans. The lean acid gas stream that was used as the basis for comparison of the process configuration test cases had an H_2S concentration of 25 mole% and an organic sulphur concentration of 1 mole%. The study noted that a lean acid gas stream such as this could be produced from sweetening natural gas with a high COS/mercaptan content and affirmed that, at such a low H_2S concentration, reliable Claus unit operation can be difficult.

The 2010 study considered the use of the acid gas enrichment (AGE) process to increase acid gas H_2S concentration, as a means to alleviate the problems associated with the lean acid gas feed to the Claus SRU/TGTU. It also addressed the fact that the conventional AGE processing scheme cannot achieve high sulphur recovery when COS and mercaptans are present, due to the fact that selective treating solvents commonly utilised for acid gas enrichment do not absorb these organic sulphur species and allow them to slip to the incinerator. Several acid gas enrichment processing schemes were compared, and it was concluded that when acid gas COS/mercaptan levels are high enough to reduce sulphur recovery with conventional acid gas enrichment below an acceptable level, an alternative enrichment design configuration should be considered.

The purpose of the previous study was to compare alternative acid gas enrichment processing schemes for a given lean acid gas stream composition and flow rate, but not to consider the impact that the upstream acid gas removal unit (AGRU) solvent selection can have on the acid gas quality. However, in most situations, it is important to consider the overall sour gas treatment flow scheme rather than simply evaluating the acid gas processing in isolation, as synergies often exist between the various processing units (AGRU/AGE/SRU/TGTU) that provide opportunities for optimisation of the overall flowsheet.

Sour natural gas feed stream used for comparison of test cases

Component	Sour natural gas, lbmoles/hr	Sour natural gas, mole fraction
H_2O	10.63	0.126
CO_2	784.69	9.300
H_2S	270.00	3.200
N_2	421.88	5.000
C1	6618.37	78.440
C_2	210.94	2.500
C_3	101.26	1.200
iC_4	4.21	0.050
C_4	4.21	0.050
iC_5	1.26	0.015
nC_5	1.26	0.015
C_6	3.37	0.040
CH_4S	4.06	0.048
C_2H_6S	1.34	0.016
Total	8437.47	100.000
Temperature, ° F	95	
Pressure, psia	870	

Table 1

Treated gas specifications

Gas stream	Specification	Value
Sales gas	H_2S, ppmv	<5
	Total sulphur, ppmv	<20
	CO_2, mole%	<1.0
Fuel gas	H_2S, ppmv	<100
Tail gas ex-TGTU absorber	H_2S, ppmv	<250

Table 2

Test cases for comparison

Test case	Description
1	Sulfinol-X main gas treating, conventional SRU/SCOT1 using MDEA
2	Sulfinol-X main gas treating, SRU/SCOT using Sulfinol-M acid gas enrichment and tail gas treating, routing of enrichment absorber overhead to SCOT
3	Sulfinol-M main gas treating with integrated enrichment step and tail gas absorber, conventional SRU/SCOT using Sulfinol-M, routing of enrichment absorber overhead to SCOT

Table 3

Test case process configurations

Test case	AGRU solvent	AGE solvent	TGTU solvent	AGE overhead routing
1	Sulfinol-X	–	MDEA	–
2	Sulfinol-X	Sulfinol-M	Sulfinol-M	To TGTU, per Case 4 from 2010 article
3	Sulfinol-M	Sulfinol-M	Sulfinol-M	To TGTU, per Case 4 from 2010 article

Table 4

This article compares three different Sulfinol AGRU options for development of the overall flow scheme for treatment of a sour natural gas stream containing significant quantities of organic sulphur (methyl and ethyl mercaptan). Although COS was an additional organic sulphur compound considered in the 2010 study, it would typically not be present in acid gas from the overhead of a chemical amine solvent or hybrid chemical/physical solvent regenerator. This is primarily due to the fact that absorbed COS is hydrolysed to H_2S and CO_2 in the solvent regeneration step of the AGRU. All Sulfinol solvents remove COS to a large extent in the main absorber of the AGRU. With Sulfinol-X, deep removal of COS can be achieved due to the presence of piperazine, which enhances COS hydrolysis. With Sulfinol-M, most of the COS would be absorbed due to the larger number of trays employed. Since Sulfinol is a hybrid chemical/physical solvent, for the reasons described above, COS captured in the absorber will not be present in the acid gas. Therefore, it is anticipated that the small variations of COS in the sales gas and treated flash gas would not be a differentiator between the three cases studied in this article; hence, COS has been omitted from the analysis.

The resulting acid gas from each AGRU configuration is processed utilising some of the acid gas treatment schemes presented in the 2010 article. The optimum configurations, in terms of relative Capex and Opex, are presented.

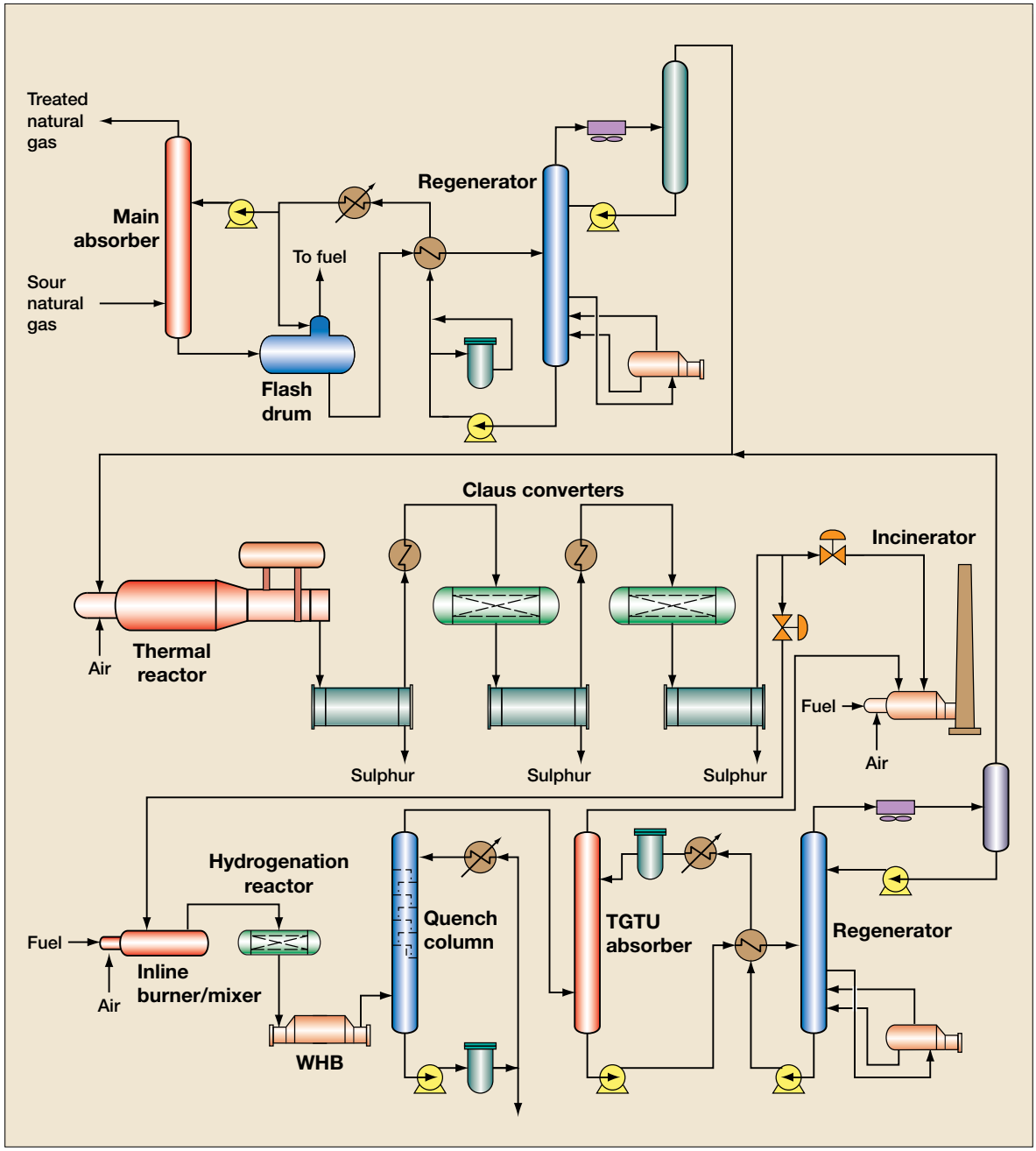

Figure 1 Case 1 process configuration: Sulfinol-X gas treating with conventional SRU/SCOT

Test cases

The sour natural gas stream used for comparison of the various process configuration test cases is shown in Table 1. Sulphur content is 96.1 t/d. About 2% of the acid gas sulphur is present as mercaptans; therefore, recovery of mercaptan sulphur is important if high sulphur recovery is to be achieved.

The treated gas specifications used for the comparison test cases are shown in Table 2. The specifications considered are typical for pipeline-quality natural gas. Table 3 and Table 4 describe the three process configuration test cases compared in this article, each of which is illustrated in Figures 1–3.

The Case 1 process configuration is shown in Figure 1. Sour natural gas is processed in a Sulfinol-X AGRU, producing a

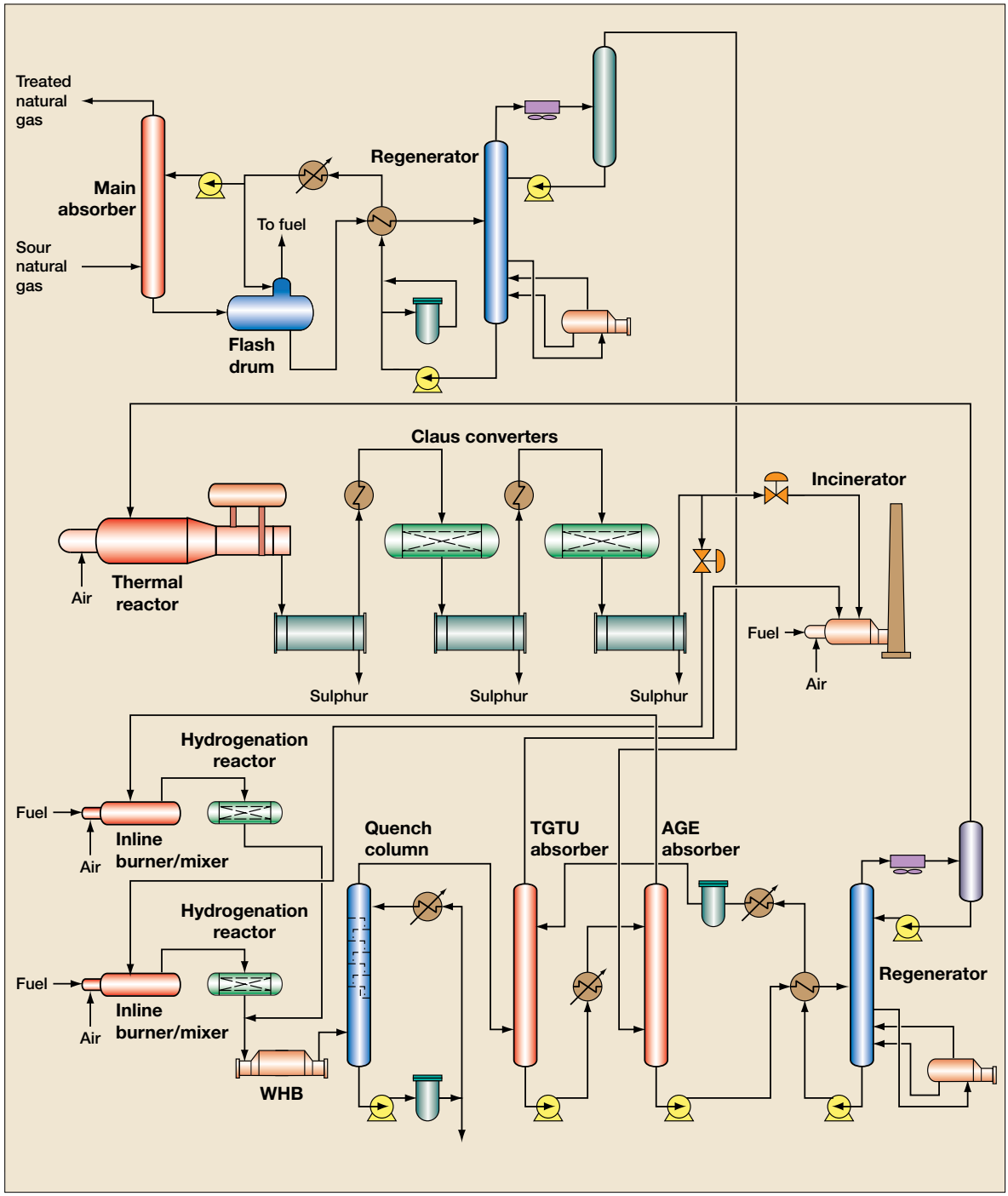

Figure 2 Case 2 process configuration: Sulfinol-X gas treating with SRU using enrichment, enrichment absorber overhead routed to SCOT

lean acid gas stream containing H_2S and mercaptans. Sulfinol-X technology employs piperazine accelerator in addition to MDEA, sulpholane and water. This solvent formulation meets both low H_2S and CO_2 specifications, as well as low specifications of trace sulphur species (such as mercaptans, COS and organic sulphides). The Sulfinol-X unit has a standard configuration consisting of a main absorber, hydrocarbon flash vessel with associated

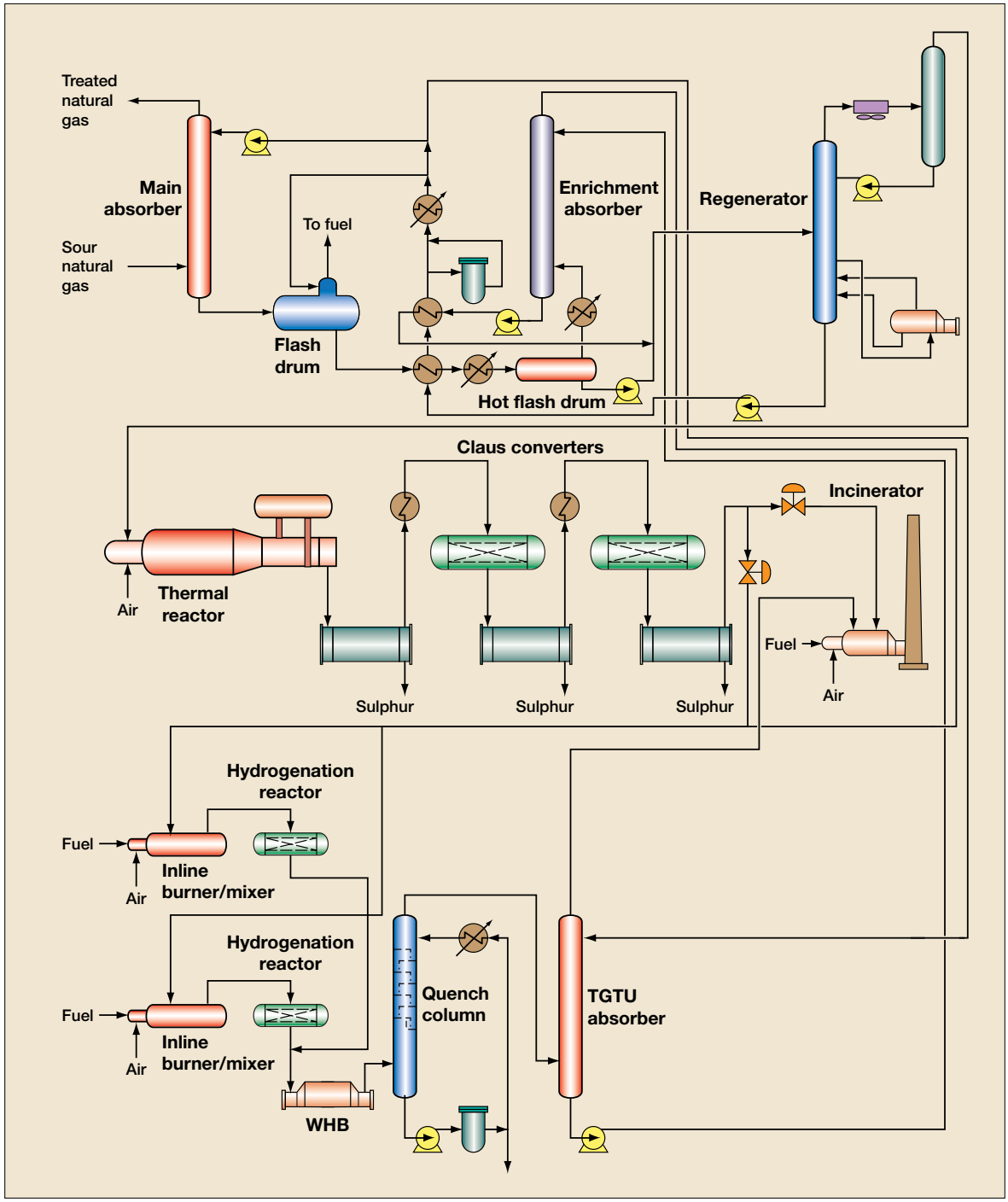

Figure 3 Case 3 PFD: Sulfinol-M gas treating with integrated enrichment step and tail gas treating, enrichment absorber overhead routed to SRU/SCOT

absorber and a regeneration section. The hydrocarbon flash minimises co-absorbed hydrocarbons in the acid gas. The lean acid gas stream from the AGRU regenerator is processed in a conventional two-bed Claus SRU. SRU tail gas flows to an MDEA-based Shell Claus Offgas Treatment (SCOT)1 TGTU, where residual sulphur species in the SRU tail gas are converted to H_2S, which is subsequently removed in the downstream TGTU absorber.

The TGTU regenerator regenerates the rich MDEA solvent, and the overhead from this tower is routed to the front of the SRU for the recovery of sulphur in this stream.

Case 1 represents a conventional base case to compare with Cases 2 and 3. The Case 1 AGRU produces a lean acid gas containing nominally 25 mole% H_2S and 0.5 mole% mercaptans, an acid gas stream similar to that used for comparison of the test cases explored in the 2010 article, with the absence of COS. As explained in the 2010 article, acid gas at or below this concentration makes sustainable Claus performance difficult due to a low thermal reactor temperature and acid gas flame instability. Cases 2 and 3 utilise enrichment to increase acid gas strength for improved Claus operation.

The Case 2 process configuration is shown in Figure 2. Sour natural gas is processed in a Sulfinol-X acid gas removal unit similar to that in Case 1. Acid gas from the Sulfinol-X unit is subsequently processed in an enrichment absorber, which absorbs H_2S from the acid gas using Sulfinol-M solvent. Sulfinol-M technology employs MDEA, sulpholane and water, without piperazine, as is the case with Sulfinol-X. This results in AGE and TGTU absorbers, which remove H_2S and mercaptans while minimising CO_2 absorption. Reduced CO_2 solubility is desirable in the AGE and TGTU absorbers to prevent excessive CO_2 flow through the SRU and TGTU, which increases their size. AGE absorber overhead gas, containing most of the CO_2 in the acid gas as well as other components not absorbed by the Sulfinol-M solvent, flows to the TGTU hydrogenation reactor rather than to the incinerator, similar to Cases 4A, 4B and 4C presented in the 2010 article. Routing the AGE overhead to the hydrogenation reactor allows conversion of the mercaptans in this stream to H_2S, for absorption in the downstream TGTU absorber, which also employs Sulfinol-M solvent. Concentrated acid gas flows from the Sulfinol-M regenerator to the SRU/TGTU for sulphur recovery.

Routing of an enrichment absorber overhead stream to a TGTU was patented by Shell in 1982. This feature is crucial to achieving high sulphur recovery efficiency when acid gas for enrichment contains sulphur species other than H_2S. With conventional acid gas enrichment, these other sulphur species are not absorbed using selective treating solvents and therefore flow unrecovered to the incinerator. Routing the enrichment absorber overhead to the TGTU allows conversion of these other sulphur species to H_2S, which can be recovered in the TGTU absorber. In order to avoid premature ageing of the hydrogenation catalyst due to the presence of heavier hydrocarbons, two parallel hydrogenation catalyst beds are employed, one for the main Claus tail gas and one for the AGE overhead gas. This is a deliberate deviation from the 2010 study, which considered only a single hydrogenation reactor for all cases, which routed AGE overhead gas through the TGTU. The reason for the inclusion of parallel hydrogenation reactors is to restrict the risk of contamination/premature ageing to the AGE overhead reactor, which is the smaller of the two. If the need for premature change-out of the catalyst in this reactor arose, it would not result in significant losses in overall sulphur recovery efficiency.

It should be noted that the Sulfinol-M solvent circulation system is integrated between the AGE and TGTU absorbers similar to the Case 4C configuration in the 2010 study; 100% of the semi-rich solvent from the TGTU absorber is cascaded to the AGE absorber. Case 4C was the optimal case from the 2010 article, hence this configuration was selected without further analysis of Case 4A or 4B configurations in this evaluation.

The Case 3 process configuration, which integrates acid gas enrichment within the AGRU, is shown in Figure 3. Sour natural gas is processed in a Sulfinol-M AGRU and the resulting acid gas is processed in a conventional two-bed Claus SRU. The Sulfinol-M AGRU contains an enrichment step, which consists of an additional hot flash vessel and an enrichment absorber. In this enrichment section, rich solvent is heated and flashed at reduced pressure. The CO_2-rich flash vapour flows to an enrichment absorber, where lean Sulfinol-M solvent absorbs H_2S and some mercaptans. The enrichment absorber overhead flows to a separate hydrogenation section of the TGTU, for conversion of mercaptans to H_2S, similar to the Case 2 flowsheet. Also similar to Case 2, the Sulfinol-M solvent circulation

system is integrated between the AGE and TGTU absorbers, as per the Case 4C configuration in the 2010 study. Case 3 employs a single regenerator for regeneration of the Sulfinol-M solvent from all three absorbers. Concentrated acid gas flows from the Sulfinol-M regenerator to the SRU/TGTU for sulphur recovery.

Compared with Case 2, Case 3 has one solvent system instead of two, which eliminates one regenerator and reduces the equipment count in the solvent storage and drain systems, as well as reducing operational complexity. The formulation of Sulfinol-M allows this solvent to be used both for the selective and non-selective removal of H_2S in the presence of CO_2, depending on the process conditions. While Sulfinol-M cannot reach the LNG-like deep CO_2 removal specification that can be achieved with Sulfinol-X, the specification of <1 mole% CO_2 selected for this article can be easily achieved.

Comparison of sulphur recovery efficiency

The overall sulphur recovery for each of the test cases is given in Table 5. The H_2S removal and sulphur recovery steps in each case have been modelled on a consistent basis. As a result, differences between cases reflect their particular process characteristics, without influence from the inconsistencies associated with variations in parameters such as H_2S removal efficiency, reboiler duty or circulation rate.

Overall sulphur recovery reported in Table 5 considers the sulphur balance envelope around the entire gas treatment facility (AGRU/AGE/SRU/TGTU) and includes sulphur lost in the treated natural gas stream, while sulphur recovery of the sulphur complex figures reported in Table 5 considers only the sulphur balance around the sulphur production facilities (AGE/SRU/TGTU). It is important to note that the 2010 study reported sulphur recovery efficiency figures for the sulphur recovery complex only (ie, the second set of figures in the table) and not for the overall gas treatment facility. Furthermore, the sulphur complex recovery efficiency figures reported in the last row of Table 5 should not be used in direct comparison with the recovery efficiency figures reported in 2010 for assessment of solvent performance. This is because the 2010 study considered a lower TGTU absorber overhead H_2S specification than that in the Sulfinol schemes of this study (approximately 180 ppmv versus 250 ppmv, respectively).

All three cases are similar in sulphur recovery efficiency (see Table 5). The sulphur balance for each case is illustrated in Figures 4–6.

Comparison of sulphur recovery efficiency for test cases

Case	1	2	3
HP flash gas to incinerator, lbmol/hr	0.083	0.080	0.031
TGTU H_2S to incinerator, lbmol/hr	0.425	0.410	0.391
TGTU COS to incinerator, lbmol/hr	0.163	0.152	0.143
Pit sweep sulphur to incinerator, lbmol/hr	0.045	0.045	0.045
Total sulphur to incinerator, lbmol/hr	0.716	0.687	0.610
Incinerator stack SO_2, ppmv dry and air-free	266	269	249
Total sulphur in treated natural gas, lbmol/hr	0.043	0.043	0.044
Overall sulphur recovery, %	99.72%	99.73%	99.76%
Sulphur recovery of the sulphur complex, %	99.77%	99.78%	99.78%

Table 5

Comparison of solvent systems

Solvent circulation rates and other solvent system design data for each of the test cases are shown in Table 6.

Solvent flow rate to the main absorber is about the same in all cases, with only a slightly higher requirement for the Sulfinol-M case (Case 3). In Cases 2 and 3, lean Sulfinol-M solvent flows to the TGTU absorber with subsequent cascading of the semi-rich TGTU absorber bottoms to the AGE absorber. Cases 2 and 3 have the same lean solvent flows to the TGTU absorbers and the same semi-rich solvent flows to the AGE absorbers. Thus, Case 2 has essentially the same total solvent flow as Case 3, with the only difference being a minor incremental increase in flow for the Sulfinol-M main absorber in Case 3. Sulfinol-M requires more steam for regeneration than Sulfinol-X; therefore, Case 3 has a higher solvent regeneration steam consumption rate than Case 2. Case 1, because it does not perform acid gas enrichment, has the lowest total solvent circulation and steam consumption rates.

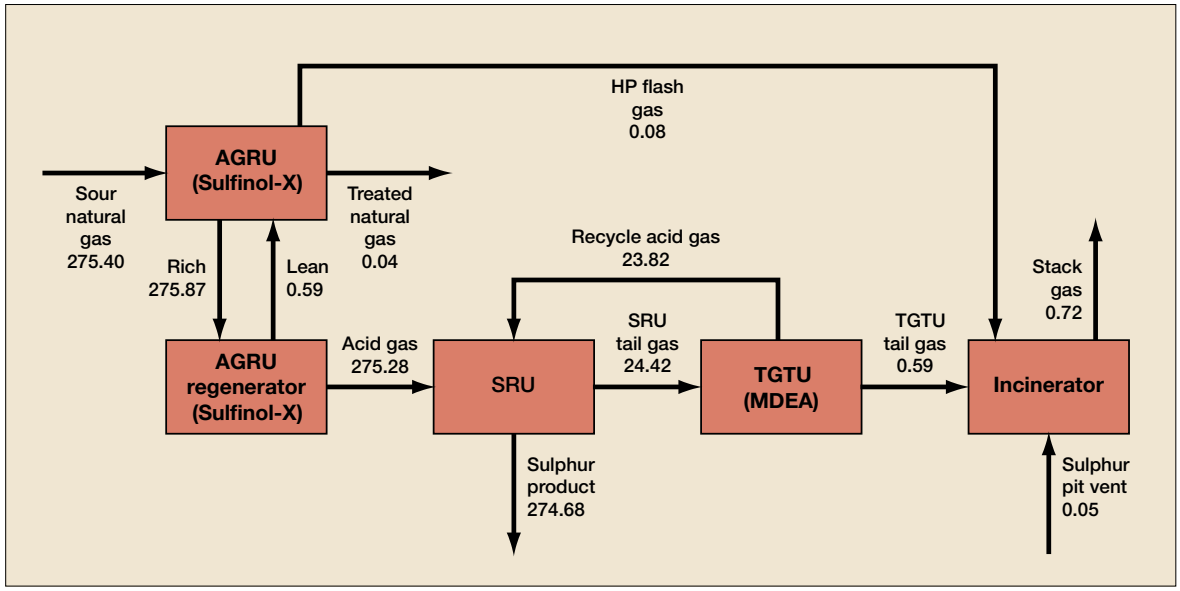

Figure 4 Sulphur balance for Case 1: Sulfinol-X gas treating with conventional SRU/SCOT (sulphur flows in lbmoles/hr)

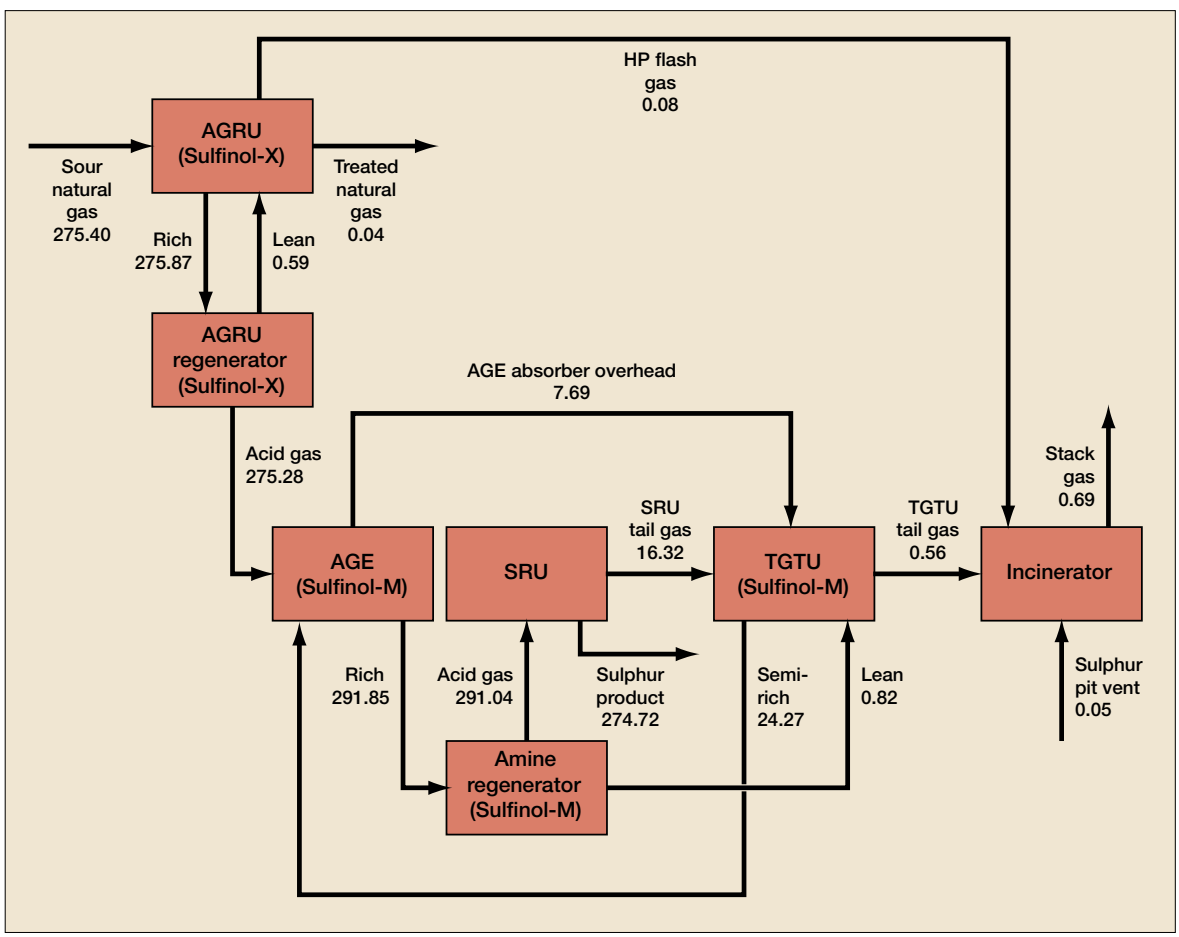

Figure 5 Sulphur balance for Case 2: Sulfinol-X gas treating with SRU using Sulfinol-M enrichment, AGE overhead routed to SCOT

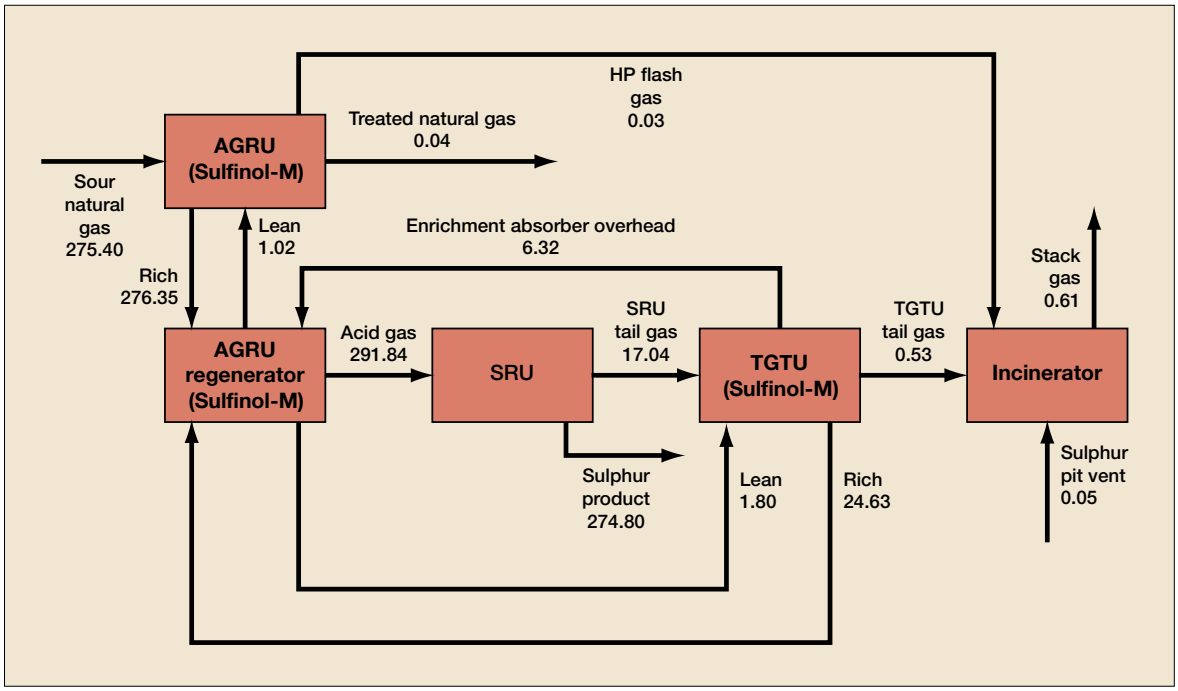

Figure 6 Sulphur balance for Case 3: Sulfinol-M gas treating with integrated enrichment and tail gas treating, AGE overhead routed to SCOT (sulphur flows in lbmoles/hr)

Comparison of SRU/TGTU train size

Most SRU and TGTU equipment sizes are primarily determined by the process gas volumetric flow rate. SRU, TGTU and incinerator volumetric gas rates for each test case are given in Table 7.

Case 1 requires the largest SRU/TGTU train size due to the fact that it processes SRU feed gas with the lowest H_2S concentration; flow rates are similar to those for Case 1 from the 2010 study. Cases 2 and 3 significantly reduce the SRU size because these alternatives minimise CO_2 flow through the SRU by slipping CO_2 from the enrichment step with the use of Sulfinol-M solvent. Since the enrichment absorber overhead is routed to the TGTU in Cases 2 and 3, the TGTU and incinerator sizes are not substantially smaller than the Case 1 size.

Solvent system comparison for test cases

Case	1	2	3
Main absorber			
Lean solvent, gpm	1236	1236	1265
TGTU absorber			
Lean solvent, gpm	325	1015	1012
Inlet H_2S, mole%	1.35	1.31	1.35
Inlet CO_2, mole%	48.43	50.74	49.31
Overhead H_2S, ppmv	248	249	248
CO_2 slip, %	93.6	88.9	88.2
AGE absorber			
Lean solvent, gpm	-	-	-
Inlet H_2S, mole%	-	24.10	19.55
Inlet CO_2, mole%	-	69.62	74.90
Overhead H_2S, ppmv	-	6526	6562
CO_2 slip, %	-	88.1	88.7
Main treating regenerator			
Acid gas H_2S, mole%	24.20	24.10	53.15
Total lean solvent, gpm	1284	1284	2338
Regeneration steam, lb/hr	55 888	55 888	129 387
AGE/TGTU regenerator			
Acid gas H_2S, mole%	28.46	57.22	-
Total lean solvent, gpm	325	1015	-
Regeneration steam, lb/hr	19 221	53 949	-
Total solvent circulation, gpm	1609	2299	2338
Total regeneration steam, lb/hr	75 109	109 837	129 387

Table 6

SRU/SCOT train size comparison for test cases			
Case	**1**	**2**	**3**
SRU tail gas, lbmol/hr	1870	1063	1108
TGTU feed gas, lbmol/hr	1870	1798	1727
Incinerator process gas feed, lbmol/hr	1713	1648	1576

Table 7

Capital and operating cost comparison

Table 8 shows estimated capital and operating costs for each case. Rough order of magnitude capital costs are provided on a US Gulf Coast basis and include engineering, procurement and installation of all process and utility equipment; storage, metering and loading facilities; plus, construction indirects, spares, engineering and commissioning. Items such as owner's costs, land costs, escalation and contingency are excluded. Operating costs are discounted for each year of plant life and are added to capital cost to form each case's net present cost.

The conventional SRU/TGTU arrangement paired with Sulfinol-X treating for Case 1 serves as a benchmark for comparison between the other cases, similar to the way in which the Case 1 conventional SRU/TGTU arrangement of 2010 served as a benchmark for the enrichment cases studied at that time. The Sulfinol-X design of Case 1 represents an optimum approach if considering only the AGRU and not the impact that the resulting lean acid gas has on the downstream SRU. However, as ascertained in the 2010 study, Claus SRU operational difficulty caused by low acid gas H_2S concentration makes the acid gas enrichment achieved in the other cases desirable, in spite of their larger amine units with higher energy consumption.

The Case 2 Sulfinol-X design is essentially the same as Case 1; however, in Case 2, the lean acid gas from the AGRU is enriched to improve Claus SRU operating performance, while also giving the benefit of reduced SRU size. The AGE/SRU/TGTU for Case 2 is similar to Case 4C from the 2010 study, but with Sulfinol-M solvent instead of MDEA. In the 2010 study, the AGE/SRU/TGTU configuration of Case 4C resulted in slightly lower capital cost than the conventional SRU/TGTU configuration of Case 1, which did not include enrichment. Here, Case 2 is slightly higher in capital cost than Case 1. The difference between the results of the 2010 study and the results reported here is explained primarily by the fact that the hydrogenation step was split into two reactors instead of combined into a single reactor, as in the 2010 Case 4 configurations.

The important comparison is between Cases 2 and 3, both of which produce acid gas with a H_2S concentration high enough to ensure stable Claus SRU

Cost comparison for test cases			
Case	**1**	**2**	**3**
Fuel			
Consumption, MMBtu/hr	32.3	26.8	30.6
Yearly cost	1.7	1.4	1.6
Power			
Consumption, kW	1314	1348	1490
Yearly cost	0.7	0.7	0.8
600 psig saturated steam			
Export, lb/hr	19 940	17 481	17 301
Yearly credit	1.4	1.2	1.2
50 psig saturated steam			
Import, lb/hr	58 964	99 383	118 769
Yearly cost	3.5	5.9	7.0
Maintenance and non-utility operating costs			
Yearly cost (10% TIC)	8.7	9.2	9.4
Cost summary			
Total yearly operation and maintenance cost	13.2	16.0	17.6
Total installed cost	86.6	92.2	93.9
Net present cost	171.9	195.6	207.6

Notes: Costs are reported in millions of US dollars.
1. Costs were prepared using the following information:
* $6.00/MMBtu LHV fuel
* $0.064/kWh power
* $6.96/1000 lb 50 psig sat. steam
* $8.31/1000 lb 600 psig sat. steam
* 355 operating days per year
* 15% annual rate of return
* 25-year plant life

Table 8

performance. In both of these cases, the SRU, TGTU and incinerator portions are similar in size and cost; therefore, the difference in capital cost is in the AGRU/AGE/TGTU treating sections. Although Case 3, with its single Sulfinol-M solvent system, requires fewer equipment items in these sections, some of them are larger and therefore slightly more expensive than the equivalent equipment items in Case 2. Sulfinol-M requires more regeneration energy than Sulfinol-X, making the regeneration system larger. Additionally, Sulfinol-M requires a larger absorber in the AGRU.

Despite the fact that this analysis shows a slight preference for Case 2 over Case 3, the capital cost differential is small and quite possibly within the margin of error of the estimates. When operating costs are considered, there is a greater departure between the net present cost of the two options, with Case 2 still emerging as the preferred configuration. However, the small difference in net present cost suggests that a detailed analysis between these two options should be carried out when selecting the preferred scheme for a specific sour natural gas-treating application.

Summary and conclusions

A 2010 analysis by Black & Veatch acknowledged that acid gas enrichment should be considered when upstream AGRU configurations produce lean acid gas with H_2S concentrations lower than that required to achieve reliable Claus SRU operation (<25 mol%), and concluded that alternative acid gas enrichment schemes must be considered to achieve high sulphur recovery efficiency when organic sulphur compounds are present. The preferred enrichment scheme from the 2010 study incorporates recycle of the unabsorbed enrichment absorber overhead organic sulphur to the TGTU for high recovery efficiency, and employs maximum solvent integration between the AGE and TGTU absorbers for minimum capital and operating cost. The preferred enrichment scheme from the 2010 study has been selected in combination with two different Sulfinol gas-treating schemes to examine the lifecycle cost of the entire sour natural gas treatment facility.

In the current analysis, Case 2, Sulfinol-X main gas treating with Sulfinol-M acid gas enrichment and tail gas treating, results in a slightly lower lifecycle cost than Case 3, which is a fully integrated Sulfinol-M approach for main gas treating, acid gas enrichment and tail gas treating. Although the Case 2 lifecycle cost is lower, minimal cost difference between the two schemes suggests that a detailed analysis should be carried out to determine the preferred option for a specific sour natural gas treating application. Additionally, it is important not to overlook the somewhat intangible operational and maintenance benefits associated with operating a single solvent system in Case 3, versus two separate systems in Case 2, when selecting the best configuration to meet a sour gas processor's needs.

Further reading

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