Low cost and reliable sulphur recovery*

By combining a selective oxidation process with a wet gas scrubber technology, Jacobs and MECS have developed a cost effective alternative to amine-based Claus tail gas treating. Sulphur recovery and SO_2 emission reduction requirements can be met at significantly lower capital and operating costs. This article compares the capital and operating costs of a typical 140 t/d SRU with an amine-based TGTU versus a SUPERCLAUS® /DynaWave®.

Selection of an appropriate and cost effective tail gas treatment process to follow existing Claus plants is a challenge facing refiners and natural gas plant owners around the world. New emission regulations, interest in increasing sulphur recovery and processing of higher sulphur crudes are the main drivers.

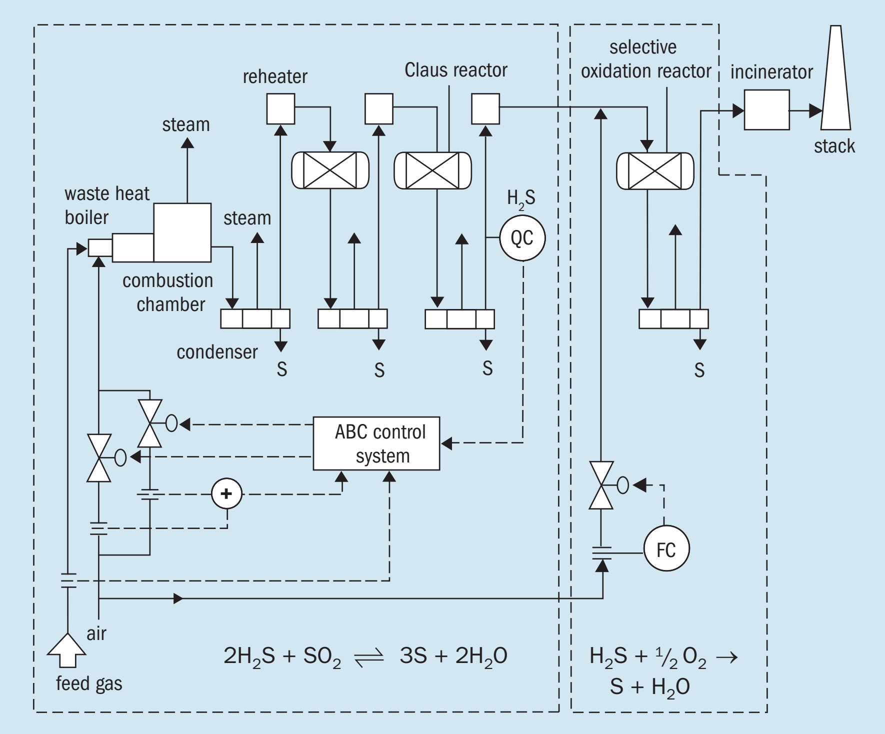
The most common approach is to install an amine-based Tail Gas Treatment Unit (TGTU) however lower installed cost and higher reliability can be achieved by combining two well established processes, Jacobs SUPERCLAUS® selective oxidation process and MECS' DynaWave® wet gas scrubber technology. Owners can lower capital and operating costs significantly with this solution.

SUPERCLAUS®

The SUPERCLAUS® process was developed to catalytically recover elemental sulphur from H_2S containing Claus tail gases to improve the overall sulphur recovery level of the sulphur recovery facility. The process was commercially demonstrated in 1988, and today more than 160 units are under license and over 140 are in operation.

The SUPERCLAUS® process achieves high sulphur recovery levels by suppressing SO_2 formation in the Claus stages, and selectively oxidising H_2S in the presence of oxygen over a proprietary catalyst (see Fig. 1). Claus tail gas from the last Claus condenser is reheated, mixed with air and then enters the SUPERCLAUS® reactor for selective oxidation of the H_2S to elemental sulphur. The formed sulphur is then condensed and recovered by the SUPERCLAUS® condenser. Tail gas from the SUPERCLAUS® stage is typically routed to an incinerator for thermal oxidation of the residual sulphur components and venting of the flue gas to atmosphere via the incinerator stack.

Fig 1: **SUPERCLAUS® process**



Unlike the conventional Claus process, the SUPERCLAUS® process controls to a set H_2S concentration entering the SUPERCLAUS® stage. This is achieved by implementation of Jacobs proprietary control system called the Advanced Burner Control (ABC system), which controls the thermal stage combustion air through combined feedforward and feedback logic. The

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required quantity of combustion air is calculated by measuring the amine acid gas and the sour water acid gas (SWS) flows. The total air demand is then compared with the feedback signal from the air demand analyser (located upstream of the SUPERCLAUS® reactor) to adjust air supply to the thermal stage. The ABC system ensures that the required H_2S content is achieved at the inlet of the SUPERCLAUS® stage for optimum sulphur recovery efficiency of the unit.

SUPERCLAUS® catalyst is not sensitive to excess O_2, nor the presence of SO_2 or H_2O because the selective oxidation reaction is not equilibrium based like the Claus reaction:

Claus reaction

$$2H_2S + SO_2 \leftrightarrow 3S + 2H_2O$$

SUPERCLAUS® reaction

$$H_2S + \frac{1}{2}O_2 \rightarrow S + H_2O$$

SUPERCLAUS® is compatible with conventional SRU designs that properly destroy ammonia present in the SWS feed gases with no added risk to ammonia salt deposition. Close to 50% of the SUPERCLAUS® installations in the world are effectively operating in ammonia processing Claus units.

SUPERCLAUS® is a non-cyclic process that has repeatedly shown simplicity of operation, high online reliability, and sulphur recovery guarantees up to 99.3%.

DynaWave® reverse jet scrubber

DynaWave® is a unique wet gas scrubber technology which offers a number of advantages in the SRU application. The most important challenges in the SRU scrubber application are turndown, the need for a high liquid to gas (L/G) ratio, and the requirement for oxidation. An SRU tail gas scrubber must be able to handle a varying range of inlet flow conditions and inlet SO_2 concentrations which occur during the critical stages of startup, shutdown and malfunction (SSM). Oxidation of the liquid effluent may be required in order to reduce chemical oxygen demand (COD) to levels acceptable to wastewater treatment facilities.

Wet gas scrubbers circulate a liquid reagent which absorbs SO_2. The liquid-to-gas (L/G) ratio is a key process parameter for a scrubber, and must be high enough in the SRU application to fully quench the hot process gas and absorb the SO_2 without suppressing the pH in the absorber reaction/contact zone. Momentary pH depression in the contact zone can be avoided with high L/G ratios. In general, higher liquid-to-gas ratios will result in higher SO_2 removal efficiencies.

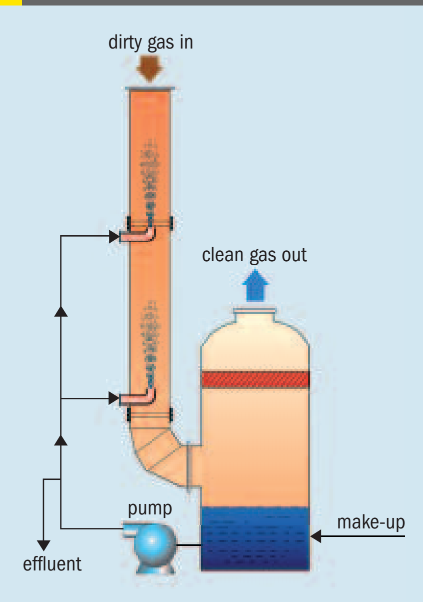
The DynaWave® achieves high L/G and infinite turndown using reverse jet technology. Tail gas from the SRU incinerator, or waste heat boiler, enters the scrubber inlet duct and collides with the circulating scrubber liquor (see Fig. 2). The liquor is injected countercurrent to the gas flow through a large bore, open throat nozzle known as the reverse jet nozzle. The contact zone where the gas and liquor collide is referred to as the froth zone.

The froth zone is an area of high mass transfer and turbulence where quench and acid gas absorption take place simultaneously. The amount of recirculation liquid required to develop the froth zone is calculated based on the maximum process conditions. The liquid flow is constant, which means that when the inlet gas flow decreases, the L/G increases and acid gas removal efficiency increases.

Compared to packed towers, where high liquid flow rates can cause flooding, the DynaWave® can operate at liquid circulation rates which are 5 to 7 times normal packed tower flow rates. This allows the DynaWave® to handle extremely high levels of SO_2, present at SSM when a portion of the SRU must be bypassed.

To react with SO_2, owners prefer to use sodium based reagents such as caustic (NaOH). The reaction between SO_2 and caustic is a strong acid-base reaction and is practically instantaneous. Once the SO_2 is in solution, the reaction proceeds as follows:

Fig 2: **DynaWave® reverse jet scrubber**



$$SO_2\,(v) + NaOH\,(l) \rightarrow NaHSO_3$$

$$SO_2\,(v) + 2NaOH\,(l) \rightarrow Na_2SO_3 + H_2O$$

In most cases, the sodium sulphite/sodium bisulphite salts formed in the above reactions must be further oxidised to sodium sulphate in order to reduce the COD of the scrubber effluent to acceptable levels. The reactions are as follows:

$$NaHSO_3(\text{soluble salt}) + 0.5O_2 + NaOH \rightarrow Na_2SO_4\,(\text{soluble salt}) + H_2O$$

$$Na_2SO_3\,(\text{soluble salt}) + 0.5O_2 \rightarrow Na_2SO_4\,(\text{soluble salt})$$

After the gas exits the inlet duct, it flows through the top portion of the vessel and exits to atmosphere through an integral stack. Before exiting the vessel, the clean, saturated gas flows through a set of chevrons which maximise liquid droplet removal from the gas stream.

The scrubbing liquor falls to the bottom of the scrubber vessel which is used as a reservoir for continuous feed to the recirculation pumps. The vessel also provides the oxidation zone for in-situ oxidation of sulphite salts to sulphate salts.

The DynaWave® wet gas scrubber has been installed in over 300 applications worldwide. The DynaWave® has been designed for 11 SRU tail gas treatment projects in the United States, and installed in seven. The DynaWave® is leading all other SO_2 absorption technologies in total SRU installations.

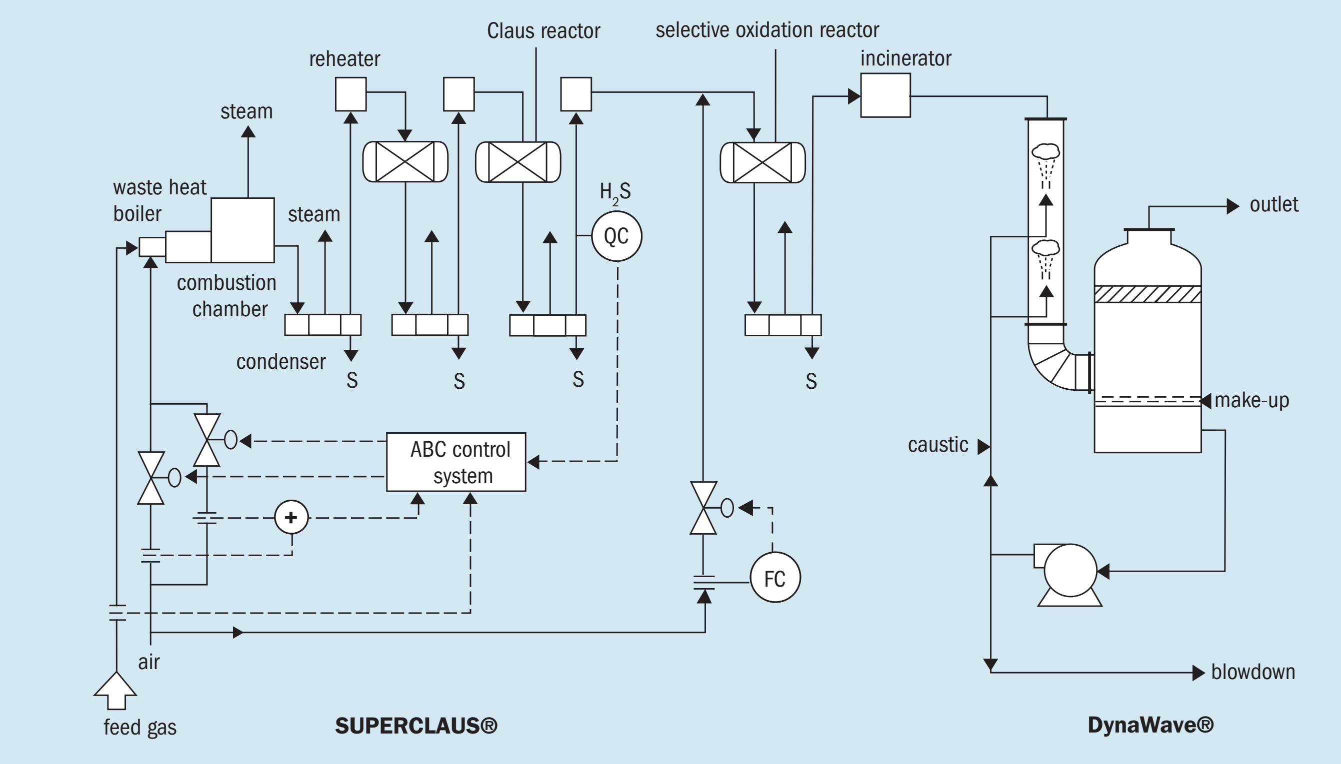
SUPERCLAUS®/DynaWave® process

By combining the SUPERCLAUS® and DynaWave® technologies, the overall system can achieve greater than 99.9% sulphur removal at compelling capital and operating costs. Approximately 99.0% of the H_2S is captured and recovered as elemental sulphur by the SUPERCLAUS® and the remaining sulphur is scrubbed and converted to Na_2SO_4 by the DynaWave®. Figure 3 is a schematic of the combined technologies:

Technology comparison

When comparing SUPERCLAUS®/DynaWave® with an amine-based TGTU, one must fully assess the advantages or disadvantages of each factor, e.g. capital costs, operating costs, number of equipment items, plot foot-print, liquid discharges, chemical requirements, achievable sulphur recovery rate and operability/reliability.

Fig 3: **Combined SUPERCLAUS® / DynaWave® process**



SO_2 emissions

The basis of the comparison assumes an EPA stack SO_2 outlet limit of 50 ppm. Both technology offerings can achieve greater than 99.9% removal of the sulphur and discharge less than 50 ppm SO_2 at their respective outlets.

To achieve this low SO_2 outlet value, the amine-based TGTU normally requires an amine additive to allow for very lean solvent stripping. Also required are additional trays in the towers, as well as increased solvent circulation and reboiler duties.

The SUPERCLAUS®/DynaWave® option achieves low SO_2 emission levels simply through the combination of the two technologies. The SUPERCLAUS® process uses proprietary selective oxidation catalyst to reduce tail gas SO_2 levels to 1,600 ppm. The DynaWave® scrubber takes the incinerated tail gas and reduces its SO_2 content from 1,600 ppm to 50 ppm or less.

Comparative capital costs

A capital cost analysis was performed based on a 140 t/d sulphur recovery facility processing acid gas containing 77 mol-% H_2S and 8 mol-% NH_3. For both the amine-based TGTU and SUPERCLAUS®/DynaWave® process, costs were calculated on a "turnkey" installed basis and include all auxiliary equipment such as waste heat boilers, incinerators, stacks, amine/caustic storage tanks, drain tanks, pumps, scrubbers, etc. Costs for catalyst, chemicals, royalties, etc. were also included for a more comprehensive comparison. No costs were included for sulphur storage or handling facilities.

Table 1 provides a comparison of the relative capital costs. In each case a grass roots installation is assumed and a thermal stage followed by a two-stage Claus unit is included. Normalising the SRU plus amine-based TGTU system cost to a relative value of 185, the combined SUPERCLAUS®/DynaWave® process cost is only 140. This indicates an overall 24% capital cost savings when choosing the SUPERCLAUS®/DynaWave® process.

When a two-stage Claus unit already exists and a TGTU is to be added, the evaluation shows that the SUPERCLAUS®/DynaWave® process provides approximately 53% savings on the capital cost of an amine-based TGTU. Most of the savings are realised through a simpler flow scheme, less complex equipment (fewer towers and pumparounds) and approximately 35% less equipment count.

Savings will depend on the size of the SRU system, however, it is reasonable to assume that the cost advantage of the SUPERCLAUS®/DynaWave® process will hold for a wide range of sulphur loads.

Operational/equipment complexity

Simplicity of operation and equipment complexity are key considerations when choosing a process to install. Compared to an amine-based TGTU, the SUPERCLAUS®/DynaWave® process has 35% less equipment and fewer complex equipment items because complex towers with pumparound systems are not required. The SUPERCLAUS®/DynaWave® process essentially requires a reheater, reactor, sulphur condenser and caustic scrubber. This translates into less maintenance costs, less operational attention and manhours and the probability of a higher on-stream factor if equipment redundancy is equivalent.

Plot footprint

A factor that is sometimes overlooked when comparing technologies is the plot footprint required of the installation. The SUPERCLAUS® /DynaWave® process requires approximately 40% less plot space than the amine-based TGTU. The equipment count is 24 for an amine-based TGTU compared to 16 for SUPERCLAUS®/DynaWave®. The SRU section with two reactors common to both process schemes has 23 pieces of equipment.

Comparative operating costs

Comparative operating costs, i.e. utilities, can be broken down into several categories; power, steam, fuel gas, water, and chemicals. For a 140 t/d SRU, Table 2 provides a utility cost comparison between an amine-based TGTU and a SUPERCLAUS®/DynaWave®.

As Table 2 illustrates, there is approximately 20% operating cost savings with the SUPERCLAUS®/DynaWave® Process.

The SUPERCLAUS®/DynaWave® process typically does not require cooling water because the only cooling needed is to condense the steam from the final sulphur condenser. The amine-based TGTU requires 2,050 gpm of cooling water for a 140 t/d SRU.

With regards to overall fresh water make-up, the SUPERCLAUS®/DynaWave® process will consume 18.5 gpm. This is the amount of water required to quench the gas from the incinerator waste heat boiler plus any effluent discharged from the scrubber system. The amine-based TGTU does not require direct fresh water make-up, but Table 2 takes into consideration water evaporated in the cooling tower.

The SUPERCLAUS®/DynaWave® process requires caustic to react with the 1,600 ppm SO_2 from the incinerator waste heat boiler. The amount of caustic required by the SUPERCLAUS®/DynaWave® process is in the order of 3.5 long t/d, dry basis for a 140 t/d sulphur processing facility. The reaction products result in a 10 gpm liquid effluent stream that contains 10% sodium sulphate which is typically sent to the waste water treatment plant.

The amine-based TGTU process effluent is a 17 gpm waste water stream, containing 20-50 ppm H_2S, which requires further treatment before being sent to the waste water treatment plant.

Table 1: **Technology capital cost comparison** (140 t/d SRU)

Item	Unit description	Relative cost	Approximate savings (%)	Comparison basis
1	2-Stage Claus SRU	100		
2	2-Stage Claus SRU + amine-based TGTU	185		
3	2-Stage Claus SRU + SUPERCLAUS® /DynaWave®	140	24%	Item 3 vs 2
4	Amine-based TGTU alone	85		
5	SUPERCLAUS® / DynaWave® alone	40	53%	Item 5 vs 4

Unique SRU solutions

Sometimes an owner does not require a complete TGTU. This might be the case when the Claus SRU is small or another TGTU technology is already installed. Both SUPERCLAUS® and DynaWave® offer solutions even in this situation.

Reducing Claus unit operating costs

For example, some owners have installed caustic scrubbers, such as the DynaWave®, directly after their Claus units. This has allowed them to meet air permit requirements without installing complete amine-based TGTUs.

When caustic is expensive, the operating costs of an inefficient Claus unit followed by a caustic scrubber can be high. The SUPERCLAUS® process offers a solution with the simple retrofit addition of SUPERCLAUS® catalyst into the third Claus reactor and possibly a new sulphur condenser for the additional heat load generated by SUPERCLAUS®. If the 3rd Claus stage does not exist, then the addition of a new SUPERCLAUS® stage would be required.

SRU process unit redundancy

In the future, process units may no longer be able to exempt emissions excesses during startup, shutdown and malfunction (SSM). Emission levels during SSM are potentially unpredictable. In the case of SRUs with TGTUs, normal emissions can be between 200-1000 ppm SO_2. During SSM, emissions can reach 4,000 to 10,000 ppm SO_2 or even higher, and gas flow rates can fluctuate as well. The technology that follows the SRU must be able to handle this wide range of process variables. As explained previously, one of the major advantages of the DynaWave® scrubber is its capability to handle very wide turndown operations.

New requirements for very low SO_2 emissions

Typical emission requirements for SRUs in the United States range between 50 to 250 ppm. The Air Quality Management District in Los Angeles, California is investigating the feasibility of limiting SO_2 emissions to below 10 ppm. The DynaWave® is a robust and reliable wet gas scrubbing process which can meet these future emission requirements at a reasonably low operating cost. In addition, since many owners will be required to retrofit a wet gas scrubber into an existing facility, the small footprint of the DynaWave® provides the possibility to install this technology where real estate is at a premium.

Table 2: **Utility comparison** (140 t/d SRU)

		Amine-based TGTU		SUPERCLAUS® /DynaWave®	
Utility type	**$/Unit cost**	**Consumption**	**$/Day cost**	**Consumption**	**$/Day cost**
Electric power	$.08/kWh	499 kW	958	485 kW	931
60 psig steam consumed	$4/1000 lb	10,200 lb/hr	979	none	0
60 psig steam produced	$4/1000 lb	none	0	7,500 lb/hr (produced)	-720 (credit)
Fuel gas (incinerator)	$3.50/1000 SCF	14,800 SCFH	1,243	16,600 SCFH	1,394
Fuel gas (heater or RGG)	$3.50/1000 SCF	3,500 SCFH	294	1,340 SCFH	113
Cooling water	$0.10/1000 gal	2050 gpm	295	none	0
Fresh water	$1.30/1000 gal	22 gpm	42	18.5 gpm	35
Amine make-up	$1.40/ lb	55 lb/day	77	none	0
Caustic make-up	$0.175/lb ($350/ton)	none	0	7,721 lb/day	1,351
Total			**$3,888/day**		**$3,104/day**