

# Ideas for better cleanup

Higher sulphur recovery efficiency, lower capital and operating costs, greater flexibility and lower CO<sub>2</sub> emissions are some of the many factors influencing the latest new process concepts and enhanced process designs for Claus tail gas treating. **Lisa Connock** reports on how these objectives are being achieved using the latest technology and catalysts.

## SuperClaus/DynaWave process

Jacobs Comprimo and MECS have combined their respective experience in sulphur recovery and wet gas scrubbing to provide a simpler and less expensive Claus tail gas treating process.

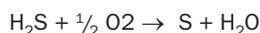
The Jacobs Comprimo SuperClaus<sup>®</sup> process, the incinerator and the MECS DynaWave<sup>®</sup> reverse jet scrubber used in series provide ultra low SO<sub>2</sub> emissions (stack emissions below 50 ppm SO<sub>2</sub>) and an overall sulphur recovery efficiency of over 99.9% (see Fig. 1).

### SuperClaus

The SuperClaus process was developed to catalytically recover elemental sulphur from H<sub>2</sub>S containing gases originating from refinery and natural gas treating plants such as alkanolamine units or physical solvent plants. The SuperClaus process has been in use in industry since 1988 and today more than 150 units are under license and over 140 in operation.

The SuperClaus process consists of a

thermal stage followed by three or four catalytic reaction stages with sulphur removed between stages by condensers. In the thermal stage, the acid gas is burned with a substoichiometric amount of controlled combustion air so that the tail gas leaving the last Claus reactor typically contains 0.5 to 0.9 vol-% of H<sub>2</sub>S. The first two or three reactors are filled with standard Claus catalyst while the last reactor is filled with a special, proprietary catalyst developed for selective partial oxidation of H<sub>2</sub>S directly to sulphur. The reaction occurring over the SuperClaus catalyst is:



The above reaction is a non-equilibrium reaction, and therefore is not limited by an approach to equilibrium. The SuperClaus catalyst is very selective in the formation of sulphur, resulting in limited SO<sub>2</sub> formation. A certain amount of air is injected into the process gas entering the SuperClaus stage and about 98% of the H<sub>2</sub>S present in the gas is converted. Since the final cat-

alytic stage is not equilibrium limited, an overall SRE of 98.8-99.2% can be achieved when preceded by two Claus catalytic stages (basis: at least 60-70 mol-% H<sub>2</sub>S in the acid gas feed). When a third Claus catalytic stage is added, an overall SRE of 99.2 to 99.4% can be achieved.

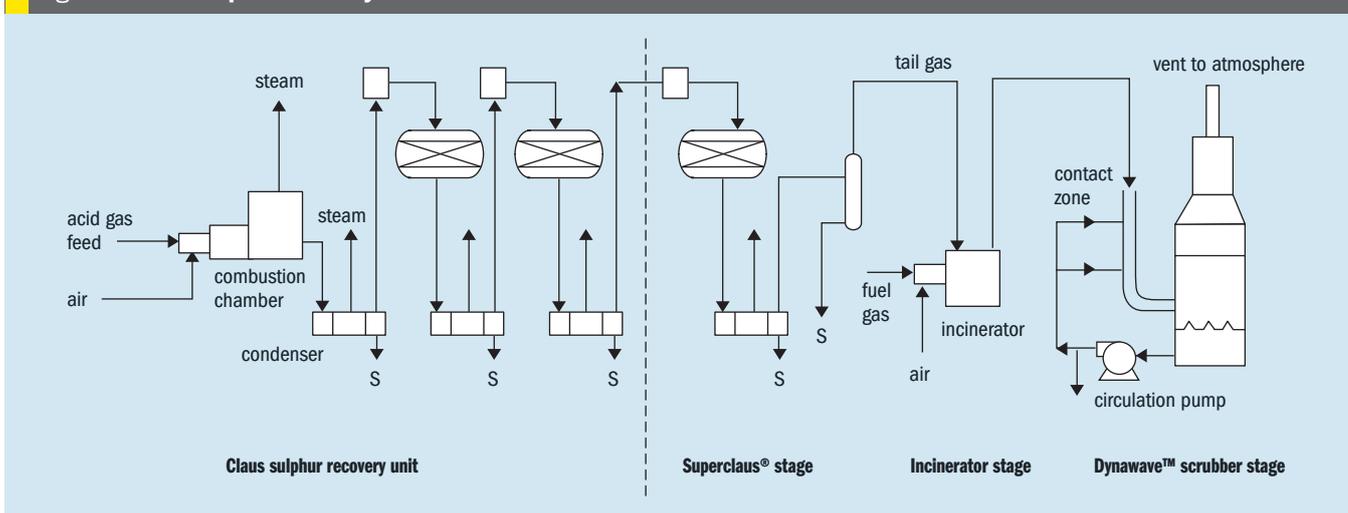
Two main principles are applied in operating the SuperClaus process:

- operating the Claus plant with excess H<sub>2</sub>S to suppress the SO<sub>2</sub> content in the Claus tail gas;
- selective oxidation of the remaining H<sub>2</sub>S by the SuperClaus catalyst selectively converts the H<sub>2</sub>S in the presence of water vapour and excess oxygen to elemental sulphur only.

### DynaWave process

The DynaWave scrubbing process was developed to remove SO<sub>2</sub> from flue gases and vent gas streams in general. The DynaWave wet gas scrubber is a unique open bore, reverse jet scrubber that utilises froth zone technology to perform desulphurisation in a wet gas environment. Since its introduction

Fig 1: Claus – SuperClaus<sup>®</sup>-Dyna Wave<sup>™</sup>



in the 1970s, over 300 DynaWaves have been installed worldwide on various flue gas and process vent streams, both for removal of SO<sub>2</sub> and other components.

For SRU applications, DynaWave is installed after the incinerator and before the stack. In the DynaWave, scrubbing liquid is injected through a non-restrictive jet nozzle counter current to the inlet incinerator flue gas. Liquid containing caustic reagent (NaOH) collides with the down-coming gas to create the froth zone, a region of extreme turbulence with a high rate of mass transfer. Quench, SO<sub>2</sub> removal and particulate removal occur in the froth zone. The clean, saturated gas and charged liquid continue through a separation vessel.

The saturated gas continues through the vessel to mist removal devices. The liquid descends into the vessel sump for recycle back to the reverse jet nozzle. In-situ oxidation of the scrubbing effluent to a benign Na<sub>2</sub>SO<sub>4</sub> solution is achieved by air spargers in the bottom of the separation vessel. This represents a cost saving compared to other scrubbers which require separate oxidation tanks. Sulphites are oxidised to sulphates which can be sent to waste water treatment without increasing chemical oxidation demand (COD) load.

To date, four DynaWave scrubbers have been installed and are in operation on SRU tail gas streams for SO<sub>2</sub> removal, three for Sinclair Refining Co. and one for Marathon Refining Co. All of these DynaWave scrubbers are installed on the tail gas from conventional SRUs with two or three catalytic stages, and which are achieving a sulphur recovery efficiency of about 95-96% in the upstream SRUs. In each case, a waste heat boiler is used to reduce the gas temperature and to produce 450-550 psig steam, and thus recover waste heat from the hot gas stream. However, the cooling or quench step is not required, since the hot incinerator effluent can be handled directly by the DynaWave scrubber. If waste heat recovery is not desired or feasible, the waste heat boiler can be eliminated, thus saving the capital and operating cost of this step.

If a Claus SRU achieves an overall SRE of 95% and a DynaWave scrubber is used to remove the last 5% of the SO<sub>2</sub>, the caustic consumption and operating cost is relatively high. However, if a SuperClaus stage is employed upstream, and a SRE of 99.0% is realised, this leaves only 1.0% of the SO<sub>2</sub> to be removed by the DynaWave stage, and its operating cost is reduced by

about 80%. In most applications, the operating cost of the SC/DW TGPU process is expected to be very competitive with that of an amine-based type TGPU.

The estimated capital cost of the SC/DW TGPU process is projected to be only 60-65% or less of the capital cost of an amine-based type TGPU process.

The SC/DW TGPU process has been selected over a conventional TGPU process for three new 150 long t/d SRUs, each with two Claus stages, followed by a SuperClaus stage, followed by a DynaWave scrubber (using caustic) for the final tail gas cleanup at the Sinclair refinery in Tulsa, Oklahoma. Licensor packages are complete and the project is scheduled for construction in the near future.

Extremely low stack emission limits are being imposed on new sulphur recovery plants in some US locations. In California, stack SO<sub>2</sub> limits less than 50 ppm, even as low as 10 ppm, are possible. The SuperClaus/DynaWave process can be operated to SO<sub>2</sub> emission levels as low as 10 ppm without equipment changes by simply increasing the liquid to gas ratio in the unit, with only a slight increase in caustic consumption.

The typical TGPU process train requires 24 different pieces of equipment compared to 16 pieces of equipment for the comparable SuperClaus/DynaWave process. The smaller equipment count indicates less complexity, lower capital cost, lower maintenance cost and smaller footprint. Flexibility is also important for tail gas clean up. With the SC/DW process the SuperClaus can be temporarily bypassed and the DynaWave scrubber can handle the full Claus tail gas SO<sub>2</sub> load and still maintain the required SO<sub>2</sub> stack limit allowing refiners to meet regulations at all operating conditions.

### **RCTI (Rameshni Catalytic Tail Gas Incineration)**

RCTI (patent pending) is one of the latest technologies developed by WorleyParsons as an alternative to the conventional WorleyParsons BSR-Amine tail gas unit. It is a tail gas incineration process that has the advantage of operating at lower temperatures, which can provide savings in reduced fuel gas costs.

The conventional thermal oxidiser/incineration scheme operates at high temperatures requiring high quantities of fuel and thus generating high CO<sub>2</sub> emissions.

WorleyParsons offers the catalytic Selectox™ oxidiser as an alternative to reduce fuel consumption and reduce CO<sub>2</sub> emissions.

Selectox catalyst was developed by WorleyParsons and UOP many years ago for sulphur/TGU applications. It is a rugged, proven catalyst, also suitable for promoting the Claus reaction in combination with in situ oxidation of dilute H<sub>2</sub>S.

The concept of the catalytic Selectox™ oxidiser is to heat the Claus tail gas to meet the required inlet temperature to the reactor. The tail gas feed is heated by indirect heat exchange with HP steam. The temperature required for oxidation is much lower than that of a conventional incinerator. The heated gas enters the reactor and all sulphur compounds are converted to SO<sub>2</sub>.

The stream leaving the reactor is processed in the caustic scrubber where the majority of SO<sub>2</sub> is absorbed by the caustic. The overhead of the caustic scrubber is routed to the conventional incinerator where less fuel will be used to operate the system, and therefore less CO<sub>2</sub> emissions.

The RCTI process consists of low-temperature catalytic reduction of Claus tail gas and subsequent low-temperature oxidation of H<sub>2</sub>S using a selective direct oxidation catalyst such as Selectox™. The tail gas feed is heated indirectly by HP steam or hot oil. Eliminating the reducing gas generator will eliminate natural gas consumption and reduce CO<sub>2</sub> emissions. If necessary, resultant SO<sub>2</sub> is captured by non-regenerable caustic, or a regenerable solvent such as Cansolv.

RCTI uses two proven catalysts – the new low temperature TGU hydrogenation catalyst and the long established Selectox™ catalyst. Compared to other oxidation catalysts, the active components of the Selectox catalyst, bismuth and vanadium, are particularly effective for the gas phase oxidation of H<sub>2</sub>S to SO<sub>2</sub> in the presence of water vapour below about 600°F/315°C. At the proper operating conditions, oxidation of H<sub>2</sub>, CO and NH<sub>3</sub> is minimised while simultaneously suppressing the formation of SO<sub>3</sub>.

The RCTI process consists of three sections. In the first section, tail gas feed from the sulphur recovery unit(s), is heated to the appropriate temperature before entering the downstream reactors. The heating system may be any appropriate heating system such as indirect heating systems, fired reheaters, or any commonly-used type of reheater, such as a steam reheater or a moisture separator reheater (MSR).

The second and the third sections comprise two different catalysts, which can either be installed in one vessel with two separate catalyst beds, or in two separate vessels. Preferably, the catalysts are contained in a single vessel to reduce the capital cost of the overall unit.

The second section of the system is a hydrogenation reactor. The heated gas flows to a catalytic reactor using hydrogenation catalyst of the type commonly employed in the Claus tail gas hydrogenation unit (cobalt-molybdenum hydrogenation catalyst) preferably low temperature hydrogenation catalyst such as those employed in units that treat tail gas from Claus sulphur recovery units.

The catalyst promotes the Claus reaction and shifts CO and H<sub>2</sub>O to CO<sub>2</sub> and H<sub>2</sub>, consumes residual H<sub>2</sub> to further reduce SO<sub>2</sub> to H<sub>2</sub>S and hydrolyses COS and CS<sub>2</sub> to H<sub>2</sub>S and CO<sub>2</sub>.

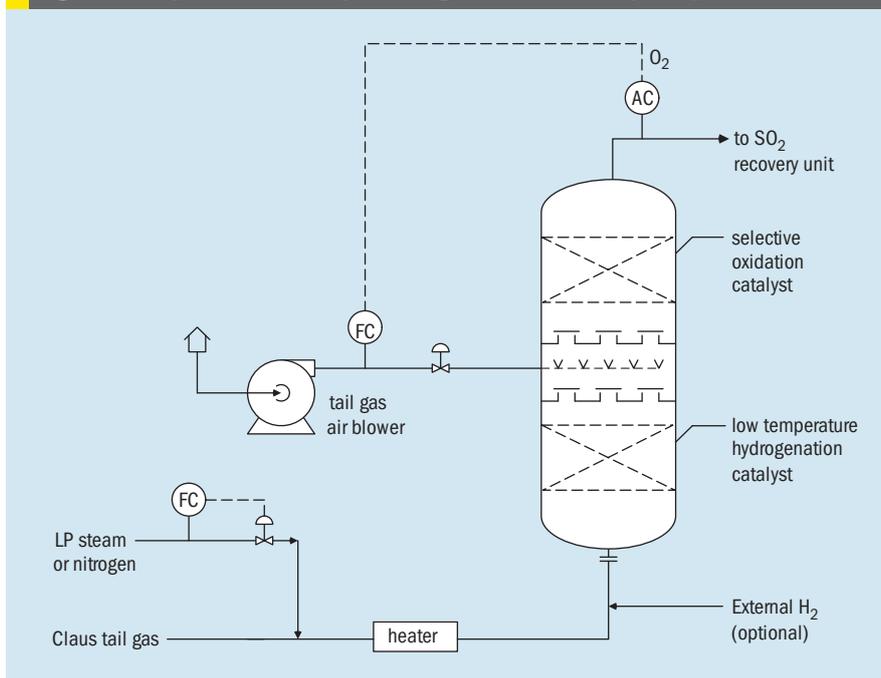
Hydrogen is required in the hydrogenation reactor. The hydrogen is supplied as an external source to the reactor, or if the heating system is a commonly-used BSR reducing gas generator, then hydrogen will be produced or if the sulphur plant operates as off ratio the adequate amount of hydrogen exists in the gas entering the reactor.

The third section is the direct oxidation catalyst reactor. Gas from the first reactor enters the second reactor where external air from a low-head blower promotes the oxidation of H<sub>2</sub>S to SO<sub>2</sub>. A key feature of the process is the utilisation of reaction heat from the first bed to achieve the initiation temperatures necessary for subsequent oxidation.

Different configurations of the RCTI process are available, for example, the outlet stream from the second reactor can be vented to the stack, based on the allowable emission regulations. Alternatively, the outlet of the second reactor is routed to a unit for SO<sub>2</sub> recovery (Fig. 2).

Table 1 shows a heat duty comparison for conventional versus RCTI tail gas treatment.

Fig 2: WorleyParsons catalytic tail gas incineration (RCTI)



### Ammonia destruction in a Claus TGTU

Crude oil from several areas in the world, including Brazil and Venezuela, contains high levels of nitrogen, which results in a very high level of ammonia in the sulphur recovery unit feed. Traditionally, high levels of ammonia have been combusted in the Claus reaction furnace, where the amount of NH<sub>3</sub>, which can be processed, is generally considered to be limited to 30-35% of the total Claus feed on a wet basis. Any additional NH<sub>3</sub> not processed in Claus units is typically converted to ammonium thiosulphate fertilizer, or purified in order to be suitable for marketing or incineration.

WorleyParsons offers a new approach to handling gaseous NH<sub>3</sub> streams – the RAC™ (Rameshni Ammonia Combustion) process for ammonia destruction in a Claus tail gas treating unit.

Ammonia destruction in a Claus tail gas treating unit has several advantages:

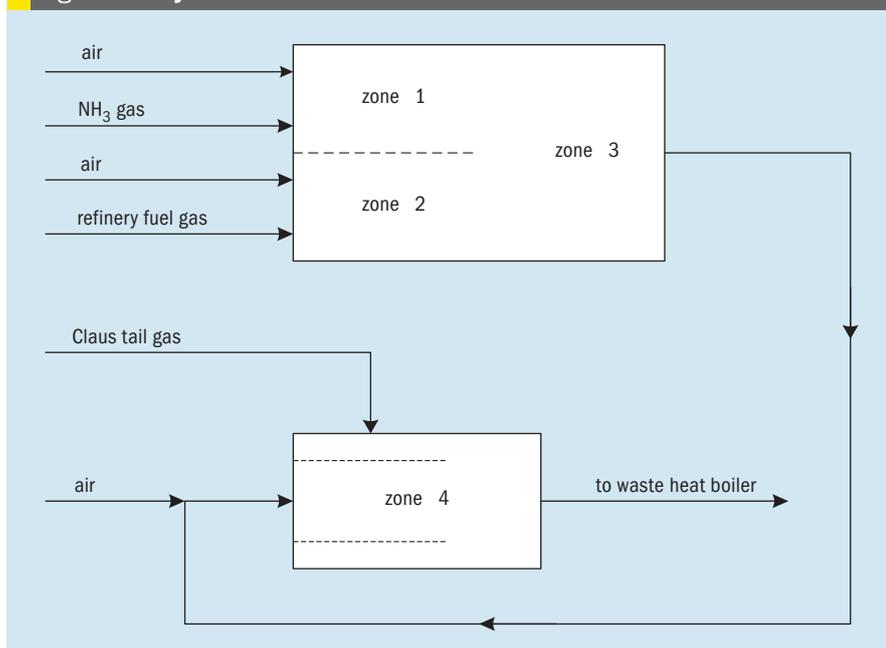
- the sulphur recovery and tail gas unit together have the capabilities of ammonia destruction beyond 30 to 35% for any new or existing Claus unit;
- a proven and established process that does not require any pilot testing;
- flexibility of mode of operation with air only, oxygen-enriched air, or oxygen only;
- plant flexibility for turndown, ability to handle different feeds, and changes in production rate;
- high reliability and easy maintenance;
- reduces plot space with fewer modifications, less impact on downstream equipment for revamp applications;
- no concerns about plugging of downstream equipment;
- no oxygen enrichment required for high ammonia content;
- reduces capital and operating costs compared to alternatives.

This new approach may find applications in many situations. For example, purification

Table 1: Heat duty comparison for conventional versus RCTI tail gas treatment

Heat input	Conventional			RCTI		
	T1 (°F/°C)	T2 (°F/°C)	MMBtu hr	T1 (°F/°C)	T2 (°F/°C)	MMBtu hr
TGU reheat	280 / 138	600 / 316	4.2	280 / 138	450 / 232	2.2
Incinerator	100 / 38	1,100 / 593	8.3	n/a	n/a	0
<b>Total</b>			<b>12.5</b>			<b>2.2</b>

Fig 3: WorleyParsons ammonia destruction in an oxidative CTG unit



facilities may have been installed to produce saleable NH<sub>3</sub> where such markets no longer exist, or elimination of expensive purification steps may be desirable. Also, with bulk H<sub>2</sub>S removal from the NH<sub>3</sub> gas via established processes, it provides an economical means of increasing Claus sulphur recovery capacity or processing greater quantities of NH<sub>3</sub> than otherwise practical. Two variations have been presented depending on whether the associated TGU is reductive or oxidative.

A process description of RAC in a reductive Claus tail gas unit has been reported in *Sulphur 314 and 316*. A process description of RAC in an oxidative tail gas unit is given below.

### RAC in an oxidative TGTU

In an oxidative TGTU scheme, a fuel is typically burned, with excess air, so that subsequent combination of the flue and Claus tail gas streams will result in a net temperature sufficient for thermal oxidation of all combustible sulphur compounds. In some cases the resultant SO<sub>2</sub> can be discharged to atmosphere, but environmental regulations will more typically require that the SO<sub>2</sub> be recovered by an absorption medium. In the latter case the hot tail gas stream will typically be cooled in, for example, a waste heat boiler prior to gas/liquid contact in the absorber.

In this case (Fig. 3) the NH<sub>3</sub> gas is combusted sub-stoichiometrically in zone 1, thus supplanting most of the fuel oth-

erwise required, usually a hydrocarbon gas. The ratio of air to NH<sub>3</sub> gas is automatically adjusted to oxidise most of the NH<sub>3</sub>, while maintaining sufficiently reducing conditions to avoid, or at least minimise, NO<sub>x</sub> formation.

A supplemental fuel, typically a hydrocarbon gas, is combusted with excess air in parallel zone 2 at a rate necessary to achieve the desired temperature elevation of the Claus tail gas stream. When no supplemental heat is required, a minimum fire is preferably maintained to facilitate a prompt increase in the firing rate in the event of NH<sub>3</sub> gas curtailment.

Combustion gases from zones 1 and 2 are combined in zone 3, where residual H<sub>2</sub> and potential CO, H<sub>2</sub>S and other miscellaneous combustibles are thermally oxidised by excess O<sub>2</sub> from zone 2.

Zone 3 effluent gases are combined with the Claus tail gas stream in zone 4 to achieve the net average temperature necessary for the desired oxidation of combustibles, which will typically include H<sub>2</sub>S, S<sub>x</sub>, COS, CS<sub>2</sub> and CO. The temperature required for thermal oxidation will typically be in the range of 425-815°C, depending on prevailing environmental regulations, residence time and the nature and concentration of key combustibles. If necessary, additional combustion air may be injected to supplement residual O<sub>2</sub> in the zone 3 effluent.

A typical target would be 1-3% residual O<sub>2</sub> on a molar wet basis in the combined tail gas stream.

## Improved HCR™ process

Siirtec Nigi's HCR™ technology has been improved in order to reduce the fuel gas consumption in the sulphur recovery block, thus reducing CO<sub>2</sub> emissions while achieving more than 99.9% sulphur recovery efficiency. The cut in CO<sub>2</sub> emissions has been achieved without the need for additional investment by utilising the latest catalysts and by plant optimisation to reduce operating costs (Fig. 4).

HCR is a tail gas treatment based on the catalytic reduction with a reducing gas (CO + H<sub>2</sub> or a mixture of both), of the oxidised sulphur compounds present in the Claus off-gas species. The resultant H<sub>2</sub>S is removed from the off gas by absorption using an aqueous solution of MDEA.

Traditionally, the catalyst used for the reduction reactions required a feed at a temperature of 280°C, thus a heater was required to raise the temperature of the tail gas from the final sulphur knockout drum of the Claus unit from 130°C up to 280°C.

In general, in-line burners were used to supply heat to the system while also generating the reducing gas needed for the reducing reactions.

The operating condition of the Claus, unique to HCR, eliminates the generation of the reducing gas with the in-line burner, thus the energy consumption of the HCR, and in turn the equivalent carbon dioxide emission, is intrinsically less than other tail gas treating units based on the catalytic process.

At the outlet of the reducing reactor, the sulphur in the process gas is present mainly as hydrogen sulphide. This species is eventually removed and returned to the SRU by means of a regenerative absorption using MDEA.

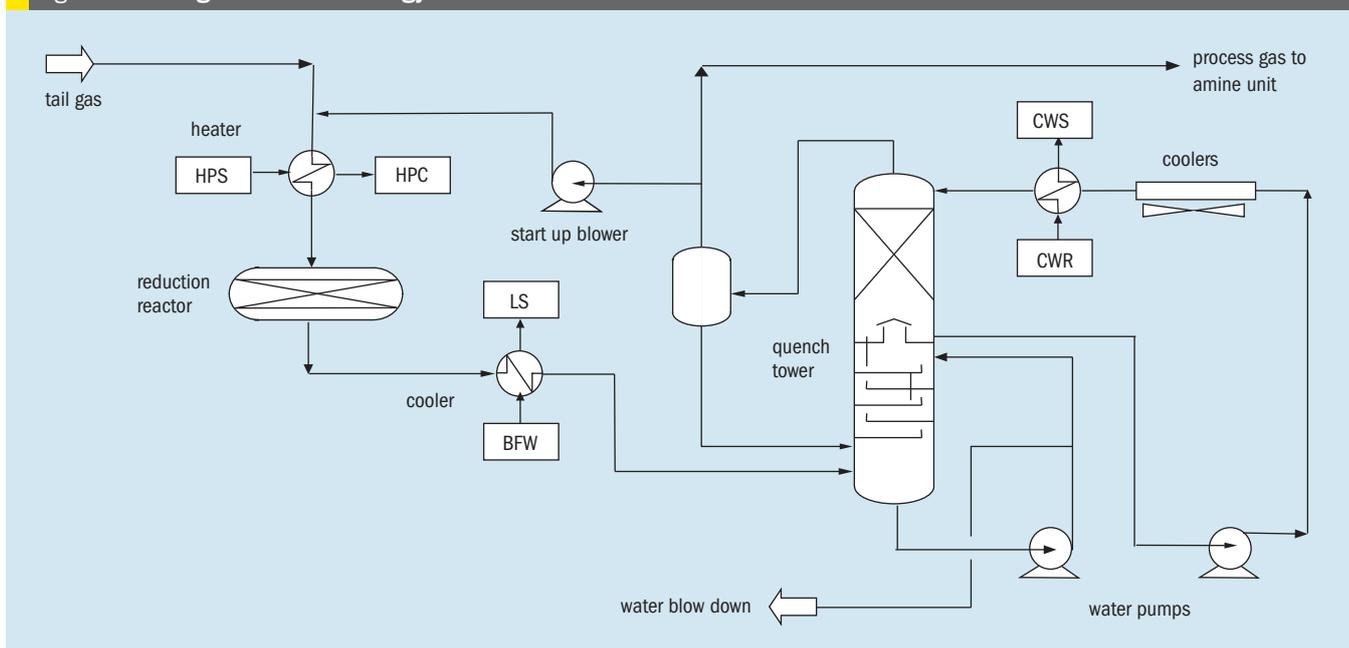
Typically, the low pressure steam consumption of the regeneration section is in the range of 100-110 kg of steam per m<sup>3</sup> of solvent when 50 wt-% MDEA is used and the targeted sulphur recovery efficiency is 99.9+%; herein lies a potential energy saving.

In order to enhance the environmental impact of HCR the technology has been improved by using a new generation catalyst and by improving the MDEA regeneration section.

### Implementation of new catalyst

The catalyst most widely used for the reducing step has for a long time been an aluminum oxide catalyst containing about 2 wt-% cobalt and 6 wt-% molybdenum. The activity of this catalyst is of industrial inter-

Fig 4: Siirtec Nigi's HCR™ technology



est at a temperature greater than 270 °C.

In addition to the reduction reactions, the above catalyst also promotes the shift reaction: the conversion of H<sub>2</sub>O and CO to CO<sub>2</sub> and hydrogen, and the hydrolysis of COS and CS<sub>2</sub> to less harmful species.

Recently a new catalyst has been introduced to the market that contains significant more cobalt (1-5 wt-%) and much more Mo (10-20 wt-%). At 230-240°C this catalyst shows catalytic activity towards both the reduction and the hydrolysis reactions equivalent to that of the "old style" catalyst at 280°C. Siirtec Nigi has modified its way of designing the HCR technology and adapted the design of the Claus section in order to accommodate this new catalyst into the sulphur recovery unit.

The implementation of the new generation of catalyst has been tested in an industrial plant for two years and has now become a standard for HCR.

The operation of the plant at a lower temperature brings a number of advantages including:

- lower duty of the heat that brings about a reduction of the fuel consumption when an in-line burner is used;
- simpler integration of the tail gas clean up unit with the other sections of the SRU making possible, for example, the supply of heat directly from the heat recovery section of the Claus unit.

From the environmental standpoint this means that for a 135 t/d Claus unit arranged with an in-line burner in the tail gas unit, the

reduction of 40°C leads to a saving of about 320 kW, equivalent to a reduction of about 550 t/a of carbon dioxide emissions. Greater emissions reduction can be achieved by replacing the in-line burner with an indirect heater integrated with the Claus unit. This arrangement results in the reduction of CO<sub>2</sub> emissions by about 1,860 t/a (equiv. 44,640 Euros/year in the CO<sub>2</sub> market).

### Regeneration of MDEA.

As mentioned earlier, the regeneration of the solvent is an energy consuming process and improvements in this area can help reduce environmental impact.

Since the first commercial application of the HCR in 1988, more than ten units are in operation, therefore a consistent set of data has been collected from the field that have allowed Siirtec Nigi to improve the correlations between steam consumption and residual acid gas in the lean amine solution.

The residual acid components in the lean amine is the key parameter upon which the performance of the tail gas scrubbing depends, thus the accurate identification of the asymptote in the curve lean amine content versus steam rate provides a valuable tool for the prediction of the marginal benefit each kilogram of steam brings to the stripping section.

On the other hand, the steam rate is related to the stripper arrangement and operating conditions, more specifically to the tower feed temperature and the stripper overhead system adopted: a refluxed recti-

fying section reduces steam requirement.

The feed temperature is typically raised against cooling the lean amine in a feed-bottom heat exchanger: the higher the efficiency of this heat transfer, the higher the temperature at the stripper inlet and thus, the lower the steam demand.

Combining the implementation of a high efficiency feed-bottom heat exchanger and the adoption of a refluxed rectifying section under the conditions suggested by the updated correlations has led to a significant reduction of the steam consumption in the stripper reboiler. For the 135 t/day SRU, this means a further reduction of about 1,250 t/year of carbon dioxide emissions.

Overall, the improvement achieved in both the reaction section and the solvent regeneration end, results in a global CO<sub>2</sub> cut of 3,110 t/year equivalent to more than 80,000 Euros per year in the CO<sub>2</sub> market. ■

### References

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