Gerrit Bloemendal, Frank Scheel, and Juste Meijer, Jacobs Comprimo Sulfur Solutions, the Netherlands, explain why low temperature tail gas treating is going prime time.

Conventional SCOT type tail gas units operate with inlet gas temperatures to the reduction reactor of 280 - 300 °C in order to achieve a full conversion of the sulfur species to H₂S. In most cases this temperature requires using an inline burner as typical steam conditions in refineries and gas plants are not high enough to raise the temperature of the gas to this level.

Comprimo Sulfur Solutions¹ and others² recognised that the ability to operate at a lower temperature offered the potential to reduce energy costs and equipment sizes, and eliminate the high maintenance burner from the tail gas treating plant. A catalyst was sought that could achieve high levels of sulfur species reduction at lower temperatures,
and has been ordered for at least a dozen other tail gas treating units (TGTU). Low temperature SCOT is sufficiently mature for application in most operating environments.

Presulfiding
The catalyst was installed in June 2004 and the unit was started up in the normal way, starting with the presulfiding step. During presulfiding, the temperatures were kept as low as possible to demonstrate that for future units a steam heater using typical refinery steam pressures of 40 bar could do the job. The presulfiding step went smoothly, and within a couple of hours the unit was ready for Claus tail gas intake. A test programme was put in place, initially on a weekly basis, and later on a biweekly, then monthly basis. This test programme was run for almost two years, and the major findings are reported below.

Low H₂ requirement
It was found that when the SCOT unit is operated with 3% hydrogen in the quench column overhead gas, a continuous supply of reducing gas is required. In further testing the catalyst operation at 220 °C, reactor inlet temperature was aimed at and the setpoint for the hydrogen analyser was reduced down to 2%, in order to minimise the use of external hydrogen. The samples showed no slip of SO₂, and ultimately no external hydrogen was required anymore, as the Claus tail gas contained sufficient reducing components (CO and H₂) to sustain this level of hydrogen downstream the quench column.

After over two years of operation the SO₂ and COS conversion remains high. A good measure to determine the aging of the catalyst is to trend the top temperature rise of the catalyst bed divided by the total temperature rise. If this trend shows no decline and stays close to 100%, it means almost all the reaction takes place in the top half of the bed and no aging has taken place. For the BP Gelsenkirchen plant, this trend is plotted in Figure 1 versus the number of the sample. It can be stated that the catalyst is almost as fresh as when it was installed. The scatter in this data is largely attributable to slight changes in operating parameters such as plant load, inlet temperature and SO₂ content in the tail gas.

CO shift and incinerator emissions
The samples from the Gelsenkirchen plant show a very good conversion of CO to H₂. The CO level in the absorber offgas is similar to that from conventional SCOT catalysts, thus no operational changes for the incinerator have been noticed. The measured CO shift as function of temperature is given in Figure 2, which shows that in the higher temperature range the CO conversion is practically complete.

SO₂ and COS Slip
Samples taken with Dräger tubes downstream the SCOT reactor showed no SO₂ and consistently no drop
of pH was found, indicating that SO₂ slip is negligible. This was confirmed by the lab analyses, which initially showed good SO₂ conversion at temperatures even below 220 °C. Later, the lowest temperature samples showed some slip of SO₂, which can either be attributed to relatively high SO₂ content in the feed gas, some aging of the catalyst, or, most likely, a contaminated sample due to reuse of drying tubes. In order to avoid risk of SO₂ breakthrough, the inlet temperature was set to 230 °C and the catalyst showed no further SO₂ slip. An additional benefit of the slightly higher inlet temperature is to better hydrolyse the COS as this is kinetically limited at the lower temperature ranges, thus reducing the overall slip of sulfur species and improving recovery.

The COS kinetics effect has been studied for the plant at BP Gelsenkirchen by plotting the measured COS hydrolysates versus the average bed temperature, as shown in Figure 3.

Although other parameters that influence the COS equilibrium varied over the series of samples taken (causing the scatter in the data), it can be seen that there is a trend for a better COS hydrolysis (i.e., closer approach to equilibrium) at higher average bed temperatures. Note that the increased conversion with increasing temperature is a purely kinetic effect; the chemical hydrolyses equilibrium, which is discussed below, would predict lower residual COS at lower temperatures. However, equilibrium is not reached at these low temperatures.

Catalyst analyses

After more than one year satisfactory operation, the sulfur plant was shut down for some modifications to the Claus part. This raised the opportunity to take a catalyst sample. This sample was analysed for its performance as well as for its chemical composition. After one year of operation, the catalyst performance in the laboratory was almost as good as for fresh catalyst. Furthermore, the physical and chemical properties had hardly changed in this period, indicating the catalyst is very stable and has a high runtime expectancy.

Operational benefits

No flame eyes, no flow trips, no igniters, no turndown limitation

It may be obvious from the above that for new units, an inline burner is no longer mandatory in a SCOT unit: a simple 40 bar steam re heater can provide sufficient temperature for this catalyst. This makes it possible to eliminate all the problems associated with an inline burner, such as trips caused by falling flame scanners, low flow on either fuel gas or air, failing igniters at startup, etc. Furthermore, turndown is no longer limited by the turndown of the inline burner or by the small recycle system from the quench column to the heater inlet using a steam ejector. The turndown of the unit can be unlimited.

As the hydrogen excess required for TG-107 is lower than for conventional SCOT catalysts, the steam re heater technology can also be applied in a natural gas treating plant. As was shown at Gelsenkirchen, the tail gas of the Claus section normally contains sufficient reducing gas to reduce all sulfur species to H₂S, but the hydrogen line was kept for backup situations. For gas plants that typically have no hydrogen available, a more reliable approach (more on H₂S side, resulting less SO₂ to the reactor) is advised to reduce the risk of upsets from the Claus unit resulting in SO₂ breakthrough. In combination with a stainless steel quench system (which is almost mandatory in high CO₂ applications anyway), this yields the highest plant availability possible.

Energy saving: a first step

As indicated above, the TG-107 enables the SCOT unit to operate at less than 240 °C inlet temperature, providing excellent conversion of all sulfur species, including COS and CS₂. Considering that the tail gas from a Claus unit typically enters the SCOT at 120 - 160 °C, the heating requirement is reduced from approximately 140 °C to 80 °C. The direct energy savings expressed as fuel gas demand is proportional to this difference, therefore a reduction of fuel gas flow of approximately 30 - 50% is achieved. Additional indirect savings occur from eliminating the combustion air, thus saving blower energy, and from the fact that the SCOT unit has a lower back pressure due to the lower total gas flow. The reduced gas flow also simultaneously reduces the quench water and the amine circulation requirements; a 5% reduction of amine flow is achieved.

Energy savings alone can pay for the swap to a low temperature SCOT catalyst, typically less than a one year payback. The TG-107 is slightly more expensive than the conventional SCOT catalyst, mainly due to its higher molybdenum content and due to additional handling at manufacturing. For scheduled replacements of fully depreciated conventional catalyst, the additional cost for installing TG-107 instead of conventional pays off in less than two months.
Steam saving for units with HP steam
For units that already use indirect heating in conventional SCOT, such as (superheated) 80 bar (VHP) steam or hot oil systems, converting to TG-107 is worth considering because of the energy saving only. The plant can change the heating medium from high value superheated steam to ‘normal’ high pressure (HP) steam and use the high value steam elsewhere.

Energy saving: a second step
In the Gelsenkirchen plant, a weak interaction was found between SO2 emissions in the stack and SCOT reactor inlet temperature. This effect was attributed to the reduced conversion of COS caused by kinetic limitations at very low reactor inlet temperatures, and consequently the lower average bed temperature. If energy conservation is to be optimised even further, the inlet temperature of the SCOT reactor can be further reduced provided little or no COS is present in the tail gas of the Claus unit. Applying this strategy, the fuel gas demand for the inline burner or steam to the reheater can be further reduced to less than 50% of the conventional flow. However, at such low temperatures the COS conversion becomes kinetically limited, and it is almost mandatory to install a layer of TiO2 catalyst in the first Claus reactor if very high overall recoveries are to be met. This requires a marginal additional investment, as TiO2 catalyst is more expensive than plain alumina catalyst but yields a great return on investment. The return on investment is not only achieved by the energy saving in the downstream SCOT unit, but also in the first Claus reactor bed itself. The TiO2 catalyst is not sensitive to sulfation, therefore the lifetime expectancy of this catalyst is much longer than for plain alumina catalyst. Taking this longer lifetime and the better performance into account, the payout time of this catalyst plan is still less than a year. At this point in time, this combination of catalysts is considered to be the best available technology, as it combines very high recoveries in the Claus and SCOT combination with the lowest energy use.

Investment saving: a third step
Conventional SCOT plants are frequently provided with a waste heat boiler downstream the reactor generating low pressure steam. The economics of such a boiler is questionable, as LP steam is usually of little value because it is in excess in the refinery. With the low temperature SCOT catalyst, the recoverable heat leaving the reactor is roughly cut in half. As a result the low temperature SCOT design allows the waste heat boiler to be eliminated and the excess heat removed in quench. The net result is to delete an expensive piece of equipment and simplify the process.

Industry applications
Debottlenecking pressure drop
The TG-107 catalyst can play an important role in debottlenecking existing sulfur plants. As the catalyst is made in 2 - 4 mm spheres, the pressure drop across a catalytic bed is relatively low. Compared with extruded catalyst, a pressure drop reduction across the bed
of approximately 20 - 30% is readily achieved. In addition, the catalyst can be applied with a high space velocity, usually requiring less catalyst volume than with conventional catalyst. This makes it an ideal catalyst for debottlenecking hydraulically overloaded plants. Furthermore, eliminating the dilution to the tail gas from fuel fired in the burner, 5 - 10% TGTU capacity can be gained without any equipment modifications.

**Debottlenecking re heater capacity**

In many sulfur plants the feed gas flow has increased in the course of time due to higher desulphurisation requirements or changed feedstock. An example is the sulfur plant linked to a coal gasification plant in Europe, which was faced with increasing loads of CO₂ in the Claus feed gas. As a consequence, the inline burner became a bottleneck, as it could no longer heat the tail gas to the required inlet temperature. Simply replacing the catalyst and operating at the lower temperature freed up sufficient operating capacity without losing recovery. Considering this is a coal gas plant with substantial amounts of COS in the Claus tail gas, the operator chose to maintain the reactor inlet temperature at 240 °C. The plant is now able to process so much more acid gas that slowly but surely the next bottleneck is starting to appear: the incinerator burner. Due to the increased load this burner is now running short of capacity.

**Operational flexibility**

In some remote areas, natural gas for firing the inline burner is not available and refinery fuel gas is used. Although refinery fuel gas is not a preferred TGTU fuel gas source due to its variable composition (which may lead to sooting of the catalyst or oxygen slip from the burner), there is essentially no alternative for conventional SCOT unit as the inlet temperature is relatively high. By switching to low temperature catalyst, refineries could replace the inline burner with a 40 bar steam heater, creating a more flexible operation. The 40 bar steam is usually readily available, either as a byproduct from other refinery units or generated in a boiler, which can handle the changing fuel gas composition. For new plants the strategy would be to fire the fuel gas in a boiler and use the steam generated with that, rather than using an inline burner. In many instances, however, 40 bar steam is also generated in the Claus and/or incinerator waste heat boiler, making the sulfur complex self supporting.

**Retrofit in SUPERCLAUS® plants**

The SUPERCLAUS® process was introduced in the mid 1980s with great success and has increased the sulfur recovery in many sulfur plants to beyond 99.0%. However, tightening legislation is driving some plants to increase sulfur recoveries. The low temperature SCOT process presents a cost effective way of doing so.

The SUPERCLAUS stage typically consists of a reheater designed to heat the Claus tail gas to 240 °C, a reactor and a gas cooler/sulfur condenser. In addition, a SUPERCLAUS unit always includes a bypass that is opened in case of upsets. In this respect the SUPERCLAUS stage closely resembles the hydrogenation stage of a low temperature SCOT unit, and only a catalyst change, a quench system and an absorber are required to convert such a unit to a low temperature SCOT. The new SCOT absorber offtags can be processed in the existing incinerator without any major modification. Whether a new regenerator is required to provide solvent for the SCOT absorber, or whether an existing amine system can be debottlenecked to provide the solvent, is to be investigated on a case by case basis.

The low temperature SCOT process can be applied to both refinery and gas treating applications in both new and retrofit projects. It offers a solution to some of the costly challenges the industry faces, as discussed below.

**Increased sulfur recovery for natural gas plants**

As the low temperature catalyst requires less gas heating, the Claus tail gas will be less diluted with burner combustion gas, and also contain (marginally) lower concentration of CO₂. In a gas treating plant where acid gas CO₂ content is typically high, low
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temperature catalyst helps reduce the total sulfur slip from the SCOT unit in four ways:

- The lower CO₂ concentration allows for a better hydrolysis of COS, provided equilibrium is reached. The equilibrium constant for COS hydrolyses can be written as:

  \[ K = \frac{(CO_2 \times H_2S)}{(COS \times H_2O)} \]

  Although eliminating fuel gas firing reduces both the concentrations of CO₂ and H₂O in the tail gas, the relative contribution of the CO₂ reduction is usually the larger part. For a typical refinery application, the CO₂ would reduce from 3.0 - 2.8%, whereas the H₂O content would reduce from 33.0 - 32.6%; this would reduce the equilibrium COS content by 6%.

- The lower temperature will also have its influence on the equilibrium. According to the rules of thermodynamics, the logarithm of the equilibrium constant K varies with reciprocal temperature:

  \[ \ln(K) = -\Delta G^0 / (RT) \]

  where:
  - \(-\Delta G^0\) is the Gibbs free energy at standard conditions.
  - R is the gas constant.
  - T is the absolute temperature.

  Figure 4 illustrates the effect of the thermodynamics. It shows that at a (bottom bed) temperature of 300 °C the value of K is 500, whereas at 250 °C it is 800. This means that under otherwise identical conditions the temperature reduces the equilibrium COS content by a factor 1.6. If equilibrium is met at such low temperatures, the actual slip of COS from the reactor will also be reduced by the same factor.

- The lower CO₂ content in the top of the absorber will give a lower 'competition' for H₂S absorption, therefore lower H₂S specifications can be obtained with equally stripped solvent (the selectivity effect).

- The lower gas flow will give less slip of H₂S, even if the same spec was met (the dilution effect).

These parameters can be key in regions where emissions are critical, although their effect for refinery applications is limited. For natural gas plants, however, where COS levels typically are high and hydroysis is poor due to the high CO₂ content in the feed gas, this effect can be substantial. Calculations show the total reduced sulfur from the SCOT absorber can be reduced by approximately 15 - 20% for a plant with a typical feed of 44% H₂S and 50% CO₂ to the Claus unit, depending on the selected temperature level for the SCOT reactor.

Mercaptans conversion in gas plants

In several gas fields in the Middle East, the raw natural gas contains several unwanted species, such as H₂S, CO₂, mercaptans and some BTX. Various gas treating strategies have been applied to such gas plants, some more successful and efficient than others. In order to minimise overall capex for such units, it is interesting to keep the number of high pressure process of equipment as low as possible. The Shell Sulfinol technology is applied in several locations for this treating challenge, which allows all the H₂S, the CO₂ and mercaptans to be removed. A drawback of the technology is that it also absorbs substantial amounts of BTX. The acid gas from the Sulfinol regenerator is usually lean in H₂S, and contains all the other species removed from the raw gas (Table 1).

The low H₂S content makes it virtually impossible to process the gas directly in a Claus unit, therefore an enrichment unit applying a selective solvent such as MDEA or Flexsorb is installed. The fact that all the equipment in the enrichment unit is low pressure equipment makes this route an attractive one from TIC perspective. However, the enrichment unit offgas still contains all the mercaptans (as they are not absorbed in the aqueous solvent), as well as most of the CO₂ and BTX. The mercaptans content precludes routing the offgas to an incinerator, as burning the mercaptans would result in excessive SO₂ emissions. On the other hand, the BTX content in the enrichment offgas makes it impossible to convert the mercaptans at the relatively high temperatures that are encountered in a conventional SCOT unit, as the BTX starts to crack, rooting the catalyst bed in relatively short time.

This is where the TG-107 catalyst could fill a gap: laboratory tests show that the conversion of mercaptans to H₂S is very high at the typical operating temperatures of the catalyst (below 240 °C), whereas at the same time the reduced operating temperature would strongly suppress the cracking and/or polymerisation of BTX, allowing for acceptable run lengths. Calculations show the overall sulfur recovery for this system, including the sulfur in the mercaptans, could be higher than 99.0%.

**Conclusion**

The TG-107 catalyst has been tested extensively as a low temperature SCOT catalyst, and it has proven to be at least as good as the conventional SCOT catalysts at temperatures vastly below 240 °C. The success of TG-107 as a low temperature reduction catalyst provides a compelling economic and operational opportunity for sulfur plant tail gas treating. The benefits can be realised both in existing units by replacing the old catalyst for energy saving and/or debottlenecking purposes, and in new units plants, providing a simplified and more robust design.

**References**