

Better control of SCOT TGT units

By combining detection techniques, electronics and the sample system, Ametek has developed a single, integrated, continuous $H_2/H_2S/COS$ analyser for SCOT tail gas treating units.

Randy Hauer of Ametek P&AI describes the initial installation of the gas analyser at a Texas refinery and the subsequent improvements that were made to the instrument following field testing.¹

The tail gas treater (TGT) is the basic unit operation of removing sulphur compounds from Claus SRU tail gas. There are several types of TGTs, including production of byproduct sulphates, but by far "closed loop" amine-based TGTs where the H_2S -rich stream is recycled back to the front of the SRU are the most prevalent. The analyser experience described here is based on the experience for a SCOT tail gas treater but the analyser and sample system has been applied to many variants of the amine-based TGT.

The process consists of three basic steps (see Figure 1):

- **Catalytic hydrogenation and hydrolysis of all sulphur components** (H_2S , SO_2 , COS , CS_2 , S_{vap} , S_{liq}) in the Claus tail gas to H_2S . The catalyst is cobalt molybdenum and this stage is sometimes referred to as the CoMo reduction or SCOT reactor. Reduction of all the unreduced sulphur compounds to H_2S requires an excess of H_2 at the outlet

of the CoMo SCOT reactor, hence the need for a H_2 analyser.²

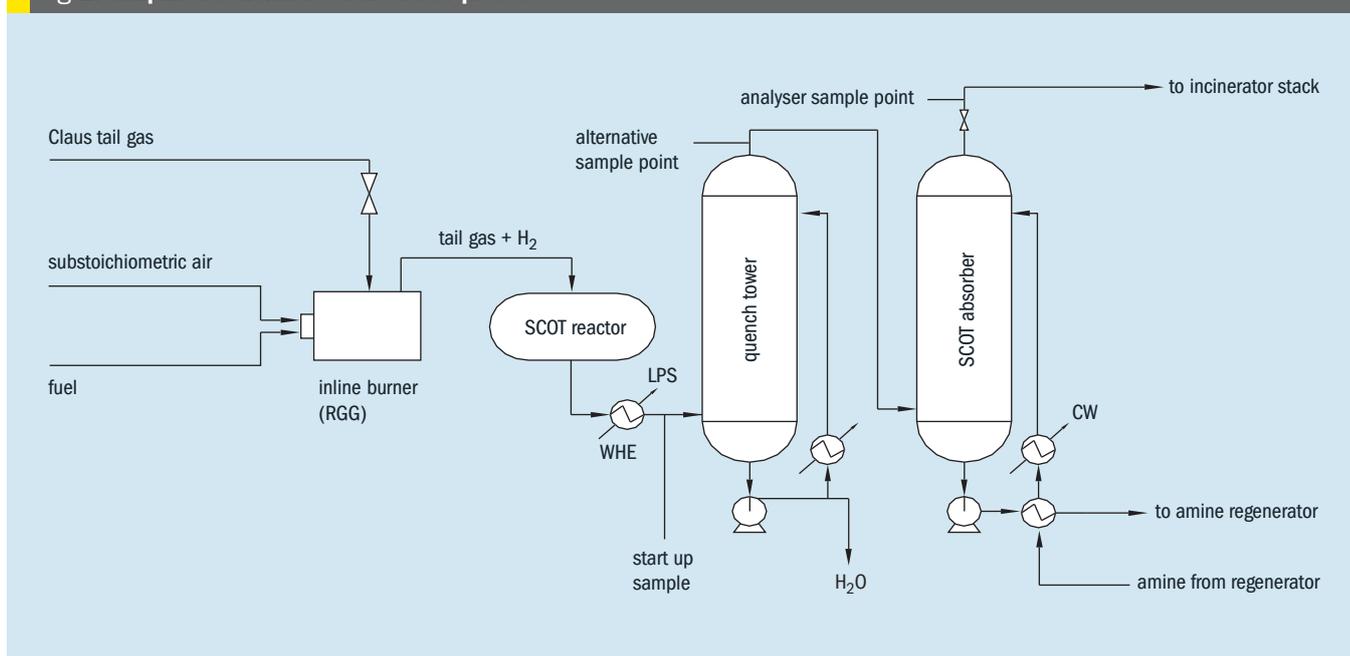
- **H_2S is selectively absorbed** from the tail gas by means of an amine solvent, after cooling. This stage is sometimes referred to as the (SCOT) absorber or contactor.
- **Amine is regenerated** (H_2S is desorbed from the solvent). The high concentration H_2S stream from the regenerator is recycled back to the input of the Claus SRU. The off-gas from the absorber is sent to the incinerator (operating permits are usually 250 ppm SO_2 with typical operation at 100 ppm SO_2 or below).

H_2S+H_2 measurement in a SCOT TGT

The process requires the measurement of hydrogen to control the reduction gas to a CoMo catalytic reactor and the measurement of hydrogen sulphide and carbonyl sulphide to monitor the efficiency of the amine contactor and CoMo reduction reactor.

There are two common sampling loca-

Fig 1: Simplified schematic of the SCOT process



sitivity. These performance specifications are desirable in applications where a single component is being measured at low concentrations with no interfering compounds present and especially when measuring multiple components with overlapping absorbance ranges. Further details on the design of this spectrometer and discussions on the advantages in comparison to other designs are available in References 3 and 4.

A cell length of 81 cm was used for the first installation measuring H_2S in the amine contactor overhead of the SCOT unit, where a full-scale measuring range of 0-500 ppm was required. Since that original installation, the most common full-scale measuring range for H_2S in the contactor overhead applications is 0-1,000 ppm, so a 40 cm cell length is often used.

Thermal conductivity sensor

The thermal conductivity sensor uses a Wheatstone bridge type circuit with matched heated-wire elements on both sides of the bridge. One of these heated elements is used as a reference and is sealed inside a compartment containing air while the other element is exposed to the sample gas. A constant voltage is supplied across the bridge and this controls the maximum temperature of the elements. The measuring element loses more heat than the reference element if the sample gas has a higher thermal conductivity than the reference air. Increased heat loss reduces the temperature and lowers the resistance of the measuring element. The reduction of measuring element resistance unbalances the bridge circuit, resulting in an increase in the bridge output voltage which is read as increasing thermal conductivity of the sample gas. Both heated elements are located in a compartment behind a sintered stainless steel flame arrestor, with the sample gas flowing past the sintered disk and diffusing into the area around the elements as shown in Fig. 3.

Thermal conductivity sensors can be used to measure the composition of binary gas mixtures, if the two components in the mixture have sufficiently different thermal conductivities. However, sample gas in the amine contactor overhead in a SCOT unit is not a binary gas mixture. A typical stream contains approximately 10% water vapour, 10% carbon dioxide, and 3% hydrogen, with most of the balance being nitrogen. There are small quantities of hydrogen sulphide, various hydrocarbons, carbonyl

Fig 3: Layout of thermal conductivity sensor

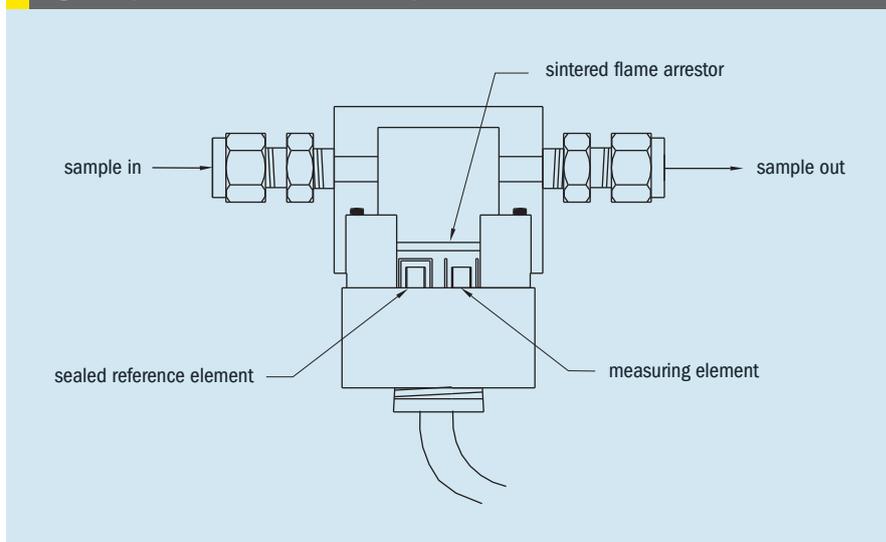
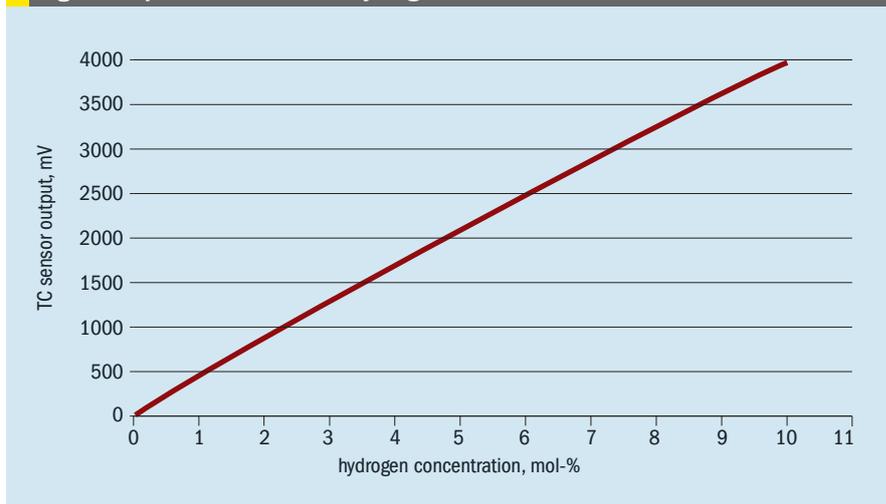


Fig 4: Output of TC sensor vs hydrogen concentration

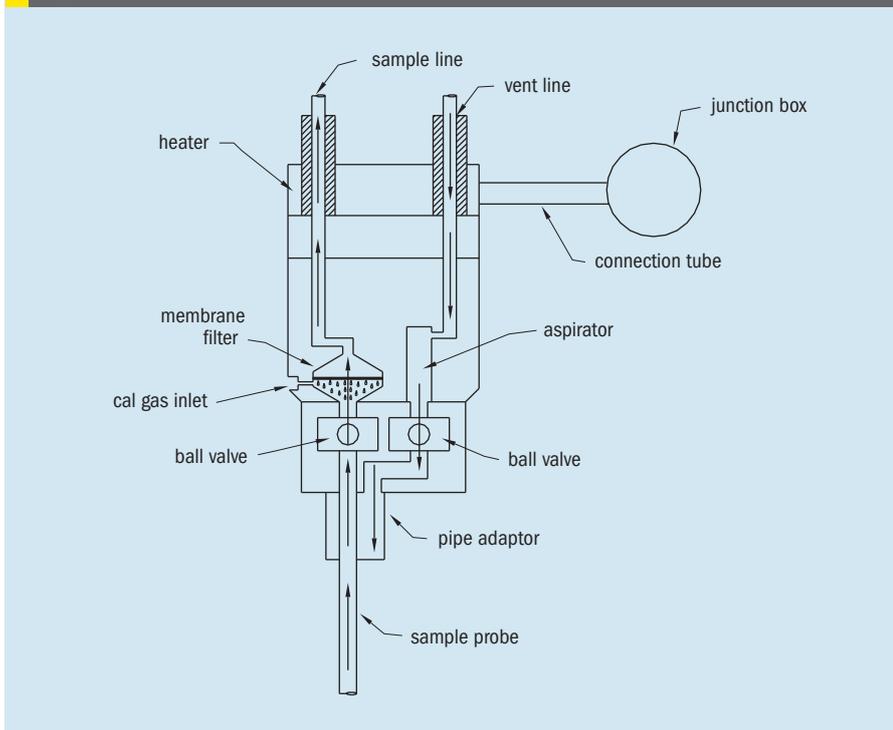


sulphide, and carbon monoxide, but these do not have a significant effect on the thermal conductivity of the mixture because their concentrations are low relative to the major constituents. It is still possible to make the hydrogen measurement by considering the sample gas to be a binary mixture, if the concentrations of water vapour and carbon dioxide are stable, or if the impact of their variation can be minimised. Water vapour concentration is a function of the temperature and pressure in the amine contactor since the sample gas is essentially saturated with water in the contactor. Good control of the amine temperature and stream pressure will result in a relatively stable water vapour concentration. Carbon dioxide concentration is affected by changes in the composition of SRU plant feed and swings in SRU air demand. It can also vary with the duty cycle of the reducing

gas generator (RGG) that is typically used to add hydrogen to the stream before the SCOT catalyst bed. Carbon dioxide concentration varies more than the water vapour, so it is desirable to operate the TC sensor under conditions that minimise the effect of changes in CO_2 .

Experiments were carried out to determine the effects of sample pressure and sensor temperature on the thermal conductivities of gas mixtures containing nitrogen, hydrogen, carbon dioxide and water vapour. It was found that the effect of CO_2 variation on the mixture thermal conductivity could be minimised at TC sensor temperatures between 400°C and 600°C where the thermal conductivity of CO_2 is closer to that of nitrogen and air than it is at lower temperatures. Higher temperatures increase the effect of water vapour concentration changes, which is not an issue in applica-

Fig 5: Schematic of heated sample probe



tions with stable water vapour content. In applications with unstable water vapour concentration or if the analyser is being switched between streams, it is possible to dry the sample gas to eliminate this issue. The output of the TC sensor is shown in Fig. 4 at hydrogen concentrations of 0 to 10%. The output is very linear with only a very small non-linearity correction being required.

After reviewing the data from these experiments, it was determined the hydrogen concentration of mixtures representative of SCOT contactor overhead sample gas could be calculated using the following equation:

$$H_2 = S_{H_2}(M_S - M_0) + Q_{H_2}(M_S - M_0)^2 - (P - P_0) - \beta [CO_2] - \gamma [H_2O]$$

Where:

- H_2 = Hydrogen concentration (mol-%)
- S_{H_2} = TC sensor linear gain
- Q_{H_2} = TC sensor quadratic correction
- M_S = TC sensor signal on sample gas (mV)
- M_0 = TC sensor signal on zero gas (mV)
- α = Pressure coefficient
- P = Pressure reading (mmHg)
- P_0 = Pressure reading during zero (mmHg)
- β = Correction factor for carbon dioxide
- $[CO_2]$ = Carbon dioxide concentration in sample gas (mol-%)
- γ = Correction factor for water vapour
- $[H_2O]$ = Water vapour concentration in sample gas (mol-%)

These tests were also used to select the supply voltage for the TC sensor that would result in the element operating temperature that offers the best combination of sensitivity to hydrogen measurement over a 0 to 10% range and also minimises the effect of CO₂ concentration changes. Since water and CO₂ are not being measured, static concentration values are used in the software to correct the hydrogen reading for their presence in the process gas.

Sample system design

Development of heated sample probe

Sample gas from the absorber overhead in the SCOT process contains moderately high levels of H₂ and H₂S that make it undesirable to vent to atmosphere, even at the low flow rates required by an analyser. The sample is typically saturated with water at a temperature between 40°C and 50°C, requiring heating of the probe and other sample handling components to prevent condensation. An aspirator was selected for the sample transport method to avoid moving parts and return the sample to the process. The sample return point was the preferred location for the aspirator to avoid the vent backpressure issues associated with long sample lines. A probe was developed that combined the sample and vent into a single sample point connection that

included two ball valves for manual isolation of the sample and vent, a 25 mm diameter membrane filter on the sample side, and an aspirator on the vent side. A heater is mounted on the top of the probe to allow all of the components including the sample and vent line connection fittings to be kept at a temperature higher than the water dew point. A flow schematic of the probe is shown in Fig. 5. A Pt100 RTD in the probe is connected to the analyser and used to provide probe temperature control. An internal temperature switch is used as a secondary over-temperature limit control. The heater is certified for use in Division 1 and Zone 1 hazardous areas.

Installation at Big Spring, Texas refinery

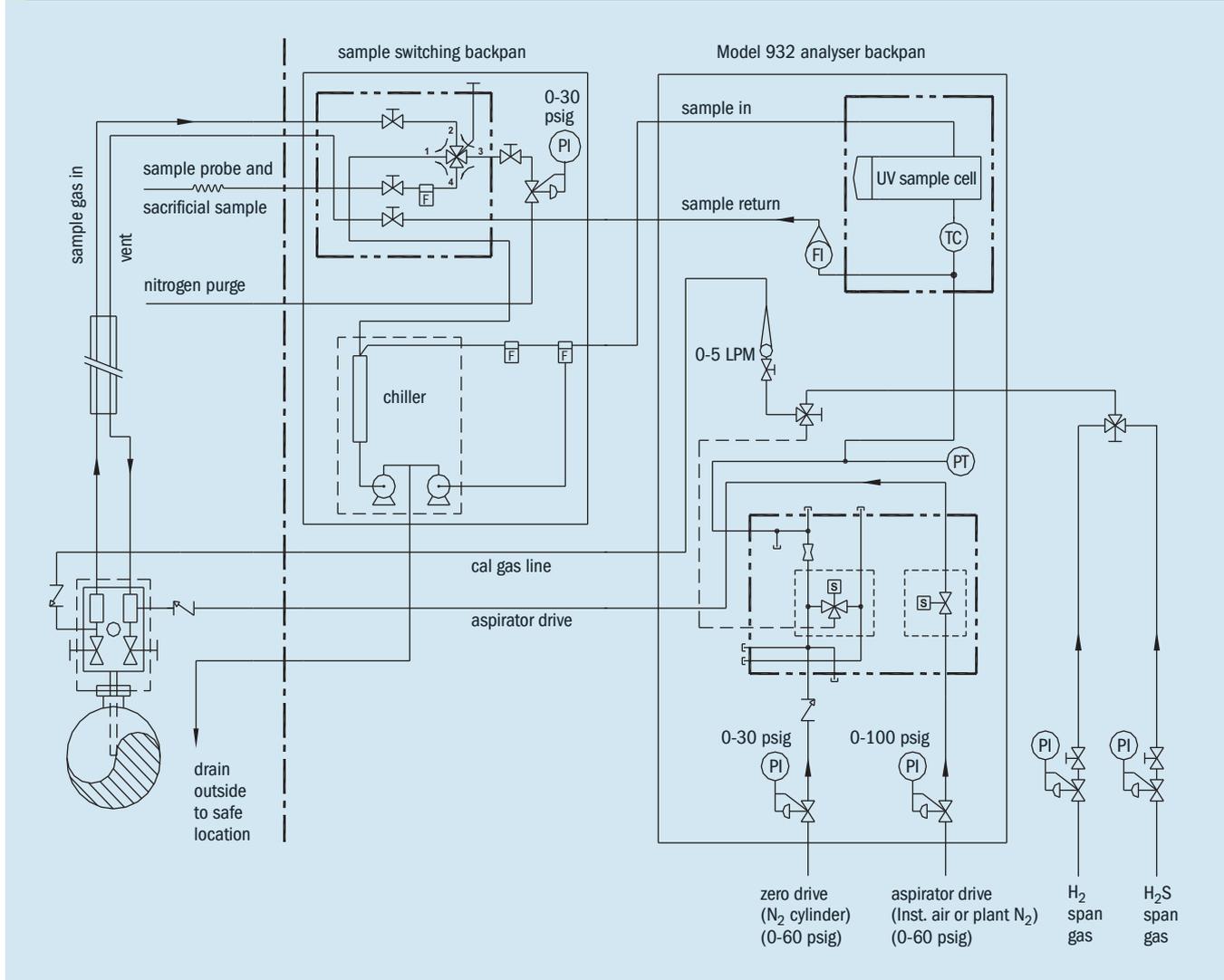
The refinery has two SRUs, (one 60 t/d and one 75 t/d capacity), both are followed by a SCOT tail gas treater. "SRU One" was operating under a grandfather clause without a tail gas treater. The load to SRU two is relatively stable with load variations being handled by SRU one. These high load variations seen in SRU One made it a good location to evaluate the SCOT H₂ + H₂S analyser. The SCOT unit was constructed as a fast track project in 2004 with Ortloff Engineers and it was brought on-line in April 2005.

Installation

The analyser included a heated sample switching system which allowed temporary manual switching between the standard sample point at the amine absorber outlet and another sample point before the absorber and the quench tower. A sample dryer was used to remove the water vapour from the sample to avoid problems with the very high water content when sampling before the quench tower. The sample system schematic is shown in Fig. 6.

The analyser was commissioned and after operating for some time, it was determined that the service life of the membrane filter in the probe could be increased by periodically switching between sample points while back flushing the idle probe with nitrogen. This back flushing seemed to be effective in temporarily removing particulate from the filter element. The probe was redesigned to allow the installation of a larger diameter membrane filter (approximately 55 mm diameter), which should result in higher sample flow rate and longer intervals before service is required. A

Fig 6: Schematic of analyzer sample system



small diameter flat element fibre filter was also added to reduce particulate loading on the membrane filter.

The redesigned heated probe was installed at the Big Spring refinery in September 2006 and operated for over three months without back-flushing. The probe seemed to be working properly at the end of this testing, but the flow rate had dropped from over 5 L/min to about 2.5 L/min. The probe was disassembled and the inspection showed that the fibre filter had a 6-mm thick coating of what appeared to be sulphur as shown in Fig. 7. It is thought that this sulphur deposited on the filter during a process upset when SO₂ breaking through the CoMo catalyst bed required that the absorber amine solution be replaced. The membrane filter was still fairly clean, in spite of the sulphur deposit on the fibre filter. A spare fibre filter was not available at the time, so the sulphur

Fig 7: Sulphur on particulate filter after process upset



Fig 8: Data from process upset in SRU/TGT

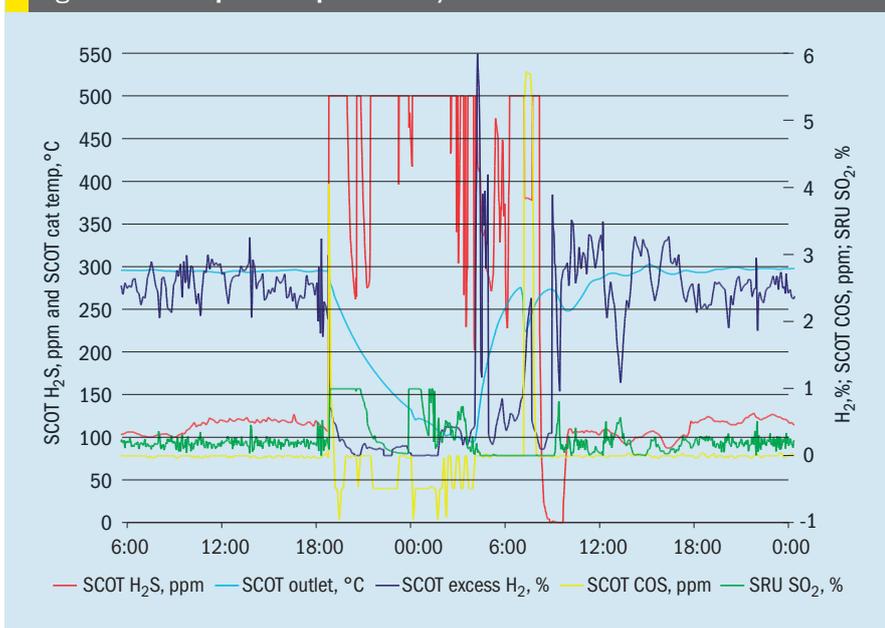
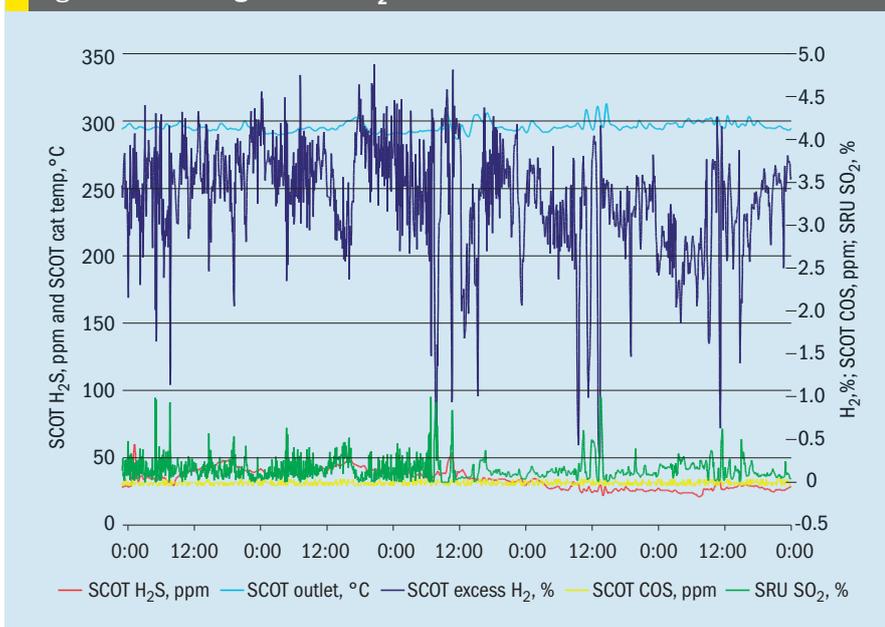


Fig 9: Data showing effect of SO₂ excursions



coating was scraped off and a new membrane filter was installed. Removal of this sulphur coating restored the flow rate to a normal value of 5 L/min.

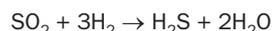
Data

Figure 8 shows some data from the analyser recorded as one minute averages. Hydrogen sulphide concentration (ppm) at the absorber outlet and SCOT catalyst bed outlet temperature (°C) are plotted on the primary Y axis. The secondary Y axis shows the H₂ concentration at the absorber outlet (%), the COS concentration (ppm) at the

absorber outlet, and the SO₂ concentration in the SRU tail gas which was measured by the SRU air demand analyser. The first section of data shows normal, stable operation, with the H₂ between 2 and 3%, the COS at close to 0 ppm, and the H₂S at 100 ppm. During this same period, the SO₂ concentration in the tail gas is about 0.2% and the SCOT catalyst outlet temperature is just below 300°C. An upset occurs in the SRU at about 19:00 which drives the SO₂ concentration up above the 1% full-scale. The flow is switched to bypass around the SCOT unit in order to protect the amine from SO₂

breaking through the SCOT reactor (sometimes determined by a drop in pH of the water in the quench tower). Once the flow is bypassed, the analyser is basically offline while the flow is in bypass mode. The temperature of the SCOT reactor drops during the period that the flow is bypassing the SCOT unit. SRU operation begins to stabilise at approximately 04:30 and after the SO₂ concentration drops down close to zero, the flow is switched back to the SCOT catalyst bed. The outlet temperature of the SCOT reactor rises up as it is heated by the hot gas stream from the reducing gas generator (RGG) and the hydrogenation reactions. Readings from the analyser show that the process quickly returns to normal operating conditions once the reactor temperature stabilises. Normally there is no COS being read by the analyser at the absorber outlet. The brief rise in the COS to just over 5 ppm occurred when the sample point was temporarily switched to before the quench tower. This COS reading of 5 ppm is consistent with the equilibrium concentration typically seen from fully active catalyst (in this case about 1.5 years old).

Although several hydrogenation and hydrolysis reactions are carried out in the SCOT reactor, the hydrogenation of SO₂ consumes a large portion of the hydrogen because it has a higher concentration than other sulphur species (with the exception of H₂S) and because three moles of H₂ are required for each mole of SO₂ as shown below:



Sulphur vapour and liquid can also consume significant quantities of hydrogen, but their concentrations do not typically vary as much as SO₂. Stable operation of the SRU and good control over the SO₂ concentration/SRU trim air are critical for successful operation of a SCOT TGT. This effect is shown in Fig. 9, where excursions in SO₂ concentration in the reactor feed result in sharp drops in H₂ measured in the absorber overhead. The reactor outlet temperature increases with SO₂ concentration because the reaction in Equation 2 is exothermic. Excess H₂ was on manual control, but was at a sufficient level during stable operation to maintain the excess during upsets.

Conclusion

Good control and measurement of excess H₂ is important to provide stable operation of a SCOT TGT. Measurement of the H₂S at

More new Ametek analyser systems for SRUs

Continuous O₂ measurement of reaction furnace

During start-up and shut-down, any time a sulphur recovery unit (SRU) transitions from ambient temperature through fuel gas warm up to the introduction of acid gas, measurement of oxygen stoichiometry is critical. Historically, operators have manually taken samples using a portable electrochemical type O₂ analyser. While giving more or less satisfactory results the requirement for more stringent operating limits, hazard exposure and the non-continuous nature were reasons to consider a permanent solution. A fixed system to draw a continuous sample during the operational transition period without intervention from operations or analyser maintenance can be rationalized. Ametek Process Instruments has delivered three continuous O₂ analyser systems to a US refiner and has interest from two other US-based refinery operators at this time.

The motivation was a combination of safety and operational requirements. The operating permit and construction of a new tail gas treating unit (TGTU) requires this particular refinery to start up the entire sulphur recovery plant (SRU + TGTU) in a single sequence with zero tolerance for exceeding emission limits. More frequent manual sampling was not a consideration, as this would bring increased exposure to personnel. The refinery consulted Ametek on available choices for a continuous system. As it turns out the continuous measurement of O₂ in an SRU process stream is not new. Ametek developed and supplied

approximately 45 systems for Superclaus™ where excess O₂ is measured in SRU tail gas before a subsequent generation of the catalyst obviated the need for the measurement. The detection principal is paramagnetic, which measures “actual O₂” and is widely applied in process O₂ applications where the background gas has flammable components. The sample handling for the continuous measurement technique could be quite conventional provided fuel gas was the only mode. However when acid gas is cut in, the sample conditioning must contend with sulphur vapour and liquid hence the sample handling requirements are similar to a tail gas “ratio” analyser.

Operational requirements vary according to local operating procedures. Sulphur Experts Inc. recommends in their seminars the fuel gas warm up burn strategy should be right at stoichiometry or no more than 0.02% excess, if possible, and to be certain to prevent free oxygen from reaching the hot catalyst. This requires “city” gas as a fuel source and accurate flow metering for both air and fuel gas. The continuous O₂ measurement is a degree of detail that ensures protection of the catalyst, prevents emission episodes and most importantly provides a level of protection for operations personnel.

Combustibles measurement in SRU acid gas⁵

Ametek has also developed a new gas analyser that combines a non-dispersive ultraviolet (NDUV) optical bench with a non-dispersive infrared (NDIR) sensor for the simultaneous measurement of H₂S

and total hydrocarbon combustibles (THC) in the acid feed gas to the reaction furnace of a Claus SRU, from a single sample point. This measurement requires a very fast response time for effective feed-forward control. A total hydrocarbon measurement is done rather than attempting speciation of the hydrocarbon mixture.

Both measurements are unaffected by common components in acid gas, including water and carbon dioxide. The hydrocarbons do not interfere with the NDUV H₂S measurement, and the interference of the H₂S on the HC measurement is almost zero.

Two different NDIR sensors have been evaluated to determine if they can be calibrated to provide a hydrocarbon concentration output which is proportional to the combustion air demand of the total hydrocarbon mixture that is present in the acid gas. Overlooking this aspect of the IR measurement may have prevented the successful use of this technology in some previous attempts at this application. The results of the in-house evaluation suggest that Sensor A, which uses a measure centre bandpass wavelength of 3.4 microns, can provide a suitable HC measurement if large amounts of non-methane hydrocarbons are present in the gas mixture and the sensor is calibrated for the predominant hydrocarbon. Sensor B, which uses a measure centre bandpass wavelength of 3.3 microns, may be suitable for applications where methane is the main hydrocarbon which changes concentration during upsets. The prototype analyser will be field tested in several different SRU acid gas streams.

the absorber outlet can be used to monitor the operation of the amine treatment section. A process analyser has been developed that combines these measurements along with optional measurement of COS. The analyser was field tested for over a year in the SRU One SCOT unit at a refinery in Big Spring, Texas. The COS reading at the SCOT absorber outlet was close to zero which shows that good hydrolysis is being achieved on the catalyst in the SCOT reactor. Feedback from this testing was used to improve the design of the sample system, resulting in a system that operated

reliably in a variety of conditions including process upsets.

While investigating the performance as well as improvements in the heated probe design, it was decided to incorporate the probe modifications into the upgrade of the SCOT unit on “SRU two”.

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