Analysers and next generation SRU control

Acid gas analysis has arrived and tail gas analysers are now coming into the third generation. **S. Simmonds** and **R. Hauer** of AMETEK discuss current trends in SRU process analysers and

The history of on-line process analytics is a relatively short one. Development was driven by the need for process control of high value hydrocarbon-based products. The first on-line analyser applications came during the second war. Rapid development came in the 1970s with the advent of the microprocessor and resultant chemometric techniques. Led by Phillips Petroleum, Union Carbide and Dupont Chemical, amongst others, these initiatives were the antecedents of today's Siemens Applied Automation, ABB Analytics and AMETEK Process Instruments.

Whether or not sulphur can be considered a high value product, in most cases the driving force for process measurement and control of the SRU is largely environmental. The US EPA Clean Air Act of 1970 and the ground-breaking study by Alberta Environment on the capability of the modified Claus process coincided with the first attempts to control the modified Claus process using an on-line analyser and closed loop control.

The first report of an on-line tail gas analyser was a technical paper based on a gas chromatograph installed at the Dow Chemical Freeport TX (USA) facility in 1970. In 1972 Amoco Oil and Dupont Process Instruments published a paper on an ultraviolet (UV) based tail gas analyser installed at the Amoco Whiting refinery, Indiana, USA. Shortly after this, in 1974 Western Research participated in a pilot study using a prototype UV-based tail gas analyser at the Shell Waterton gas plant in Alberta, Canada.

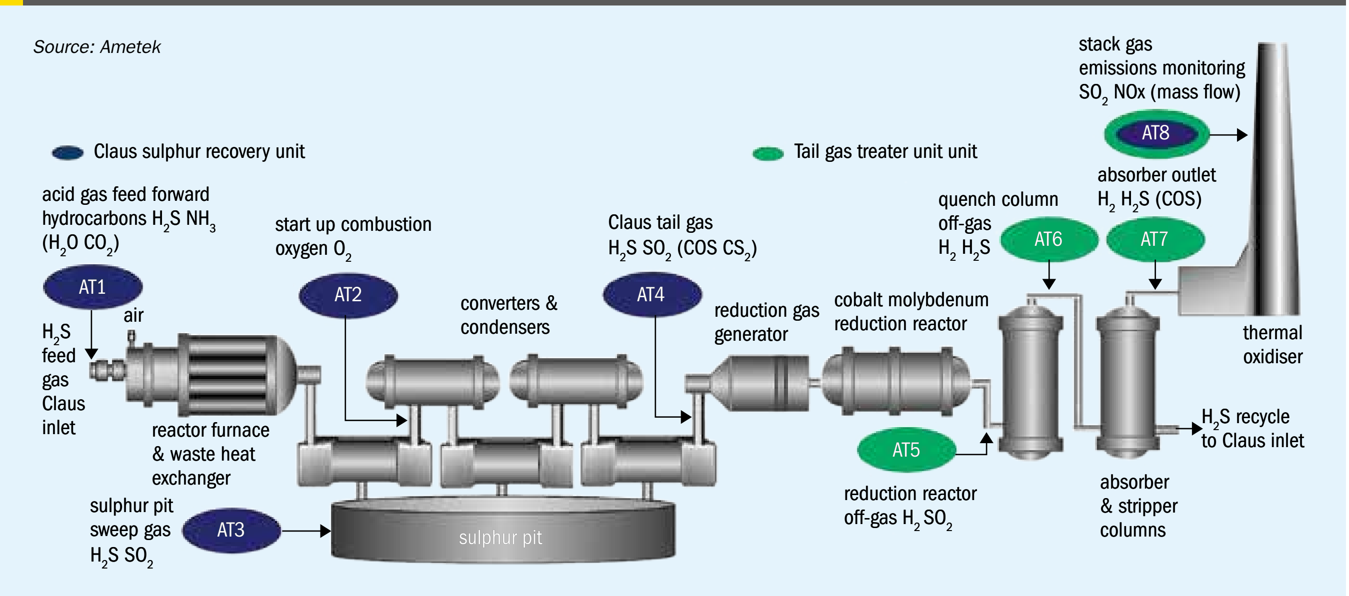
Subsequent developments by various manufacturers were all based on UV spectroscopy and extractive sampling techniques and that remains the case today.

The life cycle of an analyser is expected to be 15-25 years and some analysers can be in the field for 30 years or more if properly protected and maintained. The product life cycle of an analyser is of the same order, 15 years or more and is mostly subject to the obsolescence of the electronic components.

Process gas analysers in SRUs

The suite of process gas analysers for a sulphur recovery unit (SRU) can vary from one up to as many as eight analyser tags (see Fig. 1). The (H_2S/SO_2) SRU tail gas analyser is the most common. Every SRU (or enhanced SRU, Superclaus, sub dewpoint) will have this critical, primary analytical measurement. If the SRU has an associated amine based TGTU there is a second critical analyser and this analyser can be in one of three locations. The third

Fig 1: Simplified process flow diagram of a SRU showing 8 analyser tags



most common analyser tag is the emissions analyser, while not quite yet universal, in some cases (even when an end user is paying for high sulphur efficiency) the governing environmental authorities occasionally do not specifically require an emissions analyser, the emissions analyser is the one measurement that confirms the recovery efficiency on a continuous basis. After these three, the feed gas analyser is becoming more prevalent in front end engineering design.

As the industry drives to tighten control loops and reduce upsets in the process, the analysis of the feed-forward acid gas will become an industry standard. The results are clear that feed-forward control is both practical and worth the (relatively small) capital investment. The industry is still in the education phase and needs to be assured of certain practical implications but the need and benefits of feed-forward control are already well established. If an acid gas analyser has not been included in the FEED, then the design should be revised to allow for simple installation of a feed-forward analyser at a later date by installing the sample tap and associated heated acid gas probe, saving considerable time, effort and cost in the future.

The next most common analyser is the pit gas analyser followed by an analyser to measure the O_2 at the outlet of the waste heat boiler for exact stoichiometric combustion of natural gas during start-up and shutdown.

Tail gas analyser

There is a choice of two tail gas analysers - the "top of the pipe" (close coupled model 888 "no sample line" analyser – see Fig. 2) or the extractive (sample line analyser, model 900 ADA). Over the last five years (~600 tail gas analysers) ~80% of tail analysers for new construction have been top of the pipe (close coupled type). A "sample line" type analyser is selected for three primary reasons; firstly for installation in an analyser house for extreme climates, secondly if the sample point location is compromised due to poor piping design, and finally if the end user wishes to have the additional measurements of COS and CS_2 for process optimisation (only normally required for legacy straight SRUs with no TGTU or for enhanced Claus SRUs).

AMETEK's tail gas analyser has gone through two full generations and is about to enter a third.

Fig 2: **Model 888 tail gas analyser**

Source: AMETEK

The first generation analysers proved the measurement to be viable, the second generation analysers improved on sample handling and improved reliability to keep the analyser in cascade control, while the third generation analysers address the common failure modes external to the analyser.

The current design of the close-coupled ("top of the pipe") tail gas analyser was due for updating which presented the opportunity for some additional features. That said, given the close-coupled analyser has been installed in excess of 1,200 units and the well proven success of the technique, the goal of the update was to be evolutionary not revolutionary. The principal improvements offered in the third generation are;

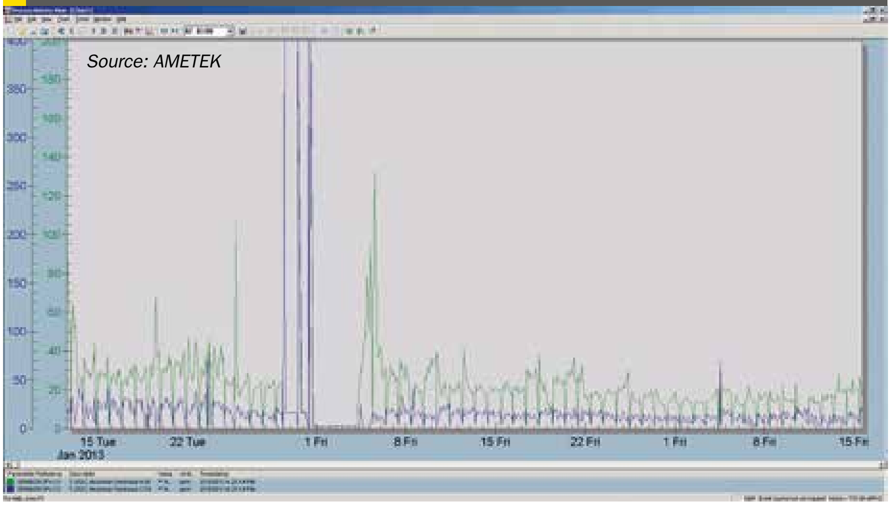
- Flange temperature RTD and alarm: An embedded RTD in the process connection flange provides an alarm for poor quality steam. This advanced warning eliminates unexpected plugging.
- Automatic flow control: This provides a method to automatically adjust the flow rate of the analyser relative to process pressure (especially important if there is entrained sulphur).
- Ambient temperature rating: Improved thermal isolation between the oven and electronics results in an increase in the ambient temperature specification from 50°C to 60°C. This makes installation in regions like the Middle East possible without the need for an air conditioned shelter (with the aforementioned need for protection from solar gain an important detail).
- Double-block isolation from the process: This provides an option for any site specific safety considerations.

TGTU analyser

The sample point location of the TGTU analyser varies depending on who is providing the front end engineering design. In 2002 AMETEK developed a combined ultraviolet (sulphur) and thermal conductivity (H_2) analyser and to date have provided ~180 analysers for various amine based TGTU processes. The measurement of the (excess) hydrogen is the primary measurement in this application. As the H_2 remains essentially unchanged after the CoMo reactor (with a slight increase across the quench tower due to renormalisation after the removal of the water) AMETEK considers any of the three sample points to be non consequential in terms of H_2 measurement based on experience. As to the sulphur gas(es), where and what to measure remains variable according to the designer, the spread of sample point locations are as follows:

- The majority (~150) are at the absorber outlet measuring H_2S and H_2. Of these 150, ~15 have added the additional analytical capability of COS measurement and it is interesting to note almost all of these have been end users upgrading an old GC and convinced of the utility of the COS measurement. The secondary measurement of the H_2S (after the H_2 measurement) (25-500 ppm) at this location is a measure of the efficiency of the amine absorber and the COS (5-500 ppm) is a measure of the CoMo reactor catalytic activity as illustrated in the process upset in Fig. 3 where the COS momentarily reached 400 ppm during an upset. Both of these sulphur values contribute to SO_2 emissions and can help to isolate the third contribution being sulphur pit sweep gas if vented to the incinerator
- Another ~25 analysers have been installed (further upstream) at the outlet of the quench tower. Here the secondary measurement of (~2.5%) H_2S after the H_2 measurement is a measure of the efficiency of the SRU as it represents all of the sulphur compounds (H_2S. SO_2, COS, CS_2, Sv, S liq) leaving the SRU. While the amount of trace COS (5-500 ppm) is the same as the absorber outlet it cannot be effectively measured at this point as it is masked by the %level H_2S
- Approximately five analysers for H_2/SO_2 have been installed further upstream yet, at the inlet to the quench. The util-

Fig 3: **COS upset data from TGTU absorber**



ity of measuring SO_2 here is to alarm for SO_2 breakthrough from the CoMo reactor before seeing a drop in the pH in the quench water. While this sample point is much less common, one advantage is the analyser can be placed in front of a diverter valve and never be dead legged in the case of TGTU bypass or a sample switching valve for this purpose if the primary sample point is at the absorber (or quench) outlet.

If there is only going to be one analyser (most FEED process packages do this in the interest of cost), AMETEK recommends locating the analyser at the outlet of the absorber. Most importantly add the COS measurement (in addition to the H_2 and H_2S) at this point as the cost is very minimal and of great value when trying to source the cause of a process upset and emission increase. Additionally, if the FEED provides for measurement at two points in the TGTU then add the H_2 measurement to the second point as the cost is again minimal and provides a back up for the primary H_2 measurement which is by far the more important variable. AMETEK has ~20 installations where there are two TGTU analysers as part of the TGTU design most of these being H_2S measurement at both the quench and absorber. Approximately half of these take advantage of adding a second H_2 measurement.

Emissions monitoring analyser

An emissions analyser is normally required as part of the operating permit. Beyond the compliance aspect, mass emission (kg/h SO_2) is a sensible and useful way to evaluate a straight Claus or enhanced Claus SRU as it can be directly related to sulphur recovery efficiency and used as an optimisation tool . Mass emission requires the SO_2 analytical measurement be made on a "hot-wet" basis because the SO_2 and corresponding velocity measurement must be on the same basis. Mass emission measurement loses some of its utility when there is a TGTU and typically the emissions in these instances are measured on a dry basis and corrected to a zero oxygen base to arrive at standardised measurement. While CO and NOx are occasionally included as a permit measurement they are not all that common. What is becoming more common is the inclusion of un-oxidised sulphurs (primarily H_2S with some COS and CS_2, 5-15 ppm total) to be included in the overall SO_2 emissions

Feed (acid) gas analyser

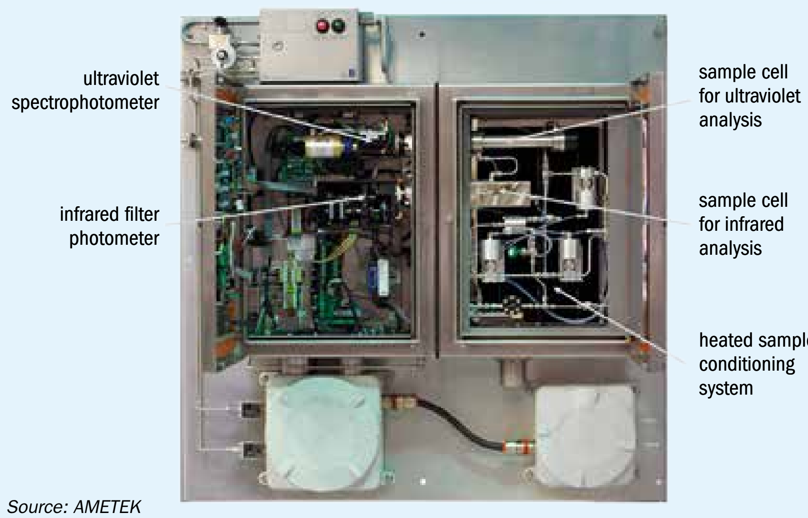
When considering the 'air demand' of the SRU process, primary air control using feed-forward flow ratio of air to acid gas accounts for ~90% of the combustion air. Secondary air control using tail gas analysis (2:1 H_2S/SO_2 ratio) controlling a trim air valve by feedback control (or cascading to the feed-forward controller) accounts for the ~10% balance of the required combustion air. Feedback control based on process analysis provides the most precision, however, it is impaired by the ~30 second process lag time, especially if the composition of the acid gas changes rapidly.

Under steady state conditions air control is stable, but in the case of sudden changes in acid gas composition it is not uncommon for air control requirements to exceed the ability of the feedback control loop. In these cases the excursion from the set point of a 2:1 H_2S/SO_2 ratio can be extreme, and the cause of a serious loss of recovery efficiency and increased emissions.

With advances in certain technology and process control, the implementation of a feed-forward analyser for real time acid gas analysis has been seen with increasing regularity, particularly on new process projects. The advanced burner control system ABC+ for feed-forward control developed by Jacobs Comprimo® Sulfur Solutions has seen a big increase in uptake in 2014. ABC+ uses real time process analysis of the acid gas to provide information to the closed-loop control.

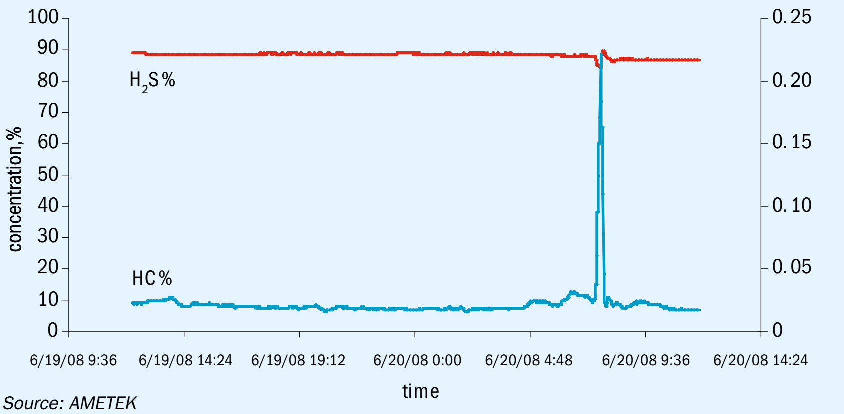
AMETEK have supplied nine analysers for Superclaus ABC+ projects and an additional 40 analysers for straight SRUs and

Fig 4: **IPS-4 acid gas analyser (open)**



Source: AMETEK

Fig 5: **Capture of transient HC variation**



Source: AMETEK

SRU-TGTU applications. Figure 4 shows AMETEK's model IPS-4 acid gas analyser and Fig. 5 shows the analyser results for a one time, sudden increase in total hydrocarbons (HC) from 0.02 to 0.25%.

While an easy case can be made to have an acid gas analyser for a gas processing SRU where variable composition in the H_2S content in the acid gas requires feed forward control and the addition of total HC can also be utilised, there is also compelling reason to add a feed gas analyser for an SRU followed by a TGTU. The problem for a TGTU is not when there is a sudden increase in HC (resulting in a dramatic rise in H_2S going to the TGTU) but the resultant dramatic rise in SO_2 going into the TGTU when the HC event is over. Additional work is being conducted to quantify BTEX in amine acid gas for SRUs related to gas processing where these components require co-firing of natural gas.

Pit gas analyser

Hydrogen sulphide exists in sulphur as dissolved H_2S and chemically bound hydrogen polysulphides. The liquid sulphur produced from Claus SRU typically contains a total of 200-350 ppm of dissolved H_2S. Spontaneous or active degassing of the sulphur results in H_2S accumulates in the gas space above the liquid sulphur. H_2S becomes progressively more dangerous as the levels incurred in handling and moving of the sulphur increases above toxic limits (70 ppm), becoming lethal at 600 ppm and reaching the lower explosive limit at ~3.25 %. A measurement tag for H_2S and SO_2 in pit gas is sometimes required for certain degassing licences or at locations where there has been an explosion incident Where there has been an incident there are records of an explosion occurring at H_2S values well below the 3.25% LEL. AMETEK has been in discussion with Black and Veatch on this subject. Based on CFD modelling Black and Veatch arrive at the conclusion H_2S can exist in pockets and stagnant areas at 16 times the mean value as measured in the sweep gas header meaning 2,000 ppm could constitute a LEL condition somewhere in the pit. There is continuous analyser data to corroborate that where an explosion occurred when there was a measured level of 4,000 ppm H_2S in the sweep gas header. Black and Veatch have asked if the sulphur pit (tank) can be measured at several points and while this is not practical for several reasons it does raise the question as to what level of H_2S constitute an alarm condition, to evaluate the gas flow in the head space and for operations to fully understand what constitutes a hazardous condition. Similarly, events of 3% SO_2 in the pit sweep header have been recorded which clearly indicates a sulphur fire where the condition prevailed for weeks without intervention, again measured values outside of the norm must be heeded

Process O_2 for start up / shut down

This measurement is made during start-up and shut-down, any time a sulphur recovery unit (SRU) transitions from ambient temperature through natural gas warm up to the introduction of acid gas. The measurement of O_2 stoichiometry is critical in order to maintain a slight excess of oxygen. Historically operators have manually taken samples using a portable electro-chemical type O_2 analyser or even mounting a "sacrificial" analyser that is discarded after start up. While giving more or less satisfactory results, the requirement for more stringent operating limits, hazard exposure and the non-continuous nature of portable grab sampling are reasons to consider a permanent solution. A fixed system that draws a continuous sample during the operational transition period, without intervention from operations or analyser maintenance can be easily implemented. The O_2 measurement is based on "tuneable diode laser (TDL) which is non contact type of analyser. The sample system is the advanced sulphur removal (ASR) probe used on the 900 ADA tail gas analyser, the analyser and sample system are maintained at 150°C so the analyser can be left on-line as the analyser transitions from warm up to acid gas mode.

Industry survey

The analytical instrumentation on a SRU plant is a highly specialised field of such critical operational performance that knowledge and experience are essential to success. In a recent wide-ranging analyser survey, with questions relating to reliability, on-line control and best practices, professionals from within the sulphur recovery industry were surveyed in order to gauge the level of understanding of the needs of the analyser application and to obtain valuable user related experiences. Three distinct stakeholder groups were surveyed who are directly involved in the purchase and maintenance of SRU process gas analysers:

- front end engineering design and start up engineers;
- operations;
- end user analyser engineers and technicians.

Reliability

The survey confirmed that the industry considers tail gas analysers to be reliable.

Trouble-shooting an analyser for sudden failure of an electronic problem is not difficult and a large refinery or gas plant complex has access to adequate skill levels for this. Specialist help is required where the problem is intermittent or electronic component failure is occurring on a frequent basis.

The primary factor affecting reliability of the tail gas analyser is heat integrity at the process connection and the second leading cause is inadequate design of the analyser shelter.

Best practices for heat integrity include:

- The process nozzle should be 150mm

(6") or less, terminating in a 2" 150 lb raised face flange (maximum).

- For top of the pipe type analysers the vendor must supply the steam jacketed ball valve. The steam needs to be of medium pressure (nominal 7 to 10 barg / 100 - 150 psig) as low pressure steam is, in practice, often wet and unsuitable.
- Use Contra-Trace™ or Contra-Heat™ to overcome any shortcomings. Do not allow the practice of wrapping steam trace tubing and insulation around a problem and thereby masking that problem.
- For sample line analysers, if possible install the analyser above the sample point and in all cases request the analyser vendor confirm the length from on-site measurements and/or isometric drawings. When sample lines are estimated and then the numbers flow through more than one set of hands, the probability the lines will be too long, is almost a certainty.

Best practices for analyser shelters include:

- Provide an adequate shelter that shades the analyser from direct sun at all times. The shelter is no different than what one would see over a local panel, quite inexpensive and almost always neglected at the EPC detailed design stage.
- Involve the analyser vendor at an early stage preferably at frontend engineering design. As end-user insist upon it and continue the dialogue into the detailed design stage. Be very wary of surrendering all analyser design to a systems integrator.

Sample point selection for both tail gas and feed gas analysers is more often than not compromised at the piping engineering stage. It is the lack of analyser specialists at the detailed engineering stage that is the root cause. A constricted and compromised sample point location can affect analyser operability which in itself is bad enough. The problem can extend to safety concerns at HazOp review, requiring an expensive piping change to make it right.

Start-up and turndown

Slow response is sometimes attributed to the analyser at turndown of the SRU when in fact it is process lag time. Although asked frequently to help configure control loops this is typically not a core competency of analyser companies and more the domain of the FEED and EPC control engineering team.

Reported analyser problems after start-up can often be related to the phenomenon of the Claus catalyst preferentially absorbing H_2S over SO_2 with the result producing values that do not represent the true air control situation. The AMETEK guideline (provided by Sulphur Experts test crews) is that the analyser should only be used for control some eight hours after start-up, perhaps more depending on individual plant conditions.

Acid gas analysis feed-forward control

From the survey it was clear that all respondents saw the benefits of feed-forward control but there were also many misconceptions that should be addressed.

Firstly, respondents were unclear whether feed-forward control can be used in the cascade control loop but from field experience this is exactly the intent. Rapid compositional analysis of the hydrogen sulphide, and a total hydrocarbon measurement provide the air demand components with the addition of a carbon dioxide and water measurement (and in the case of sour water acid gas, ammonia) provide full acid gas composition details.

Secondly, there was clear concern as to whether the information is fast enough for feed forward control, but again this is exactly the intent of these control designs. With the use of real time spectroscopic technology (a combination of both ultraviolet and infrared) the system is able to provide useful data rapidly.

Survey conclusions

The key conclusions of the survey were:

- For large scale project where a systems integrator is involved, ensure close management of the project from field proven end-user analyser technicians, in combination with close communication to the key SRU analyser vendor.
- Ensure that the SRU analyser vendor is involved in the entire project process from the early stages of the front end engineering design (FEED) right through the detailed design phase.
- A successful SRU analyser start-up requires careful thought and planning. The end-user technicians (or alternatively the contractor analyser technicians) need to be factory-trained and authorised to work on the respective analysers, alternatively the analyser vendor must be at site for start-up.

References

1. Simmonds S., Cappe S. and Hauer R. (Ametek Process Instruments) and Cicerone D. (Cicerone & Associates): “Sulphur recovery on-line analysers from front end design through life cycle ownership”, Sulphur 2014, Paris (Nov 2014).