From Vail to Vienna

2013 is a milestone year for Brimstone STS Limited, marking the 20th anniversary of its annual Vail Sulfur Recovery Symposium and the launch of the first Brimstone European Sulfur Recovery Symposium in Vienna, Austria. The Vienna Sulfur Symposium will be a regular annual event held each year in May. Lisa Connock reports on the inaugural event which took place at the Hotel Bristol on 27-31 May.

The Brimstone Sulfur Symposia series celebrates its 20th birthday this year. Over the last two decades, these annual conferences, held in Vail, Colorado in the USA, have become a well-established and highly regarded event on the sulphur industry calendar, producing informative and highly interactive gatherings for the discussion of sulphur recovery, treating and processing. The Vienna Sulfur Symposium mirrors the successful format of the Vail meeting, combining a mixture of technical papers, workshops, panel discussions, and extensive open-floor question and answer sessions. Attendees are actively encouraged to ask, answer and comment on questions related to amine treating, sulphur recovery, and tail gas treating. Topics include issues and experiences related to improving the safety, reliability and efficiency of plants.

The symposia participants are a mix of leading industry and academic experts, technology and service providers, SRU operations staff and plant managers. The overall number of attendees and the mix between operating companies and supply companies are carefully balanced to create an environment conducive to the promotion and exchange of practical ideas and information.

Approximately 60 attendees took part in the first Vienna Sulfur Symposium. In addition to the main symposium event, an optional half day gas treating seminar entitled “Meeting Challenges in Gas Treating – State of the Art” was presented by Optimized Gas Treating on the afternoon prior, focusing on:

- enhancing acid gas enrichment and tail gas treating selectivity;
- the impact of heat stable salts on the design and operation of amine units and sour water strippers.

The symposium was officially opened by Mike Anderson, President and Technical Services Manager of Brimstone STS Ltd, who gave a warm welcome and introductions, and was followed by the main programme – a mix of technical presentations, Q&A sessions moderated by Elmo Nasato of Goar Allison Ltd, a workshop on sulphur plant and tail gas unit start-ups and shutdowns presented by Greg Hanlon of Treating & Sulfur Solutions Inc. and Elmo Nasato, and a panel discussion on reaction furnace/waste heat boiler reliability by sulphur industry experts: Steve Croom (Delta Controls), Jim Hartman (Controls Southeast Inc.), Domenica Misale (Industrial Ceramics), Andy Piper (Thorpe Speciality Services) Dave Sikorski and Nick Roussakis (HEC Canada), Mike Porter (Porter McGuffie) and Elmo Nasato (Goar Allison Ltd). Shorter ‘cameo’ presentations were also given by Dave Sikorski (HEC Canada) on a CFD study of reaction furnace safety purging and by Koos Dirksen (EuroSupport) on the history of Claus catalysts.

**Reaction furnace linings**

The first presentation by Andy Piper of Thorpe Speciality Services provided a greater understanding of the limiting factors on reaction furnace linings in...
sulphur recovery units. SRU linings are complex structures that require careful consideration. They are not only the first line of defense to protect vessel shells, they are the only defense. The ultimate goal of the design and implementation process is to balance many competing factors in order to maximise the performance, reliability and life of the lining system for upset and the real world conditions that are imposed on the refractory linings.

“Twenty years service with minimal maintenance is what you would expect to achieve at a minimum if a lining is properly designed”, stated Andy. Unfortunately, the reality is far too many costly premature refractory failures, repeated time and again, all over the world. These failures can result in premature and/or frequent maintenance repairs or lining replacements between or during planned outages, longer downtimes, extended start-up times, safety and environmental issues associated with shell breaches and loss of production.

Common problems plaguing SRU linings today include a lack of understanding of refractories in general and the unique requirements for SRU applications, as well as the consequences of the technical and commercial decisions made by licensing companies, project teams and owner/operating companies.

Three keys to reliability were highlighted:
- engineered lining design;
- proper materials selection;
- experienced installation crews.

HCN in amine systems

Ralph H. Weiland of Optimized Gas Treating Inc. shared the findings of work carried out using mass transfer rate-based simulation to investigate HCN ingress and accumulation in amine systems. HCN has far reaching effects on amine system performance. After hydrocarbon contamination, its presence is one of the primary reasons refinery amine systems suffer from accelerated corrosion, operability, and reliability problems. When HCN enters the amine system, its hydrolysis produces ammonia and formate, a heat stable salt. Reaction of HCN with oxygen and H₂S generates another heat stable salt, thiocyanate. Accelerated corrosion leads to faster formation of particulate iron sulphide, which in turn leads to filter element plugging, fouled equipment, lower capacity and more stable foams.

Mass transfer rate-based simulation both confirmed and quantified previously anecdotal observations that recirculating, type water wash systems are, at best, only marginally effective in removing HCN as a feed contaminant. To seriously prevent HCN ingress into refinery amine systems, fresh makeup water is required, and a lot of it. An economic trade-off between sour water stripping capacity and energy usage versus amine system operating costs will ultimately dictate whether water washing is an appropriate choice for a specific refinery system. Finally, the buildup and accumulation of HCN and ammonia in the amine regenerator were quantified. These observations may go some way towards explaining the observed regenerator corrosion in existing plants and may inform material selection decisions for plants still in the design phase.

In-ground vs above-ground sulphur sealing

Jim Hartman of Controls Southeast Inc. (CSI) assessed the characteristic strengths and weaknesses of in-ground and above-ground sulphur sealing devices in SRUs and reported on an industry survey on sulphur sealing approaches and preferences in SRUs.

In the modified Claus process, conversion of deadly hydrogen sulphide into elemental sulphur and water occurs in the vapour phase at elevated temperature and pressure. Since the process is equilibrium limited, successive process stages are required for high conversion rates. After each stage, a condenser is used to convert sulphur vapour into liquid sulphur, which drains by gravity from the condenser into temporary storage – typically a pit or collection vessel. To prevent process vapour (with remaining H₂S and SO₂) from escaping with the liquid sulphur, some sealing means is required between the condenser and temporary storage.

Historically, SRU operators have used an in-ground device, commonly referred to as a seal leg, and/or an above-ground sealing device, such as Sultrap® and SxSeal™ devices, to achieve a vapour seal in sulphur rundown lines.

There is a wide spectrum of industry position on sulphur sealing approaches. The survey carried out by CSI indicated an industry trend (72%) toward above-ground sealing for reasons such as safety, ease of maintenance and accessibility and no potential for groundwater intrusion. The main concerns preventing universal adoption of conventional above-ground sulphur seals were reported to be concerns over supplemental pressure relief and maintenance frequency.

To address these concerns, CSI has developed SxSeal™ 2000, an improved above-ground sulphur seal that continues to provide the benefits of conventional above-ground devices but with the added features of infrequent maintenance and supplemental pressure relief of a seal leg.

SRU expansion with SO₂

Ron Schendel (CARTS) introduces SO₂Clean Technology

Ron Schendel of Chemical And Refining Technology Services (CARTS) discussed how the direct addition of SO₂ plus oxygen can double the capacity of a sulphur recovery unit, without the temperature problems associated with injection of oxygen alone. Historically, refiners wishing to increase capacity have added SRUs or debottlenecked existing units through oxygen enrichment. The benefits of using pure SO₂ to expand Claus capacity has been investigated in the past but the technology has not gained commercial acceptance due to supply chain complexities and the reluctance of refiners to build and operate a sulphur dioxide plant.

These obstacles can now be overcome as Calabrian Corporation is ready to build/operate over-the-fence plants that manufacture SO₂ utilising its proprietary commercially proven SO₂Clean Technology and deliver it via pipeline to a refinery’s SRU burner tip economically and safely, with no fugitive gas emissions, enabling refiners to
inject high purity SO₂ to increase sulphur recovery capacity with no reduction in saleable sulphur.

Ammonium salt precipitation in sulphur condensers

Muntazer Alawi of Saudi Aramco shared his experiences with the problems of ammonium salt precipitation observed in SRU condensers at Saudi Aramco’s Berri Gas Plant (BGP).

BGP was commissioned in 1977 and has five SRUs. Trains 100 and 200 can produce 654 t/d each, train 300 can produce 675 t/d and trains 400 and 500 can produce 900 t/d each. BGP is limited to 3100 t/d of input sulphur based on 62 t/d of total SO₂ emissions at 99% recovery.

SRU trains 100 and 200 were upgraded from Claus to SuperClaus in 2005 to control SO₂ emissions. Shortly after the start-up in 2006 it was noticed that the reaction furnace pressure had increased as a result of condenser no. 4 back pressure that was limiting train throughput by 50%.

During the testing and inspection (T&I) of SRU train 200 in 2007, a grey deposit consisting of mainly iron sulphate and trace amounts of ammonium sulphate was found in condenser no. 4 tubes and the demister pad. In 2008, during the T&I of SRU train 100, a similar deposit was found in condenser no. 4 and the tubes were cleaned and the train put back into service. In 2009, Saudi Aramco’s Process & Control Systems Department (P&CSD) carried out an analysis to resolve the ammonium salt deposition problem. Based on the findings and analysis it was suspected that the type of oxygen scavenger used in the boiler feed water was the source of ammonia and it was recommended to replace BFW with demineralised water as makeup to the acid gas scrubber. Despite carrying out this recommendation the problem persisted.

A study in 2010 revealed that the source of ammonia contributing to the ammonium salt formation at the condensers was mainly due to degradation products from DGA, which was carried in with the feed. However, tests performed by Sulphur Experts in 2011 indicated that only a trace amount of ammonia was found in the feed gas and the root cause of the ammonium salt formation was not clearly identified.

In-house comprehensive action plans consisting of short and long term solutions have since been developed in an effort to mitigate ammonium salt formation. The implementation of short term measures e.g. operational guidelines in the gas treating and sulphur recovery plants as well as routine monitoring of critical parameters such as acid gas temperature etc., has minimised the back pressure. Saudi Aramco is continuing its efforts to come up with permanent solutions to the ammonium salt issue.

Corrosion in sulphur pit off-gas lines

Peter Clark, Director of Research for Alberta Sulphur Research Ltd, reviewed the chemistry of air blanketed liquid sulphur storage vessels, explained how the tank off gases can corrode carbon steel above the apparent sulphur and water dew points and described some new treatment methods for tank off gases.

Sulphur pit and tank off gases, principally air contaminated with H₂S, SO₂ and sulphur vapour, pose significant challenges in terms of meeting more stringent emissions standards and for the potential for corrosion in transfer lines either to the main air supply of the plant or to the incinerator. Corrosion mechanisms appear to be complex, likely involving iron-sulphur contact corrosion mediated through acidic compounds produced on the pipe walls.

Treatment of pit off gases by catalytic oxidation over TiO₂ based materials appears to be feasible with trapping of SO₂ in aqueous caustic a fail-safe option. Return of the oxidised pit/tank off gas to the main burner air supply could be engineered as it would appear that the possibility of sulphuric acid deposition in the return line is minimal.

Preheat gun use during SRU dryout

The installed refractory in SRUs needs to be dried out to remove all moisture when initially starting up the unit or after major repairs on the refractory. The reaction furnace temperature should be increased gradually, especially during the ignition. Telal M. Hamoudah of Saudi Aramco shared his experiences of using a preheat gun during SRU dryout at Khuraniyah Gas Plant (KGP).

The preheat gun was used to close the gap in temperature between the air preheater and the reaction furnace, since it gives more control over increasing the temperature over the critical stage (149 to 538°C) when there is a greater risk of shocking and damage to the refractory.

In general, there were many advantages of using a preheat gun including:

- good temperature control, providing a gradual increase of temperature to 544°C while avoiding thermal shocks to the reaction furnace refractories;
- shorter (by 97 hours) dryout time where air preheater dryout was done independently.

Vibration, noise and combustion

Mike Porter of Porter McGuffie examined some of the physics behind vibration and the associated field of acoustics before discussing combustion noise and how to control burner noise. What should be done about excess noise or vibration? The answer is not always simple. If the acoustic resonance is simply causing noise and if that noise level is not high enough to cause and OSHA problem, the answer is probably quite simple: do nothing.

On the other hand, if the noise levels pose an OSHA problem, if a mechanical resonance is being excited, or if appurtenances are being adversely affected, something needs to change. Most burner manufacturers have developed approaches to disrupt the development of pulsation associated with acoustic resonances in the burner. There are numerous reported cases where “probes” have been inserted in the burner and adjusted until the “tone” simply goes away.

There have also been cases where the interior geometry of the burn/chamber has been altered to avoid resonance but this is a rather risky option.

If there is a mechanical natural frequency that matches the acoustic resonant frequency, it may to possible to change the mechanical frequency by adding stiffness. Since adding stiffness usually involves adding mass, such a change is often not easy.

Risks of accumulated sulphur in SRUs

Unintended condensation and accumulation of sulphur in SRUs can present problems and, in the worst cases, result in a sulphur fire and serious damage to equipment. Condenser tubes and mist pads are especially vulnerable. Sometimes the fire is limited, either by available sulphur or oxygen, and will give a noticeably higher temperature but no damage. However, it
should be noted that in every sulphur fire, not only SO₂, but also SO₃/H₂SO₄ will be produced and sulphuric acid can eventually lead to extensive corrosion damage in lines and equipment. Ellen Ticheler-Tienstra of Jacobs Comprimo® Sulfur Solutions analysed the areas where sulphur accumulation may be expected and presented a series of case histories of sulphur build-up in SRU equipment, such as waste heat boilers, reheaters, sulphur condensers and coalescers. The risks involved in the accumulation were discussed, both for the operation of Claus plants and SuperClaus® plants, for which sulphur may pose extra risks.

**SRU performace monitoring and catalyst management**

Pierre Crevier of Axens SA discussed the importance of tracking SRU performance for environmental compliance reasons to avoid being shutdown, for catalyst management to get the most out of the catalyst, and for the short and long term reliability of the plant. Even with only limited process data the SRU operations engineer can track converter approach to equilibrium and predict when catalyst change out will be necessary. By using additional information from the tail gas analyser (or samples) the evaluation can be refined. The use of a process simulator allows for rigorous and sophisticated analyses to be performed.

Regular ΔP surveys will allow the operations engineer to quickly pinpoint and diagnose throughput issues when problems arise.

In all cases the key to a successful monitoring program lies in the collection and analysis of relevant process data in the first few weeks after a fresh catalyst charge has been loaded in the converters as this is the time when all beds can be assumed to be operating at equilibrium. Ideally this should be repeated a couple of weeks later to ensure the data is in agreement.

**Elastomers for gas treating service**

Patrick Holub of Huntsman Corp. gave the final technical presentation on selecting elastomers for sealing applications in the oil and gas industries, where elastomer seals are utilised in the form of o-rings and gaskets in valves, pumps, sight glasses and hose connections. Selecting or specifying an elastomer for use in an amine or glycol system is not a precise science. The variety of elastomer compounds has increased with new formulations being introduced every year making selection a more difficult task. The single most important consideration in seal selection is compatibility with the fluid(s) in the process.

A test method was described that uses readily available equipment or low cost tools to test specific elastomer compounds for their fluid resistance in an operating environment. The test method was capable of discriminating between o-rings made of similar base compounds but manufactured with different curing methods. The test method provided data that was in fair agreement with literature data with the primary exception of polyurethane rubber. Additional work is continuing in this area.