Amine and Ammonia Acid Gas Balance Lines (AGBLs) for Refinery Claus Systems

Nathan “Tex” Ritter

Flint Hills Resources LLP, Corpus Christi, Texas
Introduction:

Environmental concerns of today are even more obvious than years past and for good reason. Those of us that are lucky enough to be (or have been) Sulfur Plant engineers know how the industries’ perspective has improved over the years.

In the past, Sulfur Recovery Units (SRU’s) were considered “back-end” units, they were necessary but, hard to justify based on raw material margin. Well, this attitude has changed significantly. The SRU has now become one of the major focuses in the gas production and refining business. If you cannot effectively remove the sulfur compounds from the gas or crude then, the operation is limited to how much can be processed based on the final emissions set forth by regulatory agencies. This shifts the focus towards the SRU from both environmental and economical planning perspectives.

Summary:

The reasoning behind this paper is that most refiners’ today are to a point that they have one, two or possibly more sulfur recovery plants within their facilities. It would be nice to be able smooth out the operation of the sulfur plant so as that it would reduce the number of operational upsets that have the potential to turn into environmental concerns/events.

Several items that have been implemented to steady gas flows to the SRU:

- Sour Water Storage Tank
- Lean Amine Surge Tank
- Amine Acid Gas Balance Header
- Ammonia Gas Balance Header

An added benefit is that it is possible to shutdown and subsequently startup a sulfur plant without having an environmental event. The reduction of incinerator SO₂ emissions can be as significant as much as 95% on average, which could place facilities in a much more favorable position with regulatory agencies. On the other hand it could be a directive from the regulatory agencies as a “consent decree” item at a later date.
Another interesting point is that with a smoother operation it is actually possible to increase a unit’s processing capability by as much as ~5-10%. This is a result of maintaining stable unit operation and being able to operate closer to any existing constraints.

How is it possible and how does it work one would ask? The simple description of the principle behind the entire design is that all of the amine regenerators/strippers and tail gas unit strippers float on a common H2S header tied to various Claus plants.

**Past Operations:**

Consider the numerous scenarios where a mechanical issue forced an unplanned outage of one Claus plant, in the past the rich amine load would have to be shifted to the remaining amine regenerator(s) and sulfur shedding practices/procedures would have to begin. It could be calculated as to how much time is allowed for the amine system to sour up before any drastic measures (sulfur shedding; i.e. upstream unit reductions) are employed but it usually results in exceeding fuel gas H2S limitations. Not to mention the other contactor/absorber products being off specification for a period of time, potentially causing either in plant or off site customer concerns. Utilizing the rich amine as an adjustment knob to transfer load from one unit to the other along with sweetening of the plant feed would reduce the load on the sulfur plants. This process is effective but it takes time (as long as hours) and sometimes the time is not available.

**Today’s Operations:**

With an Acid Gas Balance Line (AGBL), it is possible to transfer the load from one unit to another in an instant with just moving a control valve. Since only the gas is utilized, the load transfer is instantaneous. Additionally, this enables the ability to shutdown one Claus plant while continuing to operate the amine processing section as the rich H2S laden gas is routed to another Claus plant. An Acid Gas Balance Line (AGBL), sometimes also referred to as “Clean Acid Gas Header”, provides the means to smooth out the operation of the sulfur plant, through more stable flows. It is also possible to reduce and in most cases eliminate the need for acid gas flaring altogether.

The attached simplified flow diagram shows how a typical AGBL could be setup with respect to two or more operating sulfur plants.
**Design Considerations:**

**Amine/Claus**

If this sounds rather simple, well it is far from that. A lot of critical information has to be considered, the hydraulics, how much pressure drop do we have to work with, this will determine the line sizing. What about potential vapor condensation, now it has to be free draining, in effort to maintain vapor state ambient conditions need to be considered, which heating medium will be required, insulation type and thickness, control philosophy, etc.

First, the required line size and hydraulics must consider, the total distance from one SRU complex to the other SRU complex (can be as far as a mile a part from one another or further), and the pressure drop from the amine regenerators/strippers and tail gas unit strippers to all of the SRU furnace(s). Additionally, every possible scenario needs to be thought of; i.e. loss of one Claus plant with its amine regenerator operating at full rate (which could be higher that what the other Claus plant can recover).

Secondly, in order to provide maximum protection from liquid slugs to the SRU furnace the line should be free draining on all ends, to ensure liquid removal prior to entering the furnaces. Thirdly, jacketed piping/control/steam tracing and insulation requirements as well as ambient conditions have to be taken into consideration for maintaining a vapor state. Additionally, determine the best control
philosophy for individual unit needs; scenarios should be well thought-out and the best option implemented.

Let’s use a two Claus plant scenario as example. The flow of acid gas to at least one unit should be set up with a flow controller that will steady the flow of acid gas to that or those units. The remaining unit’s design would consist of pressure controller or a combination of pressure/flow controller. The unit with the pressure controller would be the swing unit, usually the one with the most room or flexibility.

**Tail Gas Units “SCOT” or “TGU”**

Whether the tail gas unit is of reducing gas generator (RGG) design or of other design (indirect heat input) is of little consequence. As long as there is enough heat and H₂ reducing gas available to complete reaction to conversion of SO₂ to H₂S.

Typically, with a reducing gas generator (RGG) design, the heating process is accomplished by combusting purchased natural gas or a clean hydrogen gas and mixing with the SRU tail gas in order to provide the required heat for conversion. There are a couple of disadvantages for this design, cost of burner management and refractory.

Indirect heating by use of a conventional shell and tube exchanger has been successful to heat the tailgas to the required temperature. The use of high-pressure steam, ~1000 to ~1200psig or a heat transfer fluid, have also been very successful. However, it may now be possible to use a medium-pressure steam, ~500 to ~600psig with the newer “lower temperature” catalysts. This works quite well with the excess steam from the SRU Waste Heat Boiler as a *free* source of indirect heating medium.

The main purpose of the TGU is to convert the (tailgas) SO₂ back to H₂S to be recycled back to the Claus for the recovery of the elemental sulfur in order to comply with regulatory emission requirements. With the AGBL, it is possible to route the recycled gas stream back to another operating Claus unit for recovery.
Operating/Control Parameters:
Consideration for other portions of the operations must be evaluated as well, controlling of the excess oxygen from the Claus furnace, TGU reactor temperatures (inlet/bed/outlet), downstream control of the quench water pH, contactor/absorber overhead excess H₂ concentration, etc.

Hydrogenation reactor temperatures become most important because of the reduced mass flow of SRU tail gas. This can cause the TGU reactor to heat up quicker and higher than desired. Normally, the utilization of the startup blower, with suction downstream of the quench column is employed to increase the mass flow in controlling of the reactor temperatures is required. Other designs include the use of air in conjunction with nitrogen for maintaining mass flow and controlling hydrogenation reaction temperatures.

In the Quench column, pH of the circulating water is the most important concern, in order to protect the downstream circulating amine. SO₂ excursions can potentially ruin the amine’s ability to absorb H₂S by creating Heat Stable Salts (HSS) that bind with the amine. There are a number of ways to buffer this circulating water consisting of the use of condensate, caustic or anhydrous ammonia. Buffering this circulating water can be automated using a reliable pH analyzer.

Since sufficient hydrogen must be present to provide hydrogenation of all sulfur species, a reliable H₂ analyzer is most beneficial, providing feedback for the control of the addition of hydrogen and can be automated as well. The hydrogen supply should be of good quality (concentration), with as few contaminates (components other than hydrogen) as possible.

Emission Reduction:
Well how does it all work?
During the “shutdown” phase of one the Claus plants, any ammonia gas processing is either routed to the other operating unit via NH₃ gas header, or ceased altogether (with water routed to storage tank(s). Since all amine regenerators and tail gas strippers, float on a common header (AGBL), during the “heat soak” or “sulfur burn out”, as acid gas is removed from the Claus process and purchased/natural gas is being introduced. The tail gas continues to operate as normal, ensuring that there is enough reducing hydrogen supply to complete the reaction to conversion of SO₂ to H₂S, as this stream is normally “recycled” back to the front end (Claus plant). Now this “recycle gas” stream is routed to the front end of another operating sulfur recovery unit. This process would normally continue until all sulfur has
been removed from the unit; typically 2-6hrs after no sulfur is observed from the condenser rundown (best to follow your company’s guidelines/policies/procedures).

An additional benefit of the AGBL is to continuously recover the majority of the emissions generated by the sulfur plant that is being shutdown. As mentioned previously the incinerator emission reduction can be quite significant, as much as 95% on average in some cases.

**How it’s done**

The desired unit for shutdown slowly and simultaneously reduces the acid gas and increases or begins natural gas firing. As the Claus becomes cleaner, (sulfur removed) the TGU continues to convert the SO₂ to H₂S and route the “recycle gas” to another operating Claus plant. As long as there is a sufficient heat source and reducing gas (hydrogen) for hydrogenation, the TGU will continue the conversion without causing downstream issues.

The TGU reactor converts contaminants in SRU tailgas according to the following reactions, in preferential order:

1. \( \text{SO}_2 + 3\text{H}_2 \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O} \)
2. \( \text{CS}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{S} + \text{CO}_2 \)
3. \( \text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2 \)
4. \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \)

As earlier mentioned certain operating parameters are vital to environmental success as well as unit reliability and will need to be controlled in order to protect the downstream circulating amine units.

By monitoring the hydrogenation reactor temperatures (ensures proper hydrogenation is occurring), as well as excess oxygen (to protect the catalyst against oxidation; although reversible not desired during this phase of operation), hydrogen availability/quality (to ensure conversion of SO₂ to H₂S) and as a final check the Quench water pH (low pH indicates lack of conversion), the unit can continue to reduce the overall emissions to the incinerator, all the while ensuring the integrity of the amine.
**Sour Water Ammonia Gas Considerations:**

One might ask, “If it works for amine acid gas, can it be designed for a Sour Water Acid Gas as well”, the answer is definitively yes. The design would be similar but, only flow control to either operating Claus plant is required. It can control the flow of Nh₃ gas to either Claus plant or to isolate from one as needed, altogether. As previously mentioned, by maintaining steady flows into the Claus plant, allows operation closer to existing constraints allowing additional capacity, while minimizing operational and environmental concerns.

Again, the design will have to be well thought out and similar design conditions as that of the amine acid gas balance line and will have to be considered and implemented; considering the hydraulics (length and size of line), the amount of pressure drop (from Sour Water Stripper to Claus plant), preventing the potential for liquid slugs (free draining), heating medium (jacketed piping/contro/steam tracing), insulation type, etc. Even though ammonia gas has different physical/chemical properties than that of amine acid gas, both have similar design requirements.
**Conclusion:**

A properly designed “acid gas” or “ammonia gas” balance line can be very useful in improving unit stability and increasing unit throughout by operating closer to unit constraint(s). During an operational upset, such as the loss of a Claus plant, the ability to immediately swing the load from one unit to another becomes much more advantageous (exceeding any fuel gas H₂S limits or contactor/absorber products being off specification, potentially causing either in plant or off site customer concerns). No more shedding of upstream water injections for corrosion concerns and don’t forget about the possibility of having to store or “stack” large amounts of sour water due to the loss of a Claus plant. Not to mention no longer having to take drastic measures; significant reductions in upstream units, as means of controlling sulfur load; can not only ease the role of the operator but, is viewed to be much more advantageous by management.

The prevention of environmental events is always favored; especially by management, as well as which could place facilities in a much more favorable position with regulatory agencies. Even though our industry strives to continuously improve our environmental stewardship and gain respect from the various communities; one mishap sets us all back to an unfavorable view in the community’s eyes.