Question 25: What are your key factors around amine contactor operation in hydrotreating units?

JOE RYDBERG (CITGO)
The biggest key factor in amine contactor operation in hydroprocessing units is controlling the lean amine flow and the lean and rich amine loading. We have seen corrosion in rich amine piping likely due to elevated H2S loadings and higher velocities (both lean and rich), especially when unit rates are changed quickly.

Adjust amine circulation to maintain desired rich amine loading (Typically 0.3-0.45 mol total acid gas / mol of amine loading). Ensure sufficient amine by:
- Sampling rich amine and determining H2S loading for optimization (reduce amine circulation)
- Controlling lean amine flow based on temperature rise of amine coming in or out of contactor (relatively new)
- Set minimum amine circulation based on maximum H2S recycle content
- When pushing unit rates, amine loading, fluctuations in pressures and flows can “overwhelm” the amine and H2S can breakthrough.
- Develop calculation tools to estimate sulfur load and set lean flow rates accordingly.

Adjust amine regenerator to maintain desired lean amine loading to meet FG H2S specifications.

There have been upsets in the sulfur unit due to hydrocarbon carryover into the amine. Typically this is caused by large hydrocarbon carryover events (Loss of HPS levels, upstream Hydrocarbon fractionators). Hydrocarbons cause foaming, solids will contribute to that as well. The amine system has to be kept clean (filtered).
- Amine temperature typically controlled to 120-130F for H2S control (less critical for MDEA based systems)
- Properly designed wash water trays designed and installed to minimize entrainment / carryover of amine into recycle gas compressor (4 trays, with a water circulation to provide adequate tray loading)
- Process inlet temp should be maintained 10 degF above amine temp for vapor hydrocarbon systems to prevent condensing
  - Less of a risk of condensing Hydrocarbons in Recycle H2 amine contactors

ROBERT STEINBERG (Motiva Enterprises)
Amine absorbers that remove H2S from a gas phase stream need to be operated with the proper amount of amine, at the right temperature and without liquid hydrocarbons.

Amine rates need to be high enough to remove the H2S in the sour gas and to keep the H2S concentration in the rich amine low enough to avoid corrosion. In low pressure service, such as a stripper offgas going to fuel gas, only a limited amount of H2S can be captured by the amine and the

amine rate needs to be adjusted to control the H2S content of the sweet gas.

In a higher pressure contactor, such as in the recycle gas loop of most hydrotreaters, high concentrations of H2S can be captured by the amine. Allowing the rich amine to be saturated with H2S in a Recycle Gas Scrubber would lead to excess corrosion in carbon steel lines and equipment. Normally, the amine rate has to be adjusted to maintain the H2S loading in the rich amine within acceptable limits. Typically, at these amine rates there is minimal H2S remaining in the sweet gas and changes in the amine rate have negligible impact on the remaining H2S in the sweet gas. The maximum H2S loading in rich amine is normally expressed in units of moles H2S per mole of amine, the maximum acceptable limit depends on the type of amine used.

Liquid hydrocarbons should be avoided in gas-phase amine contactors as they tend to cause foaming. Liquid hydrocarbons are prevented by:

- Avoid carryover of liquid hydrocarbons in the sour gas to the scrubber. This requires proper sizing of the upstream separation vessel like a Cold Separator with good internals. As a minimum there should be some sort of inlet device to help separate gas and liquid in the Cold Separator and a mesh pad below the vapor outlet nozzle. In some cases, particularly if the unit charge rate has been increased, more sophisticated devices like a cyclone separator in the Cold Separator are needed. If the Cold Separator is not large enough, an additional knockout vessel on the vapor line between the Cold Separator and the scrubber may be helpful, such a vessel normally has internal cyclones to remove liquid carried over from the Cold Separator.
- Keep the lean amine to the scrubber hotter than the sour gas to the scrubber to prevent condensation of hydrocarbons. A minimum 10°F margin is typically used but in some cases such as very high pressure units, margins of 20-30°F may be needed. It is often a good practice to provide a lean amine heater to heat the amine up to required temperatures as there may be limited ability to provide additional cooling of the sour gas in the upstream Reactor Effluent Air Condenser (REAC). A lean amine heater would generally be provided upstream of the Lean Amine Pump so it can be a low pressure exchanger. Low pressure steam is normally an adequate heating mechanism. Avoid using higher temperature heating sources that would result in high skin temperatures and potentially degrade the amine – limiting maximum skin temperatures to less than 260°F or simply keeping temperatures lower than in the Amine Regenerator Reboiler is a good practice.
- Provide facilities to skim hydrocarbons from the sump at the bottom of the scrubber. Even with good upstream separation and high lean amine temperatures, some hydrocarbons will often accumulate. These hydrocarbons are generally insoluble in aqueous solutions and form a separate liquid phase, since the hydrocarbons have a lower density than amine solutions they tend to accumulate on top of the rich amine. Level control devices using a dP transmitter will give a false low level if a significant hydrocarbon layer is present. Measuring the hydrocarbon layer can be difficult as the amount of hydrocarbons in an external level gauge will not be the same as in the tower. Using a gauge with a small level range by first lowering the level until it is drained and then raising the level to the middle of the gauge will give the same amount of hydrocarbon in the gauge as in the vessel, this information can be used to decide how much material to skim. Alternatively, an overflow device can be provided in the vessel sump at around the 50-60% level to continuously skim whatever liquid is at this elevation.

ALFREDO VILLA (Haldor Topsoe, Inc.)
Several operating conditions should be maintained and evaluated to determine the condition of the

amine system. A properly operating amine contactor will yield a clean recycle hydrogen stream and minimize impact to downstream amine regeneration equipment.
Operating with a clean amine should mitigate potential foaming, corrosion, and heat stable salt build-up in the absorber system. Monitoring the concentration and circulation rate of the amine used is crucial to maintaining good operation in the absorber. These parameters will allow for adequate hydrogen sulfide absorption and maintain target recycle gas concentration. An adequate concentration of amine will reduce the potential of corrosion in the system by maintaining low rich amine loadings. A target amine strength will depend on the type of amine circulated and should be discussed with the amine vendor.
Periodic visual inspection of the amine should be conducted to note changes in color and solids content. Typically, lean amine has a pale-yellow color and should be relatively free of solids, a change in color could indicate an increase in corrosion rates. For example, a change from pale-yellow to dark green could indicate a change in the iron sulfide content of the amine and an increased solids content. Solids in the system could lead to erosion of the iron sulfide scale protecting the inside of the piping. Removal of this scale exposes unprotected metal, which could lead to further corrosion. Along with the removal of the iron sulfide scale, solids in the system could stabilize foam.
Temperature control is of importance in any amine contactor system as it can lead to poor acid gas absorption. The loading capacity of the amine is directly impacted by the lean amine temperature, the cooler the lean amine the greater its H2S removal capacity. However, it is recommended that the lean amine temperature is maintained warmer than the gas feed. Lean amine temperatures which are too low, increase the potential for condensed hydrocarbons, which could lead to foaming in the contactor. Feed gas temperature control is also recommended as a high feed gas temperature leads to a higher lean amine temperature, which reduces the capacity of H2S removal.

GARY BOWERBANK (Shell Global Solutions)
Solvent hygiene is high on the list. Poor solvent quality, which is often measured in terms of high degradation products (Heat Stable Salts) or high suspended solids, can lead to both corrosion and fouling of the system but also increase the risk of foaming events. These foaming events are the most common issue to impact operations of any amine contactor, which can result in losses of solvent (if carried over beyond KO vessel) or off specification product. Sites may often focus on treating the symptom by dosing an anti-foaming agent, however we prefer to understand the root cause and tackle that. If not linked to solvent quality; then entrainment or condensation of hydrocarbons in the contactors is the most common root cause. So, having high efficiency gas/liquid separators upstream and maintaining lean solvent at least 5oC above the gas temperature are critical.

ERIC LIN (Norton Engineering Consultants, Inc.)
Other than the type of amine used, the most important operational factors for amine gas contactors are temperature and pressure drop. Lean amine coming to the column should be at least 10°F (6°C) hotter than the sour gas to prevent condensation of hydrocarbons and cause possible foaming. Sometimes a LP Steam heater may be necessary if the lean amine is too cold from the ARU. On the other hand, if the lean amine is too hot (~25°F greater than the sour gas), there exists the possibility of appreciable amounts of amine carryover into the sweet gas. Contactors should also have alarms indicating high pressure drop normally caused by foaming. Most contactors should have the capability of periodically skimming the oil from the top of the rich amine in order to proactively prevent this from happening.

PRASAD HARDIKAR (Honeywell UOP)
The primary purpose of an amine contactor /amine scrubber is to remove H2S from the circulating recycle gas stream or remove H2S from hydrotreating unit off gases before blending hydrogen rich gas

with fuel gas.

Here are key factors to be considered in various stages:
Design/ Commissioning Stage:

- Remove oil or rust inhibitors present from construction

UOP always recommend degreasing of new/modified amine column with 2 wt% soda ash neutralization solution before putting it in service. Degreasing removes grease or protective oil layer on amine contactor /scrubber trays and internals which can contribute to foaming. Hydrocarbon layer is meant for protecting trays/internals from rusting during transportation and storage.
Operation:

- Limit hydrocarbons entering with recycle gas:
- Keep lean amine 3-5°C (5-9°F) warmer than inlet gas to prevent hydrocarbon condensation and consequent foaming
- Ensure mesh blanket in upstream knockout drum is working
- Lean and Rich amine loading:

Amine loading is expressed as mole loading of H2S per mole of Amine. Lean amine loading indicates efficiency of amine regeneration unit and capacity of lean amine to absorb H2S. Rich amine loading sets maximum H2S capacity for rich amine.
Higher rich amine loading increases potential for erosion in the rich amine lines due to two phase flow in the rich amine lines especially from downstream of rich amine control valve. This can have negative effect on the operation of the amine regeneration system as the lean amine will eventually become more contaminated with iron particles and have deficient performance. It is recommended to maintain rich amine loading < 0.4 mol acid gas/mol MDEA with KCS metallurgy lines.
It is quite tempting to reduce lean amine flow during operation from an optimization perspective. However, such reduction in flow with same acid gas (H2S) content increases rich amine concentration well beyond acceptable rich amine loading as amine will continue to absorb acid gas till saturation. Hence monitoring rich amine loading is a critical factor in amine contactor operation.

- Amine Appearance and Quality

Amine appearance and quality is one of the critical aspects to monitor.
It is observed that increase in total dissolved solids (TDS), total suspended solids (TSS), heat stable salts (HSS) enhances foaming tendency in lean amine. TSS are expected to be NIL and HSS at < 0.5% for lean amine solutions. These parameters are better controlled with mechanical filtration (with activated charcoal) and it may require replacement if foaming issue persists.
Lean amine displaying a green color is indicative of the presence of solubilized iron sulfides in the amine due to corrosion or issues with amine system filtering. Lean amine with a slight green color will continue to remove H2S from recycle gas adequately, but if soluble iron sulfide buildup in the amine is not eliminated, foaming could be a potential concern.

- Amine Color Guideline:

– Light straw = amine is in good condition
– Black or dark green = corrosion is taking place
– Light green rich amine = small particulates present

- Avoid excessive foaming inhibitor as this with increase foaming tendency
- As an operational task, regularly skim out hydrocarbon layer before it starts to build up

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