September 2010

Contamination in Amine Systems

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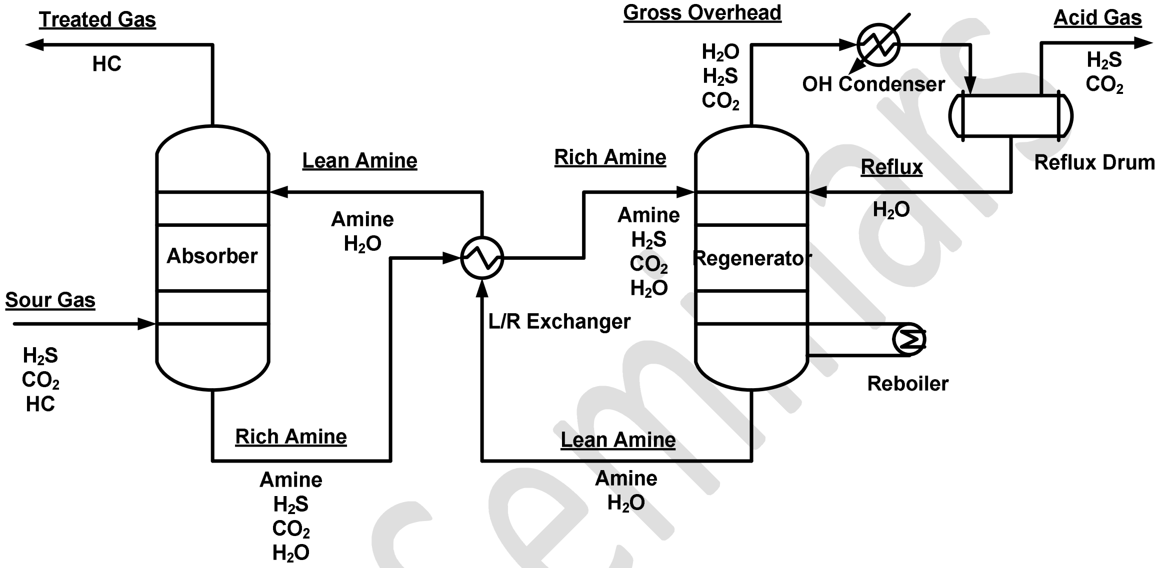
Let us consider a typical amine system:



Lean amine solution is circulated to the absorber or scrubber where it removes acid gases, hydrogen sulfide and carbon dioxide, from the feed gas to the scrubber. The rich amine flows from the scrubber to the regenerator where the acid gases are stripped out of the amine solution. Regenerated or lean amine is recirculated to the scrubber to absorb more acid gas.

Two operating truths impact the amine system. The first is the amine circulation is a closed loop. Anything that enters the solution will stay there until we do something to remove it.

The second is the absorber is often called a scrubber for very good reason. The intimate contact between the amine solution and the gas effectively removes acid gas by chemical reaction, water soluble materials since the amine solution is mostly water on a molar basis, and any solid or entrained liquid materials by contact.

The regenerator is designed to remove the acid gas. What else is there that can be absorbed by the amine solution and how will it affect operation of the amine unit and perhaps downstream units?

IMPACT OF CONTAMINATION

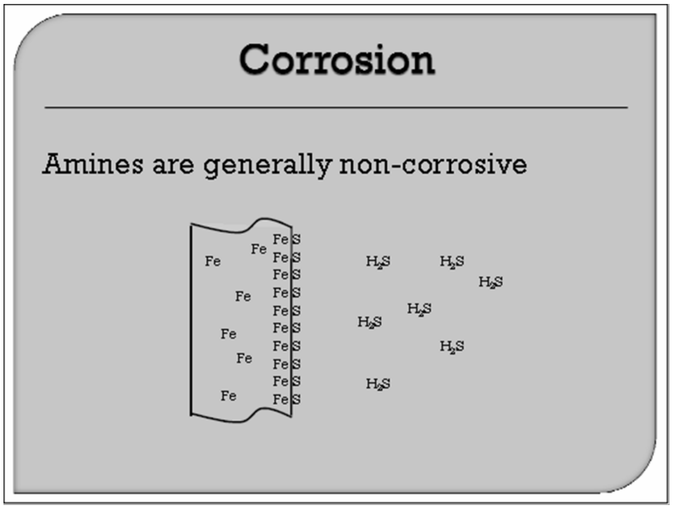
Amine Degradation

Amine quality has a strong impact on the good operation of the amine unit. Amine that is weak, dirty, or partially spent by heat stable salts (HSS) cannot do a good job of cleaning gas. “Free” amine, amine not bound by HSS, is the active ingredient for acid gas pick up. Target free amine strengths depend on the type of amine used. Heat stable salts (HSS) in amine solution are those amine salts that do not break up at regenerator conditions. These salts tie up amine molecules, which then cannot react with acid gas, and can lead to fouling and corrosion.

Acidic anions can come from the gases being treated (HCl, HCN, SO_2, formic acid, and the like), from oxygen in un-blanketed tanks or from vacuum columns, and can be formed in the amine solution. For example, formic acid can form from CO and the OH^- in the alkaline amine solution and several organic acids (including formic acid) are products the hydrolysis of nitriles formed in cat crackers. Though they are not strictly speaking salts, polymeric and other organic amine degradation products are often included in the HSS category.

Foaming

Amine solution becomes frothy when vigorously agitated as on a tray in a gas absorber or regenerator. Fortunately, this froth quickly subsides in good quality amine solution and the column functions normally. However, this froth can be stabilized by altering the surface properties of the amine solution or more commonly by the presence of a third phase in the column. The third phase can be solids such as iron sulfide or it can be a second liquid phase such as hydrocarbon. The third phase occurs at the gas-liquid interface. The froth does not break in the tray downcomer as it does in normal operation and a situation analogous to jet flooding occurs. Pressure drop increases across the column, operation becomes unstable, and capacity is reduced.

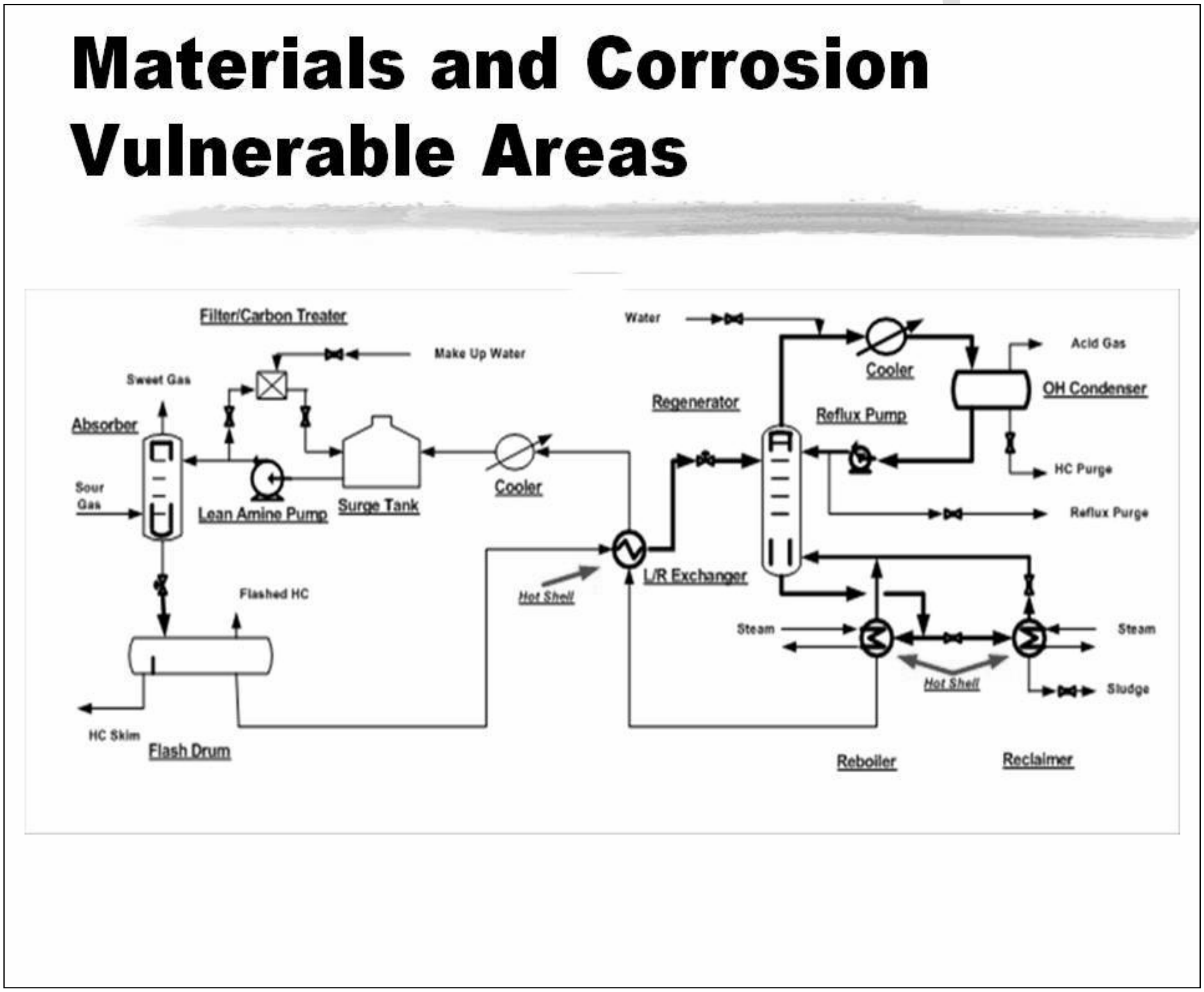


Corrosion

Amines are generally non-corrosive

Corrosion

In general, all amines are considered non-corrosive. Much of an amine unit is built of carbon steel. Steel reacts with H_2S to form a layer of FeS on the surface that protects the steel from further attack. As long as the layer of FeS is intact, the overall corrosion rate is quite low. The iron sulfide layer is soft and friable; it can be worn away by high flow velocity or turbulence. High HSS content increases the viscosity and density of the amine solution. At the same time if higher amine solution circulation rates are required to circulate enough free amine to pick up the acid gas, solution velocities go up. This combination can result in erosion of the protective iron sulfide layer exposing bare steel to further sulfidic attack and higher rates of corrosion.



Materials and Corrosion Vulnerable Areas

This figure shows areas prone to accelerated corrosion. These are generally areas that are hot, exposed to flashing acid gas, and areas subject to turbulence.

Other contaminants that could accelerate corrosion include:

- Excessive ammonium bisulfide or cyanide in the regenerator overhead; both compounds can penetrate the iron sulfide protective layer and attack steel.
- High levels of chloride ions in the amine solution can attack the stainless steel alloys used in corrosion prone areas of the amine unit.
- Excessive acid gas loading, above 0.5-0.6 m/m in the rich amine; not really a contaminant since the objective of the amine unit is to pickup acid gas. However, loadings above about 0.5 moles of acid gas per mole of amine forms the amine-bisulfide salt. The bisulfide ion can penetrate the iron sulfide protective layer and cause accelerated corrosion of carbon steel.
- Oxygen and wet steel rapidly can result in scale or rust formation. This is most likely to happen during startup or turnaround. The oxidized iron in the pipe scale is immediately converted to iron sulfide. This iron sulfide is not bonded to the pipe wall so does not form part of the protective iron sulfide layer. The iron sulfide formed in this manner is free to circulate in the amine solution.
- Solids in the solution, primarily iron sulfide, can be abrasive to the iron sulfide protective layer, exposing new steel surface to sulfidic attack.

Fouling

A common problem in amine systems is the accumulation of sludge or scale on column trays and in still or low velocity areas of the unit. Scale formation on trays leads to gradual choking of the hole area that gas needs to flow up the column. This can result in jet flooding and loss of gas capacity in the column. Areas with low flow velocity such as the rich amine flash drum often accumulate sludge; as the sludge accumulates it robs volume from the vessel and if re-entrained adds to the solids load of the circulating amine. This sludge is often referred to as “shoe polish”; it looks and feels much like black shoe polish or wax. It is thought to contain a mixture of contamination products – iron sulfide, heavy hydrocarbons, polymeric amine degradation products, and other solid material.

SRU Problems

Some of the contaminants that enter the amines system get removed in the regenerator and then get sent to the sulfur recovery unit. Of primary concern to the SRU is ammonia and hydrocarbons in the acid gas feed. The sulfur plant uses oxygen from air that is pumped into the unit to convert H_2S to elemental sulfur. Overall reaction is:

$$H_2S + \frac{1}{2} O_2 \rightarrow S + H_2O$$

The amount of oxygen, generally provided by atmospheric air pumped into the sulfur unit by an air blower, added to the sulfur plant is the essential control variable for efficient sulfur plant operation. On a volume basis, both NH_3 and hydrocarbon consume more oxygen in the sulfur unit than required for the conversion of H_2S to sulfur.

$$NH_3 + \frac{3}{4} O_2 \rightarrow N_2 + H_2O$$
$$C_2H_6 + 3\frac{1}{2} O_2 \rightarrow 2\ CO_2 + 3\ H_2O$$

Typically, the first limit in sulfur plant capacity is volume and pressure the air blower can deliver. So both ammonia and hydrocarbon rob the sulfur plant of capacity.

In refineries, ammonia is often intentionally disposed of in the sulfur unit. Even though sulfur capacity is given up, the sulfur plant can be designed and operated to effectively destroy ammonia, a noxious and toxic gas. A necessary condition for this operation is introducing the ammonia properly to the sulfur plant so it can be destroyed. If ammonia enters the sulfur plant in the acid gas feed it may not be destroyed and can lead to deposition of ammonium salts in cooler parts of the sulfur plant with resulting plugging, pressure drop and localized corrosion issues.

Hydrocarbon in the acid gas feed is not controlled by the sulfur plant operators. And a bigger problem is the amount of hydrocarbons in the feed will change with time. This presents a control problem at the sulfur plant.

Another problem caused by hydrocarbons in the sulfur plant feed is the potential to form soot in the main burner flame. Any soot formed will eventually be collected on the catalyst bed. The soot can physically block the active sites of the catalyst reducing bed activity. If enough soot accumulates, the pressure drop across the bed increases and affects the unit capacity.

Environmental Violation

Should the level of contamination rise to a point where they interfere with good operation of the amine unit, direct violation environment permit may occur. For example, high sulfur in fuel gas system in the refinery. Poor treating in a gas plant can result in the sales gas failing to meet pipeline specification.

Poor control of air in the sulfur plant caused by contaminants in the acid gas feed can lead to poor sulfur recovery in the sulfur plant and resulting high SO_X emissions from the tail gas thermal oxidizer. Classic upset in a sulfur unit results from a slug of hydrocarbon in the acid gas. The hydrocarbons consume the oxygen at the main burner resulting in a high H_2S to SO_2 ratio in the SRU tail gas. The tail gas analyzer calls for more air to the burner to correct the off-ratio operation. The hydrocarbon slug passes through the sulfur unit; the air rate remains high driving the SRU tail gas to high SO_2. During this swinging air supply scenario, the sulfur unit is operating inefficiently and so leaving excessive unrecovered sulfur compounds in the tail gas. There is a strong possibility for high SO_X emissions in the stack during such an episode.

In a worst case scenario, there is a selective amine based tail gas treating unit removing sulfur from the SRU tail gas. During the air control upset high concentrations of SO_2 can be sent to the tail gas treating unit. If the SO_2 reaches the tail gas treating unit amine system it will react with the amine to from heat stable salts.

SOURCES OF CONTAMINATION

Feed Gas

Most contaminants probably enter the amine system in the feed gas. Ammonia is a gas that is readily absorbed by the aqueous part of the amine solution. Ammonia can cause corrosion in the amine unit and operability problems in the SRU. Organic acids like formic acid and mineral acids like HCl that can contribute to heat stable salt formation are found as volatile materials in the refinery. Amine is an organic chemical so there is some natural affinity for hydrocarbon gas to dissolve in the amine solution. This is a physical phenomenon favored by the higher molecular weight amines such as MDEA or DGA, higher concentration amine solutions, and at higher pressures such as in gas plants or in high severity hydrogen processing units in the refinery. Oxygen can contribute to amine degradation and to corrosion.

Hydrocarbon

Hydrocarbons can enter the amine system in the liquid phase. Feed gas to a scrubber is almost always a hydrocarbon gas from a single-stage flash operation separating vapor and liquid. In a perfect separation, the vapor is at its dew point. A poorly designed or overloaded separator will allow some liquid to flow out in the gas phase as a mist of liquid droplets. Any cooling of the gas stream will likewise result in condensation of the heavier components in the gas stream. The intimate gas-liquid contact in the scrubber will remove any liquid droplets from the gas stream.

A special case is liquefied Petroleum Gas treating. LPG can be physically absorbed by the amine solution. It can also be carried under from the LPG contactor in the rich amine stream exiting the treater.

Make Up Water

Fresh amine is usually delivered to the plant as 100 % or 85 % amine and must be diluted to target solution strength. Virtually all amine systems lose water from the amine solution during normal operation. The amine solution loses water as water vapor in treated gas at the absorber and some water is continually lost to the sulfur recovery unit in the acid gas from the regenerator. Water is frequently purged from the regenerator overhead to control ammonia in the reflux system.

Therefore, water is added to the amine system routinely. Contaminants in the water will accumulate in the amine solution. Steam condensate is the water of choice. Boiler feed water may contain sulfite oxygen scavengers, phosphate corrosion inhibitors, and filming amines. City water may contain considerable calcium hardness, sodium, some chlorine, and may be high in chlorides. The key is to know what is being added to your amine, and how to remedy to contamination.

Oxygen

The most obvious source of oxygen contamination is an amine surge tank breathing freely to atmosphere. Less obvious sources involve the feed gas. Leaks in compressor suction piping can occur in natural gas collection networks. In refineries, vapor recovery systems and flare gas recovery systems are common sources of oxygen in the gas feed to a fuel gas scrubber.

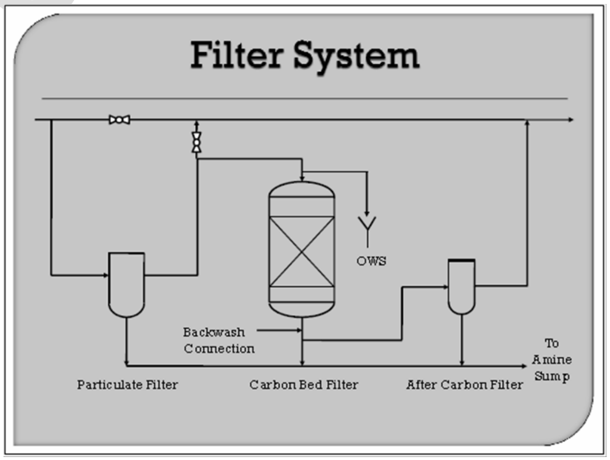
Startup/Turnaround

Pipe scale readily forms on steel exposed to air, especially in the presence of moisture. This is a common occurrence at unit startup and during maintenance turnarounds. Any pipe scale or rust in the unit when H_2S is introduced gets immediately converted to iron sulfide. And this iron sulfide is not bonded to the pipe and equipment walls so it is carried away by the circulating solution.

REMEDIES FOR CONTAMINATION

Particulate Filtration

Corrosion in the amine system produces fine iron sulfide particles. Solids can also enter with the treated gas. Excessive solids (> 200 - 400 ppm wt) can cause foaming. Solids also tend to scour off the protective iron sulfide scale in piping and promote corrosion. Removing these solids by filtration is essential to reliable operation of the amine unit. Filtration is typically done on the lean amine to minimize odor and potential safety problems when opening the filter vessel. Filtering the rich stream is done, and may be marginally more efficient. A variety of filtration systems are in use.



Wound cartridge filters, bag filters, and automatic backwash filters are the most popular filters. Filter element change out is done on a pressure drop basis. The rate of filter change out is a rough measure of the corrosion rate in the unit.

Carbon Beds

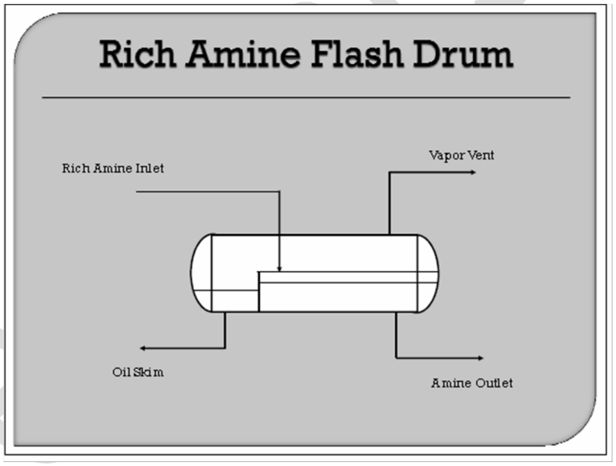
Soluble, surface active contaminants in amines may cause foaming. Because they are dissolved, these contaminants are not removed in the particulate filter system. Many amine systems use activated carbon treaters to remove surface active contaminants and traces of hydrocarbon. Particle filters are provided upstream of the carbon filter to avoid plugging of the carbon bed with solids.

Life of the carbon should be monitored by visually inspecting the amine in and out of the carbon filter. There should be a perceptible color change and reduction of amine foaming tendency across the carbon filter. Typical carbon life is six months to a year. Carbon filters are generally not effective in controlling hydrocarbon content of the amine solution. The carbon will only hold about 30% of its weight in contaminants. The principal reason for using carbon filtration is to remove dissolved surface active materials that would cause foaming.

Hydrocarbon Skimming

Rich Amine Flash Drum

Rich amine from gas and liquid absorbers is saturated with hydrocarbon and has the potential to upset the regenerator and the sulfur recovery unit. To remove most of the hydrocarbons, rich amine from various absorbers is collected in a flash drum. The drum should be designed with enough amine residence time to allow complete separation of hydrocarbons. Skimming facilities should be provided to remove and recover the hydrocarbon.



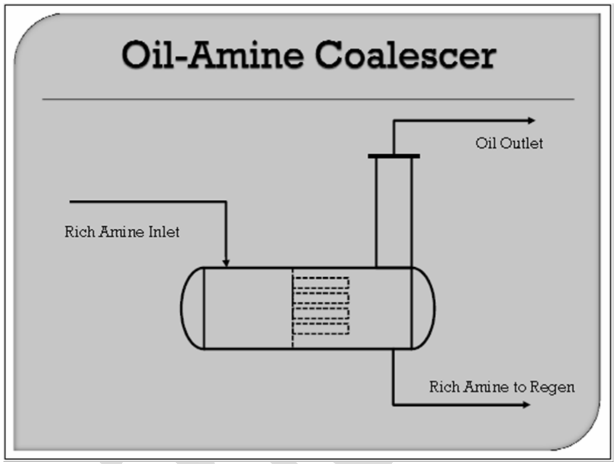
Skimming can be done with a system of over-and-under baffles or with a simple nozzle. This will depend, in part, on where the amine circulating inventory level swings are to be taken.

The flash drum operates at a pressure high enough to get amine into the regenerator without pumps (3.2 - 4.6 BarG or 45 - 65 PSIG), or at a low pressure set by a vapor recovery system or a firebox (0.1 - 1/0 BarG or 1 - 15 PSIG). Observation of operating units suggests that the lower pressure option removed more hydrocarbon and lead to fewer upsets downstream

Other skimming locations

Anywhere there is a still amine level an opportunity exists for a separate hydrocarbon layer to form. Commonly, the regenerator overhead accumulator drum has an oil overflow baffle and hydrocarbon skimming. Hydrocarbons that get stripped out of the amine solution in the regenerator and then are condensed in the overhead system accumulate in this drum. Less commonly, skimming connections are provided at levels in column bottoms – especially the scrubbers and at the lean amine surge tank.

Oil Coalescer on Regenerator Feed



Rarely seen but gaining increasing acceptance is using an oil-amine solution coalescer on rich amine feed to the regenerator. The oil-amine solution coalescer should follow a full-stream particulate filter on the rich amine stream. This arrangement protects the amine regenerator from fouling and is effective in limiting hydrocarbon contamination of sulfur plant acid gas feed. One user with this arrangement processes refinery amine solution and reports ten-year turnaround cycle on the amine regenerator with virtually nil hydrocarbons in sulfur plant feed.

Handling Heat Stable Salts

If the waste water treating facilities can handle it, HSS content of amine solution can be controlled by purging amine solution to the WWT and making up with fresh amine and water. Unfortunately, this option is not available at most locations. Various amine reclaiming processes can be used to reject the HSS. The primary amines, MEA and DGA, can be thermally reclaimed at amine unit operating conditions. DEA and MDEA will start to decompose before they reach their ambient pressure boiling points so other techniques must be used.

Vendor Reclaiming

All amines can be reclaimed by vendors who bring specialized equipment to the plant. Techniques include vacuum distillation, ion exchange, or electrodialysis (membrane). There are potential issues to be considered when using on-site reclaiming. If they bring in their own heater; permitting might be required to account for emissions and there is also the hassle of setting up mobile facilities onsite.

Increasing use is being made of “kidney units”. Kidney units are small, permanently installed ion exchange systems that continuously treat a small slip stream of the circulating amine solutions to control HSS buildup.

Amine Regenerator Reflux Purge

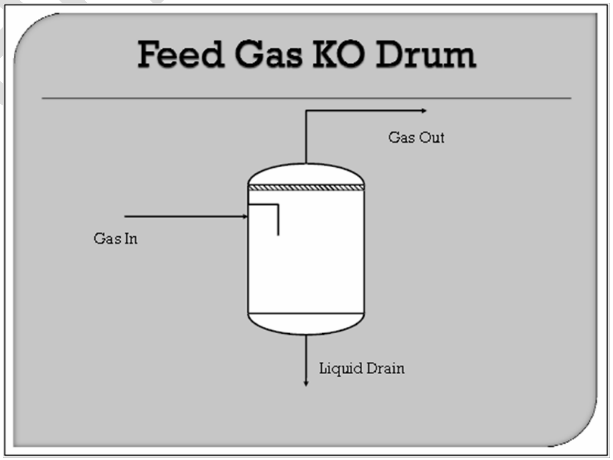
Volatile contaminants, in particular ammonia, will accumulate in the regenerator overhead reflux system. A controlled purge of this stream can control the concentration of ammonia to limit the corrosion potential of ammonium bisulfide. The purge can also be used to limit the ammonia content of the acid gas feed to the sulfur unit.

PREVENTION OF AMINE SYSTEM CONTAMINATION

A better approach to limiting the operating problems of contamination in amine systems is to prevent the contaminants from getting in the amine solution. Gas streams fed to gas absorbers typically come from a column or exchanger saturated with water and hydrocarbon liquids. Any cooling of these streams will cause these materials to condense. If they are not removed, they will cause foaming or contamination of the amine in the absorber. For these gas streams, commonly used equipment includes knockout drums, filter-separators or a water wash drum or column.

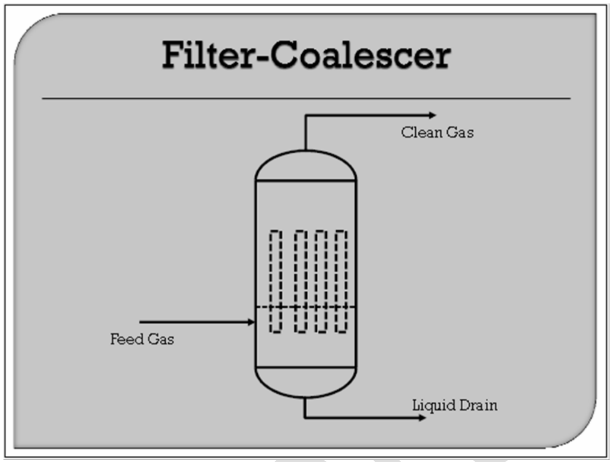
KO Drums on Feed Gas

A scrubber inlet knock-out drum functions to catch entrained hydrocarbon liquids and occasional slugs from the feed gas. A KO drum is essentially a wide spot in the pipe allowing liquids to drop out of the gas flow. Demister pads are commonly used to facilitate the separation of mist or liquid droplets from the gas stream. Demister pads are effective over a limited range of gas velocity.



Filter-Coalescer on Feed Gas

Proprietary filter-coalescers are common in natural gas plants and gaining increasing use in refineries. Proprietary Filter-Separators are available from several vendors. They are typically two-stage devices with replaceable filter elements. The first stage removes solid material from the gas stream. The first-stage filtration protects the elements in the second-stage coalescer from being blinded by the solids. The second stage coalesces any fine droplets or mist in the gas stream into larger, heavier drops that are easily separated from the gas stream. Proprietary filter-coalescers can be very effective for both liquid and solid contaminants over a wide range of operating conditions.



Water Wash

A water wash drum is a column used to water wash gas streams from an FCC, Coker, or Vacuum Unit that may contain cyanides, acids, ammonia or particulates. A circulating water stream removes these contaminants. Liquid is bled to the sour water system. Sour water stripper feed is commonly used as make-up because the ammonia is a good buffer and this minimizes refinery sour water.

Lean Amine Temperature

An important absorber control variable is the difference between the inlet amine temperature and the inlet gas temperature. Most feed gas streams are saturated; if they are cooled, liquid hydrocarbons will condense. Condensed hydrocarbons can cause severe foaming in the absorber. By keeping the lean amine temperature 5°C (10°F) hotter than the feed gas temperature assures the operator that condensation will not occur in the scrubber.

Unit Preparation at Startup

An alkaline wash before putting new equipment or following a maintenance turnaround can remove pipe scale and rust from the equipment and piping. This procedure avoids converting the pipe scale to iron sulfide when H_2S is brought into the system. It will also clean up any grease or oil used for shipping protection or fabricating that would otherwise end up the amine solution and contribute to foaming. The alkaline wash must be followed by a good rinsing procedure to prevent contaminating the amine solution with caustic. The final wash is often a dilute amine solution.

Oxygen

The first step in preventing O_2 contamination is to make sure the amine solution is not exposed to air. Inert gas blanketing of the lean amine surge tank and amine sump are commonly provided. If the O_2 is entering with the feed gas to a scrubber, the oxygen leak must be found and corrected at its source.

Iron Sulfide

There is not much that can be done to prevent the formation of iron sulfide in a system that contains H_2S. Good design practice includes low amine solution velocity especially in the rich amine piping to prevent eroding the sulfide layer. Alloys such as stainless steel are used in those areas prone to accelerated corrosion.

CONCLUSION

Contamination costs are more difficult to quantify than energy costs or amine loss costs. However, if the contaminant level is allowed to get high enough to cause operating problems, the cost can be surprisingly high.

A principal contaminant of concern is the amine heat stable salts (HSS) formed when strong acids or oxygen react with the amine solution to make amine salts that will not regenerate with the limited heat available in the regenerator. HSS reduce the capacity and reliability of the amine unit. Addressing high HSS often involves bringing in a vendor to reclaim the amine solution incurring more costs.

A second major contaminant is suspended iron sulfide solids in the solution. These solids contribute to foaming, plugging and fouling of equipment. In addition, it becomes necessary to change out filters more frequently. Other solids, like carbon fines, have the same bad effect on the operation of the amine unit.

Hydrocarbons are a common contaminant in an amine system. They can affect the amine unit directly by causing foaming. Excess hydrocarbons generally end up in the acid gas feed to the sulfur plant contributing to operability problems for the sulfur recovery unit. Control is by flashing at the rich amine flash drum and skimming at the flash drum and other locations such as the regenerator overhead accumulator. A filter-coalescer arrangement on rich amine feed to the amine regenerator is an effective control for hydrocarbon contamination.

Preventing contaminants from entering the amine system is a good strategy to mitigate the operating problems posed by contaminants.

Knock out drums on scrubber feed gas provide some protection to the amine solution from hydrocarbon carryover. Filter-coalescers on the feed gas are much more effective in removing solids and liquid mist from the incoming gas.

Water wash on suspect feed gas streams has been used effectively to prevent accumulation of water soluble contaminants such as organic acids and ammonia.

Maintaining lean amine temperature hotter than the feed gas to a scrubber prevents hydrocarbon condensation in the scrubber.

Insuring makeup water is contaminant free prevents accumulation of those contaminants.

While industry has learned how to mitigate the effects of contamination on amine system operation, preventing the accumulation of contaminants in the amine system may be a better approach to good amine system operation.

This table shows a matrix of contaminants, impacts, remedies and prevention of contamination of amine systems:

Contaminant	Source	Impact	Remedy	Prevention
Heat Stable Salts	Acidic compounds Oxygen Feed gas	Binds amine Increases density and viscosity Corrosion	Purge and Makeup Reclaiming	Water wash feed gas Inert gas blanket surge tank
Iron Sulfide	H_2S Corrosion	Foaming Fouling Erosion/corrosion	Filtration	Limit amine velocity S/U Procedures
Other solids	Feed gas Pipe scale Carbon bed	Foaming Fouling Erosion/corrosion	Filtration	Filter-coalescer on feed gas
Hydrocarbons	Feed gas Condensation LPG Treating	Foaming Fouling SRU operability SRU capacity SRU Pressure drop	HC skimming Filter-coalescer on regenerator feed	Filter-coalescer on feed gas Maintain lean amine temperature
Oxygen	Unblanketed tank Feed gas	HSS Corrosion	Inert gas blanket tank	Locate and repair feed source O_2 leak
Ammonia	Feed gas	Corrosion SRU operability SRU capacity	Regenerator reflux purge	Water wash feed gas