

Causes of Amine Plant Corrosion- Design Considerations

Sidney F Bosen, Ph.D.
The Dow Chemical Company
335 Pennbright, Suite 120
Houston, TX 77090

ABSTRACT

Some mechanical designs usually found in amine plants that have been found to be the cause of corrosion are presented.

INTRODUCTION

Aqueous mixtures of alkanolamines and/ or alkylalkanolamines (amine) have been used in a regenerable process to remove acidic contaminants, usually hydrogen sulfide (H₂S) and carbon dioxide (CO₂), from process and natural gas streams for over 60 years. This activity is driven by either product specification necessary for sale, e.g. natural gas that contains less than 4 ppm(v) H₂S, or by avoidance of environmental emission permits, e.g. fuel gas with less than 160 ppm H₂S. Plant economics are negatively impacted by the loss of revenue due to unplanned corrosion caused plant outages and the cost for repair of the corrosion damage².

Figure 1 gives a generalized overview of an amine plant.. Acid gas is removed from the gas stream or light hydrocarbon liquid stream by counter current reactive absorption with an acid gas lean (lean) aqueous amine solution in a multistage (trayed or packed) absorber tower, operated at the pressure of the feed gas/ liquid stream. Since hydrocarbons and other non-reactive gases also dissolve in the aqueous amine solution, many process designs recover these by pressure reduction in a flash tank, which is configured so gases are separated from liquids and, if needed, hydrocarbon liquids can be skimmed from the aqueous phase. Some acid gas may also flash with the recoverable gases. Amine solution chemistry permits acid gas removal from the rich amine solution at elevated temperatures. The process is facilitated by counter current steam stripping in a multistage (trayed or packed) regenerator tower, operated at low pressure. Stripping steam, which is used for heating and acid gas dilution, is usually generated in a reboiler that takes its feed from the regenerator tower below steam stripping section. Condensing water from the effluent water/ acid gas stream from the top of the regenerator helps minimize water usage. Acid gas separation from the condensed water is done in the reflux accumulator. Specific plant design determines point of water return, e.g. top 4 trays of the absorber or regenerator to conserve amine losses. Energy is conserved by preheating the rich solution prior to entering the regenerator with the hot lean solution from the regenerator in the lean/ rich heat exchanger (L/R HEX). Low pressure booster pumps are sometimes used to pump the hot lean solution from the reboiler/ basin of the regenerator tower through the L/R HEX and lean amine cooler to a surge tank in front of the high pressure amine pumps. Depending on pressure and volume requirements, positive displacement or multistage centrifugal pumps are used to pump the lean solution to the top of the absorber tower.

Many of the causes of amine plant corrosion have been identified and reported earlier, see Nielson et al for a comprehensive literature review up to 1994². Among those factors identified are choice of amine, acid gas, acid gas ratio, contaminants and operating conditions. While mention of good design practice for corrosion control has been made by a number of authors, for example see Kohl and Nielson³, conflicts arise when normal design practice is applied from other engineering specialties. Examples where corrosion is caused by design are presented.

Discussion

ABSORBER

Since acid gas absorption releases heat and the majority of absorbers are not insulated, water vapor condensation on wall surfaces not wetted by the amine solution can occur. If CO₂ is the only acid gas present, or when a very low level of H₂S is also present with the CO₂, carbonic acid will form and may be very aggressive to carbon steel. This is especially true for the vapor space at the bottom of the absorber. Submerging the inlet gas distributor² reduces the possibility of carbonic acid attack by spraying rich amine solution onto places of the carbon steel vessel wall between the bottom tray or bed support and normal liquid level not usually wetted by the amine solution. If the inlet gas distributor is submerged, extra care must be exercised to ensure the fasteners do not fail from the strong vibrations caused by bubbling gas through the liquid. Failure of the fasteners of a submerged inlet distributor can also result in erosion of the vessel wall. When the inlet nozzle is above the liquid level, any entrained solids or liquids may erode the absorber wall opposite the inlet nozzle by impingement. If the absorber is too small for an inlet gas distributor and when the inlet nozzle is below the liquid level, rising bubbles can impart enough velocity on the liquid to cause erosion of the vessel wall.

Failure of the rich amine exit nozzle presents a significant safety issue. A vortex breaker above the rich amine exit nozzle helps ensure gases are not entrained with the exiting liquid. Some vortex breaker designs create sufficient pressure drop to form bubbles in the flowing liquid that leads to cavitation of the rich amine exit nozzle wall.

Tray designs may accelerate corrosion/failure of the tray deck and moving parts. Sometimes the passage of gas through the valve results in high velocity liquid moving over and eroding deck surfaces. Mechanical wear can occur in some instances when the moving part has unintended motion, e.g. a circular valve spins in addition to moving up and down. For CO₂ removal, some designers use carbon steel tray decks with fixed valves to reduce costs. During shut downs, planned or unplanned, complete drainage of the amine solution from the tray deck increases the potential of carbonic acid attack especially if the outage is long enough for vessel wall cooling and condensation of water vapor.

At the treated gas exit or top of the absorber and the outlet separator (used for amine recovery), there is also a risk of carbonic acid attack, even when H₂S represents the majority of the acid gas removed. The treated gas stream is fully saturated with water and usually cools as it flows to downstream processing equipment. Condensed water in the presence of very low levels of CO₂, still produces carbonic acid, whereas very low levels of H₂S are likely to accelerate rather than retard carbonic acid caused corrosion.

Level Control/ Pressure Reduction Valves/ Isolation Valves

Many process control engineers specify control valves that are smaller diameter than the flow lines connected to it. While this enhances control characteristics, it increases the potential for corrosion, as flow velocities in the valve body become much greater than recommend by API 945⁴ for flow lines. Upgrading metallurgy is often used to mitigate this problem in the valve body and trim. Piping transitions to and from the smaller diameter control valves are often overlooked and should also have the same metallurgy upgrade. Absorber level control valves also benefit from additional hardening of the valve body and trim surfaces, especially when there is a sizable pressure reduction which results in erosive two phase flow.

Slug or plug liquid and vapor two-phase flow is expected down stream of the absorber level and flash tank control valves as the piping is not sized to produce either stratified gas/ liquid or annular liquid flow. Flash tank level control valves should be downstream of the L/R HEX to minimize the formation a vapor phase, from acid gas stripping or water boiling, in the L/R HEX. To reduce the length of pipe exposed to erosive slug/ plug flow, the level control valves should be placed as close as possible to downstream equipment, e.g. flash tank or regenerator. Two phase flow may also be induced in pressure control valves, diverter valves and measurement orifices.

Isolation valves are necessary for safe operation of the plant. Often the design and placement of the valve is neglected. Some gate valve designs induce two phase flows in the valve, which causes excessive corrosion of the seating faces. Since most amine service is fouling, placement of the valve should be such that deposition of solids is reduced rather than accelerated.

Bypass lines around automatic valves present more opportunities for corrosion. As an automatic valve bypass is seldom active, the bypass lines are essentially dead legs. The manual valves in bypasses around absorber level control and flash tank level control valves need to be treated the same as the automatic valve. Physical placement of bypass lines at control valve stations is also important. Bypass lines above the automatic valve may collect non-

condensable gases that keep the amine solution from wetting pipe walls. When water vapor is condensed on the metal surface shielded from the amine solution, carbonic acid can be formed when CO₂ is present, even at very low levels, and when insufficient amounts of H₂S are present, significant corrosion of carbon steel can occur. Bypass lines below the automatic valves will collect sediments promoting under deposit corrosion.

Flash Tank

Material specification of the flash tank inlet nozzle is sometimes overlooked. While the flow line from the absorber level control valve may be 304 or 316 Stainless Steel to mitigate the impact of slug/ plug two phase flow, the flash tank inlet nozzle may be constructed from the same grade of carbon steel as vessel. Design of the inlet deflector plate is important to minimize the erosive effects of the two-phase flow on the vessel wall near the inlet nozzle. Since some flash tanks separate liquid hydrocarbons from the amine solution as well as the gas phase, flow velocities are lower than those in piping, which allows deposition of suspended particles. Accumulated sediment not only increases the risk of under deposit/ poulitice corrosion, but also reduces the effectiveness of the flash tank by decreasing liquid residence time in the vessel. Excessive entrainment of hydrocarbons to the regenerator degrades its performance and may cause corrosion in other equipment such as pumps. Since the flash gas stream leaving the flash tank is saturated with water and at an elevated temperature, piping design and material selection of the flash gas line must account for both condensed water and acid gas content of the flash gas.

LEAN/RICH HEAT EXCHANGER/ LEAN AMINE COOLER

A strategy to minimize energy usage is to increase the heat recovery in the Lean/R Heat Exchanger (L/R REX). Unless sufficient back pressure is present on the rich stream, two-phase flow can occur in the L/R HEX from aqueous solution boiling and/ or acid gas stripping. If the two-phase flow is slug/ plug flow and not annular liquid flow, rapid thinning of metal surfaces and excessive vibration can occur in both plate frame and shell and tube L/R HEXs.

Counter current flow is used in many L/R HEX designs to maximize heat recovery. This design has unintended corrosion consequences for carbon steel shells of shell and tube L/R HEX. The rich solution is usually piped to the tube side as experience has shown it to be more fouling than the lean solution. The preferred flow path for the rich is inlet at a lower elevation than the outlet as the rich is more likely to develop vapor bubbles than the lean. Gravity assists bubble removal on the tube side since fluid velocities are too low to sweep them out. Counter current flow requires the hottest lean tube surface to be in contact with hottest rich surface, which results in the hot lean solution entering the shell side of the L/R HEX at the top and exiting at the bottom of the L/R HEX. Corrosion problems occur when bubbles of non-condensable gases, e.g. air or hydrocarbons, accumulate in the shell. The initial fill procedure, usually done by operating the amine circulation pumps, may trap large amounts of air or inert gas in the upper portion of the shell as liquid flow velocities are too low for physical entrainment of the gas. When the lean solution L/R HEX entrance nozzle has an excessive amount of trapped non condensable gas, the entering or falling liquid can produce localized corrosion by the failing liquid entrain vapor bubbles and impinging them onto metal surfaces directly below the lean inlet nozzle. Pockets of non-condensable gases keep the amine solution from wetting metal surfaces. Trapped vapor bubbles also keep the amine solution from wetting the metal surface, but do not prevent water vapor from condensing. Even if low amounts Of CO₂ are present in the lean amine solution, corrosive amounts of carbonic acid can be formed in the condensed water, unless there is an adequate amount of H₂S present for passivation.

REGENERATOR

A common problem with many rich amine inlet liquid distributors to the regenerator is they are not designed for flashing or two phase feed. Mechanical forces present when there is flashing or two phase feed are sufficient to cause severe distributor vibration and/ or failure. Failed ladder type distributors can produce a concentrated stream of liquid that erodes vessel wall or collapses tray decks. Some inlet distributors are no more than splash plates, which can be dislodged or damaged by the force of the rich amine solution feed. Missing or damaged splash plates result in erosion of the vessel wall opposite the feed point and carryover of liquid droplets in the vapor stream leaving the regenerator.

The steam or combined steam liquid return line to the regenerator from the reboiler is another place that needs examination. If the steam or combined steam liquid return line extends into the vessel, it should be positioned so it does not impart movement to the liquid below it. It is possible to induce circular motion of the hot amine solution where local liquid velocities at the vessel wall can exceed those normally recommended for amine service. If the

line terminates at the vessel wall, a deflector plate should be placed on the regenerator wall opposite this vessel nozzle, as entrained high velocity droplets are very erosive.

In applications where CO₂ is the only acid gas or when H₂S levels are very low in the regenerated amine solution, carbon steel surfaces not wetted by the amine solution are susceptible to carbonic acid attack when water vapor condenses. The vapor composition in the regenerator is dependent on the stripping ratio, moles of water vapor per mole of acid gas, and the place in the regenerator. Since most of the acid gas is stripped in approximately the top 1/3 of the vessel, the vapor in the lower 2/3 is much closer to the water condensation point. The amount of water vapor condensation on the vessel wall is dependent on a number of factors, quantity and quality of insulation and ambient temperature. Ladder attachments or other cooling sites on the vessel wall also accelerate water vapor condensation. Carbonic acid does form even though CO₂ levels are low in the vapor and when H₂S levels are low, protective iron sulfides will not be present.

REBOILER

Two different reboiler designs are used in amine plants, thermosiphon and kettle. Thermosiphon reboilers return the heated amine solution and steam to the regenerator tower by the same pipe. Kettle reboilers return the heated amine solution and steam to the regenerator tower in different pipes.

Thermosiphon reboilers return both liquid and vapor in one line to the regenerator column below the lowest tray or bed. The line size used must be designed for annular liquid flow to avoid erosive slug/ plug or dispersed droplet flow regimes. Reboiler feed line head height is an important design element to insure two phase-flow begins in the proper place in the reboiler. Special provisions must be made if corrosion monitoring or temperature measurement is needed for the reboiler return line. Any object sticking through the slow moving liquid layer into the high velocity vapor flow will deflect the vapor onto downstream metal surfaces resulting in erosion of the pipe wall.

Kettle reboilers usually have two steam exit nozzles that are combined to one line close to the reboiler. Best design practice is to make the piping from the nozzles is completely symmetrical so there are no differences in steam flow between the two nozzles. Asymmetrical piping can induce high localized steam velocities at one exit nozzle resulting in accelerated corrosion due to liquid droplet entrainment. Occasionally one encounters tube bundle designs with inadequate tube spacing. Liquid is entrained by the generated steam and washes the tube surface at a high velocity. Inadequate vapor space above the liquid will also result in erosive liquid entrainment which can uncover the top row of tubes and/ or erodes the steam exit nozzles.

REFLUX CONDENSER

The design of the reflux condenser determines where two phase-flow becomes annular liquid. Metal surfaces exposed to erosive slug/ plug flow should be minimized. Special provisions must be made if corrosion monitoring or temperature measurement is needed for the piping between the reflux condenser and reflux accumulator. Any object sticking through the slow moving liquid layer into the high velocity vapor flow will deflect the vapor onto downstream metal surfaces resulting in erosion of the pipe wall, especially when H₂S is present, since ferrous sulfide films are easily removed.

PUMPS

Many plant operators prefer to leave the startup screens in when the plant is in normal operation. Provision for pressure drop measurements across the inlet screen should be provided, as many plant operators do not appreciate the severity of cavitation corrosion. Many believe it is permissible to operate cavitating pumps for short time periods without causing significant damage.

Often the size of pump inlet and outlet pump nozzles is overlooked and fluid velocities can be much greater than those recommended for carbon steel in amine service. Occasionally the designer will not consider important factors, such as wall shear stress, and selects the materials of construction for the pumps by using analogies to other aqueous services, e.g. high pressure centrifugal boiler feed water pumps.

Amine solution booster pumps are used when there is insufficient pressure or head height for the regenerated hot lean amine solution to flow from the bottom of the regenerator to the main circulation pump which is normally placed after the lean amine cooler. Figure 1 shows two commonly used booster pump locations. Location 2 is preferred as the hot lean amine solution at location 1 is at or close to the boiling point. It is very difficult to prevent

cavitation due to water boiling as pressure is reduced in the pump bowl. Startup inlet screens also increase the pressure drop increasing the ease of pump cavitation.

Cavitation of the high-pressure circulation pumps is usually a result of the surge tank design. A popular design has the incoming lean amine flow into the surge tank above the liquid level. The incoming fluid falls through and saturates with the inert pad gas, usually methane or fuel gas. Extension of the inlet piping below the liquid level is recommended. Gas saturated amine solution forms bubbles when the pressure is reduced in the pump inlet. The bubbles collapse when they are transported to higher pressure discharge locations, e.g. impeller tip and bowl. As the gap widens between the bowl and impeller, the amount of recirculated liquid increases, which decreases the fluid flow to the next stage. It is possible to damage all stages of a multistage pump. Excessive amounts of hydrocarbons in the reflux stream also place the reflux return pump at risk of cavitation. In this case the bubble is vaporized hydrocarbon. The source of the liquid hydrocarbon that is carried over from the regenerator is an inadequately designed flash tank or one was not specified.

Filters

Experience has shown that amine gas treatment is a fouling service. Particulates formed in the plant as well as those transported into the plant can be very bothersome. The potential for under deposit corrosion increases when the amount of circulated solids increases. Another problem exists when H₂S is present in significant amounts, circulated particles scour loosely adherent sulfide films which results in more particles and accelerates wall thickness reduction. While particulate filters and carbon filters are highly recommended, very few designs utilize full flow filtration. Slipstream filtration requires a flow diverter, e.g. orifice plate or control valve, to direct fluid flow to the filter. Design of the flow diverter should be similar to level control/ pressure reduction valves with special attention paid to downstream piping that carries the main flow.

Filter housings, both particulate and activated carbon, are excellent at removing non condensable vapors since the flow path inside the vessel is usually in at the top, out at the bottom coupled with a low fluid velocity. When a significant vapor bubble forms at the top of the filter housing, the amine solution is prevented from wetting the metal surface. Even if low amounts of CO₂ are present in the lean amine solution, corrosive amounts of carbonic acid can be formed in the condensed water, unless there is an adequate amount of H₂S present for passivation.

CONCLUSION

The root cause of amine plant equipment and piping corrosion may be a direct result of the plant design. During the material selection review of new plants still in the design stage, corrosion causing design elements can be identified. Once identified, the design team can choose the most economic alternative to minimize the impact of design induced corrosion.

For existing plants with corrosion problems, examination of design induced corrosion should be included in the root cause determination. Proactively altering the design of another piece of equipment may ensure the elimination of the specific corrosion problem.

References

1. Bottoms, R. R., U. S. Pat. 1,783,901 , 1930.
2. Nielson, R.B. et al, "Corrosion in Refinery Amine Systems", CORROSION95, Paper No. 57 1, (Houston, TX: NACE International, 1995).
3. Kohl, A. L. and Nielson, R. B., 1997, Gas Purification, Fifth Edition, Gulf Publishing Company, Houston, TX
4. API (American Petroleum Institute), 1990, "Avoiding Environmental Cracking in Amine Units" API Recommended Practice 945, 1st Edition, Aug, American Petroleum Institute, Washington, DC.

Figure 1. Typical Amine Process Flow Diagram

