Shutting Down and Starting Up an Amine System

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Abstract

The purpose of this document is to describe precautions that should be taken to prevent foaming, hydrocarbon accumulation, corrosion, and cracking in amine systems when shutting down amine systems for maintenance and vessel entry. Starting up an amine system after a turnaround and putting new equipment in service will also be addressed.

Amine System Shutdown

A smooth startup begins with taking an amine system out of service properly. It is important to circulate amine while having adequate steam to the amine regenerator so that the entire inventory of amine solution has been stripped of H_2S and CO_2. Doing this prevents safety concerns with shipping and handling the amine solution and makes the solution less corrosive to carbon steel process and storage vessels. A simple step to check lean amine loading before turning off the steam to the regenerator is advised. An alternative to the lean loading check is to dip lead acetate paper into the amine solution. The amine is adequately stripped if the lead acetate paper remains white to very light brown after contacting the amine solution. Particulate filters should remain in service during the shutdown. Reducing the micron size of particulate filters, down to 10 microns if possible, during shutdown is recommended to thoroughly clean the system.

There is no reason for excessively long stripping which is the same as putting the amine system in hot standby. A rule of thumb is to circulate for 3-5 turnovers of system volume. As all the H_2S is stripped from the amine, iron sulfide from the protective iron sulfide layer protecting the piping and equipment will go back into solution due to solution equilibrium. We know iron sulfide is back in solution when previously clear amine turns brown in hot standby (Figure 1). As more iron sulfide enters solution, the likelihood of filter plugging and future leaks from disturbing the protective iron sulfide layer increases. If an amine system has particularly high heat stable salts, the protective iron sulfide layer will be dissolved at a higher rate, which should be considered when writing shutdown procedures.

Figure 1: Amine solution turns brown after 12 hours of stripping for shutdown purposes

Pump out all contactors and L/L treaters during shutdown. Get all liquid out of them. Amines and hydrocarbons left in vessels that are not opened during turnaround will just act as contaminants that can cause foaming or make iron sulfide particulates during the startup

Storing amine

The Amine Best Practices Group (ABPG) advises that lean amine should not be stored in process vessels for more than 4-6 weeks.   One reason for this is that lean amine is mildly corrosive when sitting stagnant in steel process vessels. In addition, iron sulfide particles grow and drop out of solution when amine solution sits stagnant and cold. Lean amine solution that is sent to temporary storage tanks should preferably be blanketed with nitrogen to prevent corrosion and, to a lesser extent, amine degradation. We recommend that temporary storage containers be made of austenitic stainless steel if cracking is a concern at ambient temperatures. MDEA and DEA solutions must be blanketed with nitrogen to prevent the oxygen-assisted degradation of MDEA and DEA to bicine, a chelating agent that dissolves the protective iron sulfide layer that has been established in existing amine systems.

The ABPG is aware of at least one case where uninsulated hot steam tracing was touching a carbon steel amine regenerator used to store amine solution for a period of years. A leak occurred which was attributed to both external corrosion due to the resulting hot spot from the steam tracing and internal corrosion due to the lean amine H_2S loading. The operator must consider the risk of storing lean amine in a process vessel where bare steam tracing is applied.

Vacuum Trucks

Vacuum trucks used to transport lean amine to and from storage vessels must be cleaned before use in amine systems. Vacuum trucks are a source of contamination and have contributed unwanted caustic, hydrocarbons, soaps, and surfactants to refinery amine systems.

Cleaning the amine system

Cleaning fluids and chemicals that are not properly rinsed from amine system vessels can produce horrible foaming. A well-known H_2S scavenger used for chemical cleaning, if left in an amine system, will result in amine foaming at a concentration of only 10 ppmw. Recently a refiner found manganese sulfide particulates in a tail gas amine system that foamed weeks after startup. The manganese sulfide was attributed to residual potassium permanganate, a H_2S scavenger, used for amine system cleaning. The most important thing to remember from this document is:

- Rinse every elbow, fitting, tray downcomer, and small space to thoroughly remove any cleaning fluids used to prepare equipment for personnel entry. Cleaning fluids are normally surfactants and even 10 ppmw contamination can result in severe prolonged foaming

Preparing the Vessel for Chemical Cleaning

The Refinery Sector Rule states that a vessel should have less than 10% LEL before the vessel is opened. If a site is using close coupled wash connections as shown in Figure 2, our experience has shown that it may take a long time (days) to remove H_2S and LEL to acceptable levels before the wash connection can be installed to begin chemical cleaning.

Figure 2: A close coupled wash connection (no valve on vessel nozzle)

A simple fix to shorten the time required to install wash connections for chemical cleaning is to install double block and bleeds (Figure 3) where all wash connections are required. With the double block and bleed, only a short section of piping needs to be free of H_2S and LEL instead of an entire vessel which might be filled with sludge and pyrophoric material.

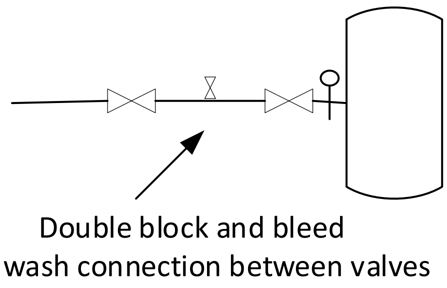

Figure 3: Wash connection location between two block valves

Considerations when Decontaminating Amine Systems using Chemical Cleaning Technologies

There are a number of different vendors that offer different chemical cleaning technologies. The ABPG has had positive experiences with almost every vendor and chemical cleaning package. Some chemical cleaning procedures use low strength acids with surfactants, others use low strength caustic (sodium hydroxide) with surfactants, and some cleaning procedures use surfactant packages only. Chemical cleanings in amine systems are completed using both vapor phase and liquid phase cleaning. The authors have historically had much better results with liquid phase cleaning procedures on vessels in amine service. Liquid cleaning should have a step in the procedures to move liquid upward in the vessel to remove materials that float on top of the liquid.

An important consideration when choosing a chemical cleaning package is the materials of construction of the pressure vessels that will be cleaned. Stainless steel vessels, whether solid stainless or clad with stainless, require low chloride water to prevent stress chloride cracking. Stainless steel is much more sensitive to chloride cracking as amine is removed from the equipment because the pH of the liquid in the tower decreases and oxygen is introduced. Some chemical cleaning procedures work better when temperature is increased so steam is used to heat the liquid in the pressure vessel. The likelihood of chloride cracking also increases with temperature and decreasing pH. At least one refining company specifies chloride concentrations below 5 ppmw prior to introducing acid or steaming procedures as steaming of systems can result in chloride concentration. Because the risk of chloride cracking increases with decreasing pH and increasing temperature, the ABPG recommends demineralized water (zero chlorides) for both initial and final washes when chemical cleaning stainless steel equipment in amine service.

Carbon steel vessels in amine service should be post-weld heat treated (PWHT) to prevent cracking. Unfortunately some refiners have found that not all of their pressure vessels and especially piping in amine service has been PWHT. For this reason, the ABPG recommends steam out procedures should be avoided in systems with non-PWHT carbon steels.

A typical caustic based cleaning procedure used by refiners is as follows:

1. Flush equipment with demineralized water. Maximum temperature 140°F.
2. Circulate a solution of 10% wt. caustic and surfactant containing chemicals. Temperature not to exceed 140°F.
3. Flush tower with demineralized water.

A typical acid based cleaning procedure used by refiners is as follows:

1. Flush with demineralized water to remove bulk amine to very low amine concentration. This step will also remove chlorides as needed.
2. Circulate H_2S scavenger to remove H_2S
3. Circulate low strength acid (< 10% wt.) Phillips 66 has seen sulfamic, sulfuric, and citric acid used for this step. H2S scavenger can been added during this step in addition to step #2.
4. Flush system with demineralized water to raise pH
5. Neutralize system with low strength (< 5% wt.) soda ash
6. Flush system with demineralized water until pH rises to neutral or greater

An advantage of using a caustic cleaning procedure is that the procedure is fast. There are no neutralization steps required. Also, caustic reacts with H_2S. It is a stronger base than amine and helps to prevent accidental H_2S releases during the chemical cleaning process. A disadvantage of using caustic for chemical cleaning is that temperatures should be limited to 140°F maximum or the likelihood of cracking is high on non PWHT steel. While most refiners use only PWHT steel in amine service, we have found that cracking on welds has occurred on legacy equipment that was never heat treated. Chemical cleaning with caustic requires more skill on the part of the chemical cleaning vendor.

Acids can be easier work with than caustic because caustic induced cracking is eliminated. However, carbon steel vessels must be neutralized after acid cleaning, adding more steps and time to the chemical cleaning procedure. Acid cleaning also removes the protective iron sulfide layer present on carbon steel equipment in amine service. Consequently, the amine solution will corrode carbon steel equipment again on startup, usually resulting in an excess of iron sulfide particles in solution which increases the chances of foaming after startup. An operator should expect filter plugging and the need for frequent filter changes during startup after acid cleaning has been utilized.

The picture below indicates extensive debris in an amine regenerator after a vapor phase cleaning using surfactants only. The debris is mostly iron sulfide (70% wt.) and iron oxide. While the regenerator was free of H_2S and LEL after the vapor phase cleaning, it took days to vacuum all the debris off the trays, negating any cost and time advantages gained by this comparatively less expensive procedure.

Figure 4: Amine Regenerator tray after a chemical cleaning fail

The authors have no preference for which type of chemical cleaning is used, provided all surfactant chemicals are rinsed from the system to prevent amine foaming. Our advice is to check references for all chemical cleaning vendors carefully.

New Equipment or Old Equipment with New Internals

New pressure vessels and new vessel internals, such as trays, random packing, and structured packing are often delivered with residual machining oils and surfactants. These materials can produce foaming in new equipment[1]. To remove machining oils, it is recommended to rinse new pressure vessels, piping, and vessels with new internals with an alkaline solution of 3-10% wt. NaOH (caustic). Alkaline solutions of trisodium phosphate or 2-5% wt. soda ash have also been used successfully to remove oil and surfactants. When using caustic, temperatures must be kept below 140 F to prevent alkaline stress corrosion cracking (SCC) if materials are susceptible to SCC. Heating caustic solutions in reboilers or thermal reclaimers prior to using in other equipment is not recommended as is easy to overheat the caustic solution. Water washing is not guaranteed to remove machining oils. The alkalinity of the solution is important. Some amine vendors recommend washing new equipment with low strength amine before starting up new equipment. A good water wash should be performed after the caustic cleaning to remove caustic and prevent sodium accumulation in the amine solution. Target neutral pH to end the water wash.   New internals can also be cleaned before installation in pressure vessels, which may be easier than internal cleaning.

Amine Import

When purchasing new amine for a startup, grab a sample of the amine from each fresh amine truck if possible.   Trucks can be contaminated.

Startup

Use the same brand and type of amine particulate filter as used before shutdown.   Use the same brand and type of activated charcoal as used before shutdown. If the amine system was stable and without foam before shutdown, don't make changes. Certain types of particulate filters and activated charcoals are incompatible with amine systems. Changing these materials just adds more items to disqualify from a root cause analysis of an event after startup.   Local vendors may be unaware that some of the items they are selling are incompatible with amine solutions.

Filter coalescers used immediately upstream of gas contactors should be changed out during the turnaround or maintenance period.   Use the same brand and type of coalescer as used before the shutdown for the same reasons as listed above for filters and activated charcoal.

Avoid loading activated carbon into an empty vessel. Fill carbon filter vessel about 1/3 full of water before adding carbon. After loading, fill the vessel with water in an upflow direction until water comes out the top to displace air. Allow water to flow to 2 to 3 bed volumes to removes fines near top of vessel. Reverse water flow for 2 to 3 bed volumes to remove carbon fines near bottom of bed. Allow at least twelve hours to wet the carbon and displace air in the carbon pores.

Normal operating amine strength should be established as quickly as possible, preferably before starting amine circulation. The easiest way to do this is to fill the lean amine surge tank, rich amine surge tank, or even a temporary Baker tank with enough fresh amine (usually 79-100% wt. amine) so that just by adding condensate to the mixing vessel amine an appropriate amine operating strength (wt.%) is achievable. Carbon steel is an acceptable material for fresh amine.

Amine solution has a specific gravity close to 1. The lean amine surge drum, rich amine surge drum, and amine reflux accumulator operate at moderate temperatures and consequently operating specific gravity isn't much different from ambient startup conditions. Calibrate level instruments when there is enough amine solution in them and before amine solution is sent to any gas or liquid contactors. Pressure up these vessels to operating pressure as differential pressure instruments can be sensitive to operating pressure. A second calibration may be necessary on the amine regenerator which operates at 250^{o}F or higher resulting in lower amine solution specific gravity.

Ensure that Operations and Technical Support know how level instruments are supposed to work in each process vessel.   Ensure that alarms are active in the DCS for all instruments.   Alarms may have been deactivated during a shutdown period. Any level instrument reading more than 80% level may really be over the top of the level instrument's range. Also, be wary of level instruments that "flatline." A level instrument with no fluctuations in level is often indicative of high level over the level instrument's range and not of a stable liquid level. A more than once repeated startup error starts by first allowing a high level in the amine regenerator bottoms which floods the reboiler with cold liquid.

Steam flow in then added to the reboiler to help reduce the liquid level in the tower bottoms. If the steam is added too quickly, large bubbles can form which quickly rise in the tower, resulting in catastrophic tray and/or packing damage (Figure 5) and even random packing getting lifted out of the tower and into the overhead piping and reflux accumulator.

Figure 5: Displaced packing support grid after high liquid level in reboiler

What should be avoided is attempting to rapidly adjust concentration after sour hydrocarbon gases and liquid have been added to the system. The ABPG has experience with foaming events associated with changing amine concentrations rapidly. Foaming has been associated with both increasing or decreasing amine concentrations rapidly. Increasing amine concentration rapidly by adding 100% wt. fresh amine will most often turn amine black as iron sulfide particles are formed with increasing pH. Iron sulfide particles can stabilize foam.

Check amine concentration in storage vessels. It should be within a few weight percent of operating strength. Adjust in storage vessels if necessary. Begin adding amine solution to process vessels after air is removed from vessels for both flammability and amine degradation concerns.

Have nitrogen connected to the amine regenerator. Add nitrogen to amine regenerator to prevent pulling a vacuum after amine solution is heated and also to have enough pressure so lean amine pumps will work (enough NPSH) or to pressure to the lean amine surge tank.

Begin slowly heating the amine regenerator. Check steam traps on reboiler for functionality. The goal is to have a hot regenerator before sending any hydrocarbon to amine contactors and liquid treaters. Heat in the regenerator will lift small amounts of entrained and absorbed hydrocarbons to the regenerator overhead where it can be purged either as liquid from the reflux accumulator or as gas to flare or the sulfur plant (if small amounts of hydrocarbon).

Begin circulating amine solution through amine contactors and liquid treaters. Take the opportunity to calibrate flow meters and level instruments on all process vessels.

When the amine solution has been circulating through all the process equipment and the amine regenerator overhead temperature is hot enough to produce reflux, begin adding hydrocarbons to selected amine contactors. Hydrocarbons should be coming from fractionators that are reasonably close to on-specification. We don't want hydrocarbons that are much heavier than normal entering the amine system and condensing into the amine system. Amine can be warmer than normal at this time. H_2S removal from the hydrocarbons might suffer but that's acceptable in the short term. What we don't want is very cold amine condensing a heavy load of hydrocarbons coming from a fractionator that is nowhere near on specification. All that will do is sent heavy hydrocarbon, likely gasoline, into the amine system, where is it likely to cause foaming and fool level instruments. The hydrocarbons will then potentially overpressure the amine regenerators and create the potential for loss of containment of H_2S at the sulfur plant.

Have additional staffing to monitor particulate and charcoal filters for plugging. It is likely filters will plug no matter what precautions are taken to prevent amine system contamination. Change particulate filters as necessary and consider preemptive filter changes. Consider using larger than normal micron sizes at startup, up to 70 microns, because smaller micron size filters may plug too frequently for personnel to keep up with filter changes. But remember to reduce to smaller micron size filters as amine unit operations stabilize. Changing filters frequently to keep the amine free of particulates will significantly reduce the likelihood of foaming and amine carryover events.

When a reasonable flow of acid gas has been established, remember to remove nitrogen from the amine regenerator. It may take a day or two before Console is confident enough to remove the nitrogen. That's Ok, don't worry about the nitrogen costs. Keeping pressure on the regenerator to avoid level measurement errors will minimize the severity of upsets.

References

1. "Investigation and Diagnosis of Startup Foaming Issues at a New Tail Gas Treater," S. Copper, B. Viceral, K. Thomas, S. Goff, J. Contreras, L. Nyadong, J. Stavros, N. Hatcher*, Hydrocarbon Processing*, April 2022, pp. 15-20.