

Influence of Ammonia on Gas Sweetening Units Using Amine Solutions

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ABSTRACT

The effects of ammonia in the feed to amine sweetening units has been investigated using a process simulation program called TSWEET®. In the cases studied, MEA and MDEA were used to treat gases contaminated with up to 0.3% ammonia. The MEA units studied were 1100 psi gas contactors sweetening 0.25 to 4% H₂S and 0.25 to 2.5% CO₂. The MDEA units were 300 and 20 psi units treating high CO₂ streams in a selective manner. Small amounts of ammonia can cause serious problems in some amine sweetening units. These problems are usually traceable to a complex of ammonia with CO₂ in the stripper. When large amounts of CO₂ are present, this complex may cause a build up of CO₂ and ammonia in the circulating amine. In MEA, ammonia tends to push CO₂ into the reboiler, increasing the CO₂ residuals and ammonia in the lean amine. In MDEA, the ammonia appears to help drive CO₂ overhead, decreasing CO₂ and increasing the H₂S in the stripper bottoms.

Presented at AIChE, Houston, TX, March 1993.

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INTRODUCTION

Ammonia is sometimes present in sour gas streams which must be sweetened such as selected refinery gases, coke oven gases and reactor outlets in tail gas cleanup units (TGCU). Whatever its source, ammonia often has a major impact on the operation of amine sweetening units treating these gases. This paper will investigate the influence of ammonia on the plant operations and examine possible mitigating actions.

As noted by Kohl & Riesenfeld (1985), ammonia may be used to remove H₂S, CO₂ and other acid gases such as HCN, COS, CS₂ and mercaptans. However, a serious disadvantage in using ammonia for sweetening is the extreme corrosiveness of concentrated ammonia solutions which requires the use of expensive alloys in construction. In addition, ammonia sweetening processes are usually more complex than amine sweetening processes, thus requiring additional equipment. Although amine units are simpler and less expensive, they have not been considered suitable to treat streams containing significant amounts of acid gases other than H₂S and CO₂. However, over the past two decades, BS&B Engineering in Houston has installed several of their Sulfiban® Units to treat coke oven gases with monoethanolamine (MEA) solutions. These gases contain a large assortment of acid gases and ammonia. If ammonia is present in the feed stream in amounts on the order of 0.5% or higher,

the stream is usually processed for partial ammonia removal before being sent to an amine unit. Accordingly, this paper will investigate situations where the ammonia concentration in the sour feed is on the order of 0.1 to 0.3 mole %.

A process simulation program called TSWEET® (Bryan Research & Engineering, 1993) was used in the present study to examine the influence of ammonia on the performance of amine sweetening units. TSWEET can simulate amine sweetening, sulfur recovery, TGCUs and sour water strippers, all in a single run. The amine sweetening capabilities include MEA, DGA, DEA, MDEA and mixtures of these amines while the sulfur recovery capabilities include Claus, Cold Bed Absorption, Superclaus®, Selectox®, and oxygen enrichment such as the Cope® process. The ability to handle ammonia was recently included in TSWEET through the use of the NRTL equation of state. The program results for ammonia have been verified by comparison to VLE data and operating data from several sour water strippers. To date, no detailed comparison of program results to operating data from amine sweetening units with ammonia in the feed gas has been made due to the lack of published data. However, general trends have been compared and the program results are believed to be correct.

PROCESS DESCRIPTION AND PROBLEMS

A flow diagram for a simple amine sweetening unit is shown in Figure 1. As shown in this figure, a lean amine stream is used to scrub the sour gas in an absorber and the rich amine is sent to a stripper or regenerator for acid gas removal. When small amounts of ammonia are present in the sour gas, nearly all of the ammonia is scrubbed from the sour gas by the amine solution. Due to the high solubility of ammonia in water, the ammonia may build up in the circulating amine solution and present several problems in the absorber and stripper.

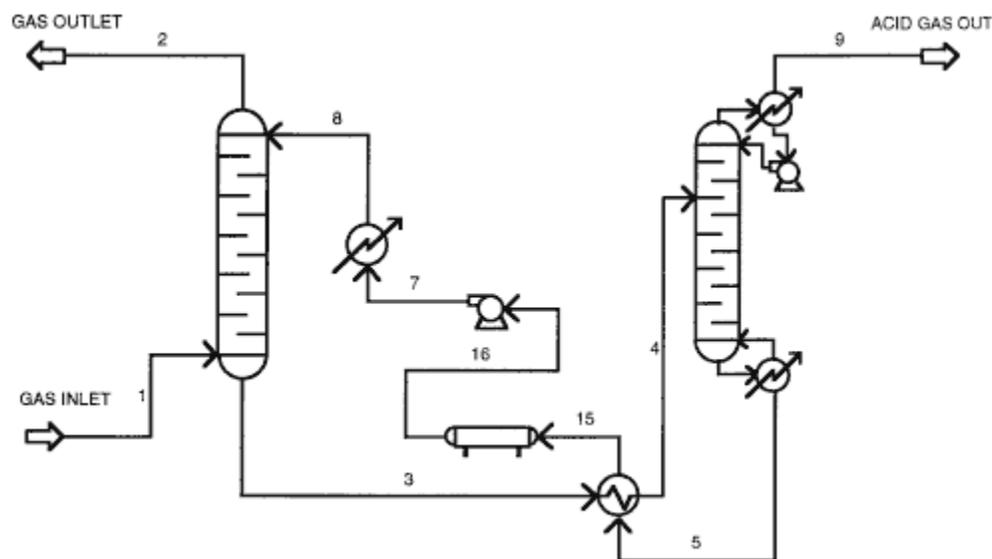


Figure 1. Simple amine unit.

Absorber

The primary problem in absorbers is failure to meet the overhead acid gas specification. This problem is actually due to poor stripping. The amine solution which is recycled may contain a large amount of ammonia. This ammonia carries significant quantities of H_2S and CO_2 which "tie up" part of the amine and reduce the carrying capacity of the solution, as well as increase the equilibrium gas concentrations. Thus, when the resulting lean amine is fed to the absorber, acid gases may either break through due to insufficient capacity or come to equilibrium at too high a level.

Stripper

Since the ammonia fed to the stripper will vaporize at stripper conditions, it tends to travel up the column with the

water and acid gases. If the column has a conventional condenser, the ammonia condenses with the water and is then returned to the column. The ammonia then tends to revaporize as it travels down the stages in the stripper and is recycled between the condenser and column until sufficient concentrations are reached to force the ammonia overhead or through the bottom. Since the amount being refluxed can be 10 to 20 times that escaping in the acid gas vapor, this clearly represents a significant change in the condenser flow rate. In addition, the condensation of ammonia is highly exothermic and thus can cause a large increase in the condenser duty.

With no ammonia present, the water is normally condensed in the condenser with small amounts of the acid gases due to their low solubility. However, because ammonia is a base, it tends to capture significant quantities of the acid gases and return them to the stripper. In those cases where this cycle builds, a large portion of the acid gases and ammonia may escape out of the bottom of the stripper and return to the absorber. These large residuals, obviously, limit the pickup in the absorber.

DISCUSSION OF RESULTS

The operational problems with ammonia are many and at first glance random. Some units may have problems meeting the sweet gas specifications. In others, the stripper may flood or be unable to hold the process control set points on the condenser or reboiler. However, as has been noted previously, all of these problems have the same root cause. Ammonia is almost totally absorbed at the temperature and pressure in the absorber, resulting in a heavy ammonia load in the rich amine fed to the stripper. Then, in the stripper, the K for ammonia in the condenser is considerably less than one, meaning that most of the ammonia vaporized in the stripper is returned in the reflux. However, the K for ammonia within the stripper is only slightly greater than one, resulting in a mild tendency to exit the tower at the overhead rather than the bottoms. Therefore, the ammonia concentrations tend to build up in the stripper as more and more ammonia tries to exit the top of the stripper, only to be captured and returned in the reflux. The concentrations continue to build up until a steady state amount of ammonia either overcomes the low K in the condenser or forces its way to the reboiler against high K's in the tower. Thus, the build up of ammonia results in composition profiles such as are shown in Figure 2. This figure shows the concentration of ammonia in the vapor phase of a typical MEA stripper operating on a rich amine from an ammonia contaminated feed. Changing the condenser temperature from 140 to 160°F does nothing but shift the K for ammonia in the condenser a little closer to one, effectively making it slightly easier to exit the system through the overheads. Yet, as can be seen in Figure 2, the primary effect of increasing the condenser temperature is to reduce the maximum ammonia concentration in the column from 20% to less than 12%. It is also interesting to note that the maximum effect occurs, not at the condenser, but rather in the vicinity of the reboiler. Clearly, the stripper is highly sensitive to changes in the condenser temperature. In order to examine the ramifications of this, it will be necessary to examine several individual cases and extrapolate the results to a wider range of applicability.

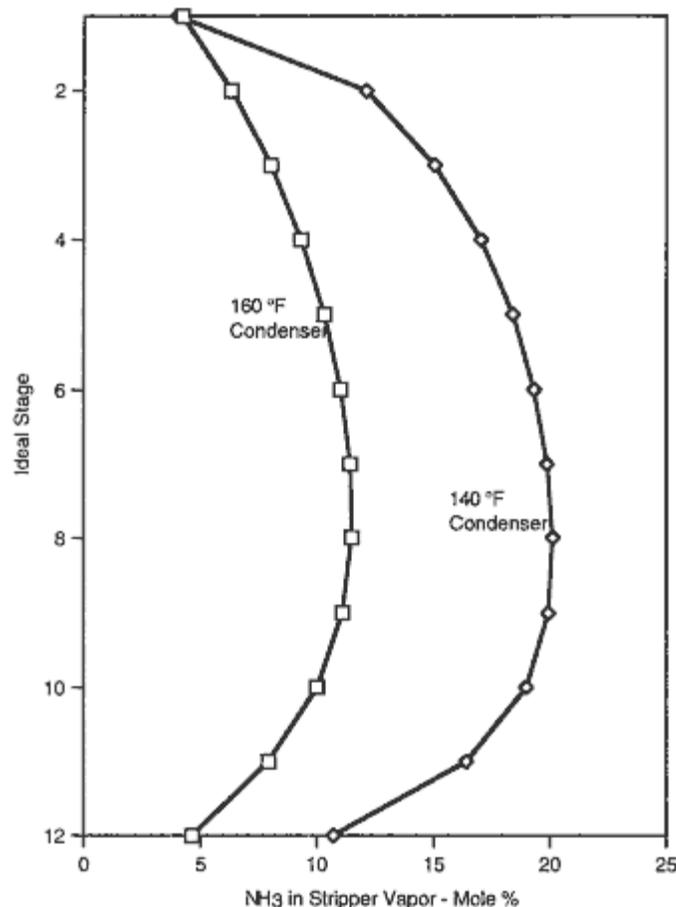


Figure 2. Effect of condenser temperature on ammonia concentration in Case 1 -- MEA stripper.

CASE 1: 15 Wt % MEA, 30 MMSCFD, 2.5% H₂S, 2.5% CO₂ at 1100 psia

For the ammonia free base case, the unit requires 920 gpm of 15 weight % MEA. The reboiler duty required is 37 MMBTU/hr, and the condenser is operating at 14.2 MMBTU/hr. In the ammonia free case, the unit will produce sweet gas containing approximately 125 ppm CO₂. However, when the ammonia concentration in the inlet has risen to 0.3 mole %, the CO₂ in the sweet product is in excess of 500 ppm. Figure 3 shows the effects of ammonia infiltration on the unit if the condenser temperature, reboiler duty, and circulation rate are held constant. Interestingly, the H₂S concentration, although changing slightly from run to run, remains nearly constant at roughly the pipeline gas specification.

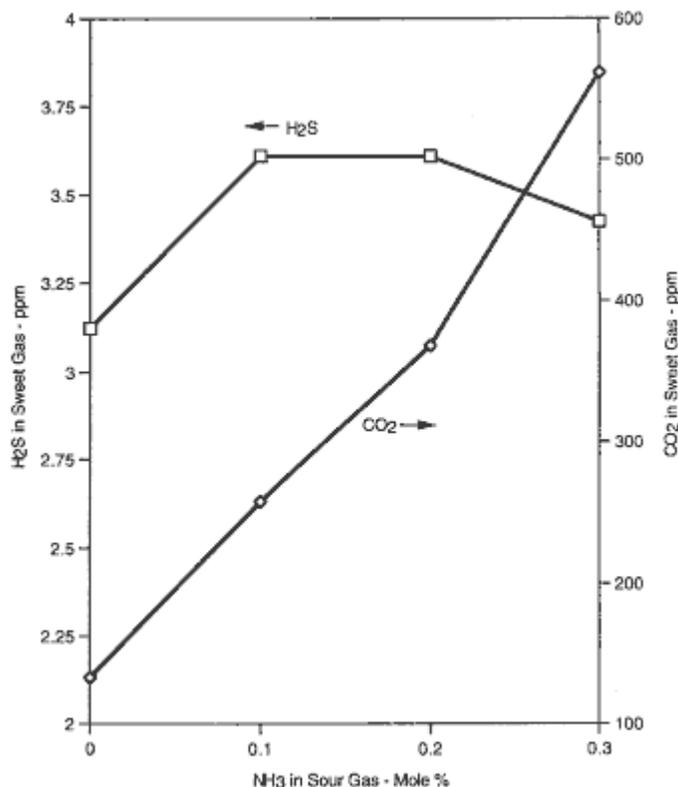


Figure 3. Effect of NH3 on sweet gas for Case 1 -- MEA unit.

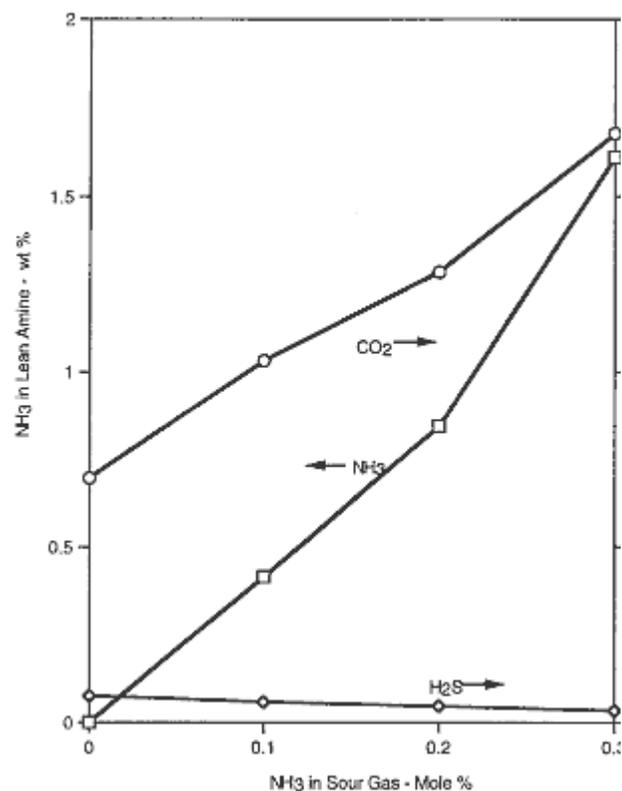


Figure 4. Effect of NH3 on lean amine for Case 1 -- MEA unit.

In order to understand how the ammonia recycle causes these effects, a detailed examination of the stripper data is necessary. The first item which should be examined is the composition of the lean amine. Figure 4 shows the concentrations of ammonia and acid gas in the lean amine. The ammonia increases from none to 1.5 weight % at 0.3 mole % ammonia in the feed gas. While 1.5 weight % does not initially sound like a large change to the 15% MEA solution, it must be remembered that ammonia's molecular weight is only 17. This small weight % causes almost a 40% increase in the normality of the solution. It is well recognized (Kohl & Riesenfeld, 1985) that although higher amine concentrations allow greater carrying capacity, they cannot be stripped as cleanly. Examination of the CO₂ residuals gives confirmation of this. In the no ammonia case, the CO₂ is under 700 grains per gallon, while in the 0.3% ammonia case, the concentration has more than doubled. The H₂S concentration, while very low, shows a minor decrease. This is due to a displacement effect from the CO₂ being carried out the bottom of the stripper. Most of the CO₂ concentration increase in the lean amine may be traced back to an effect noted by Maddox (1974). As the ammonia concentration goes up, the reboiler temperature goes down, as can be seen in Figure 5. Maddox noted that below 250°F, CO₂ residuals rise very rapidly as a function of temperature. The reason that the reboiler temperature decreases is directly related to the amount of ammonia in the column. It requires considerable heat to vaporize ammonia, and its VLE curve is such that it vaporizes more readily than water or amine, robbing the system of heat which could be used to heat the rest of the system and aid in CO₂ stripping. In addition, much of this vaporized ammonia is then condensed in the overhead condenser and recycled in the reflux. This is an exothermic process made more so as the ammonia in the reflux liquid begins to absorb acid gases. Thus, the condenser duty required to produce a constant condenser temperature rises dramatically with rising ammonia content. As can be seen in Figure 5, the condenser duty required rises from just over 14 MMBTU/hr to almost 19 MMBTU/hr, even though the stripping efficiency and reboiler temperature are dropping.

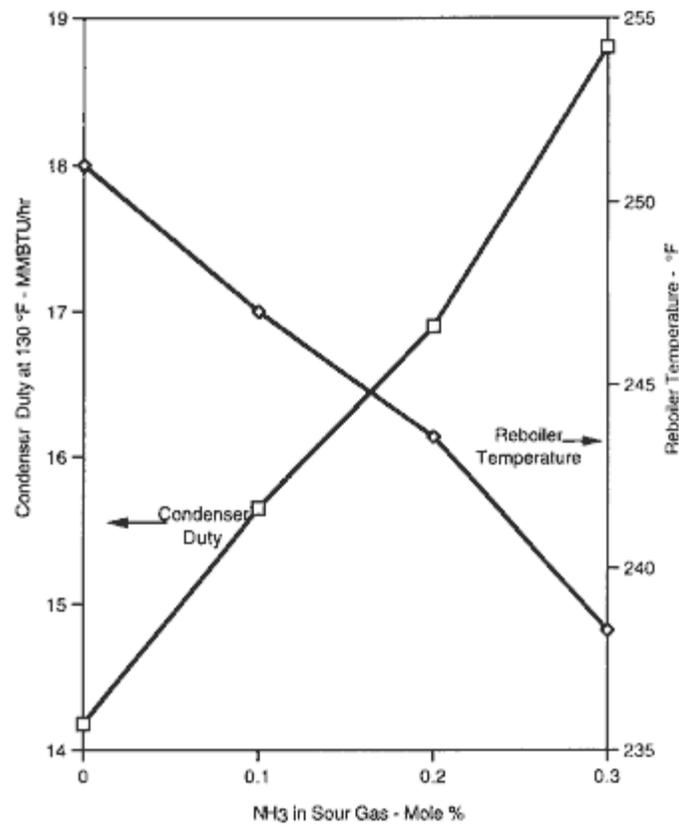


Figure 5. Effect of NH₃ on condenser duty and reboiler temperature for Case 1 – MEA unit.

There is one good thing about this effect. Because more heat is being required to vaporize ammonia and less vapor is being generated in the stripper, the percentage of flood actually drops slightly in the unit as the ammonia content rises. Although it is not plotted, it was noted that a 7 foot column would be required if no ammonia were present, but only a 6 foot 8 inch unit in the 0.3% ammonia case.

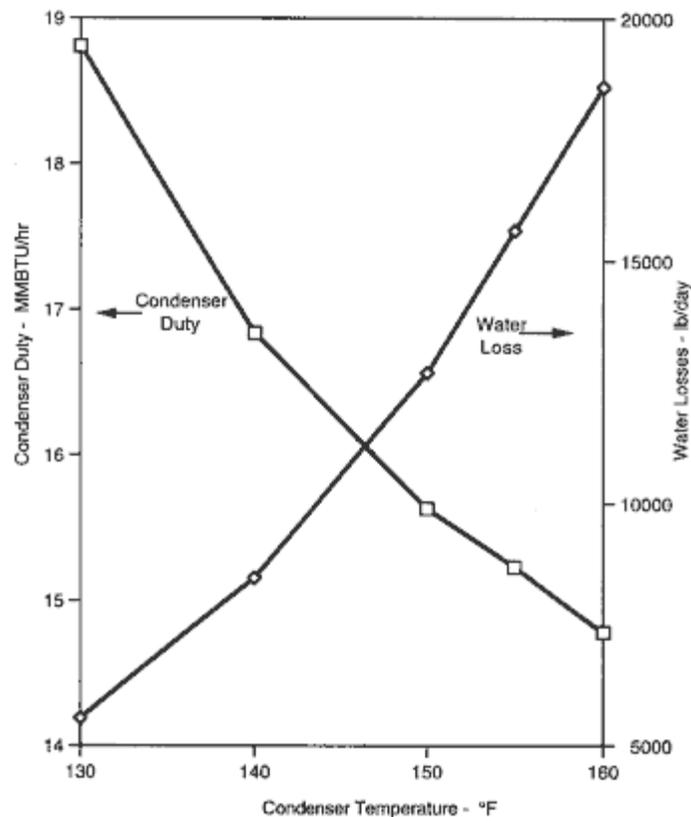


Figure 6. Effect of condenser temperature on condenser duty and water losses in Case 1 -- MEA unit.

In an operating unit, these full effects would probably not be observed. Many units do not have 30% excess capacity in the stripper condenser duty and most reboilers are operated on temperature control. In such units, the condenser would reach its maximum heat transfer load and then the temperature of the acid gas product would begin to rise. Figure 6 shows the effect of increasing the condenser temperature on the required duty at a 0.3% ammonia feed gas. This increasing temperature would then have the effect of increasing the water lost overhead from the stripper. Ammonia carried out overhead would also increase, restoring the reboiler temperature and CO₂ residuals to near ammonia free values without increasing the reboiler duty. If Figure 2 is reexamined, it can be seen how this increase in ammonia overhead reduces the ammonia traffic in the column. It can be seen that at 160°F, the maximum concentration of ammonia in the stripper is only 12% as opposed to 20% in the 140°F case. In addition, the percentage of ammonia in the lean stream is reduced by over half. However, Figure 6 shows the ultimate cost of allowing the condenser temperature to rise. The water makeup increases from roughly 5500 lbs or 750 gallons per day to roughly 18000 lbs or 2400 gallons per day as the condenser temperature rises from 130 to 160°F. This increase in makeup water can easily be a major expense in the operation of the unit. If the operator plans to use higher condenser temperatures as the mitigating method in this unit, a balance must be struck between the condenser duty and water losses. If there is a CO₂ specification below the 2% pipeline standard, it must also be taken into account.

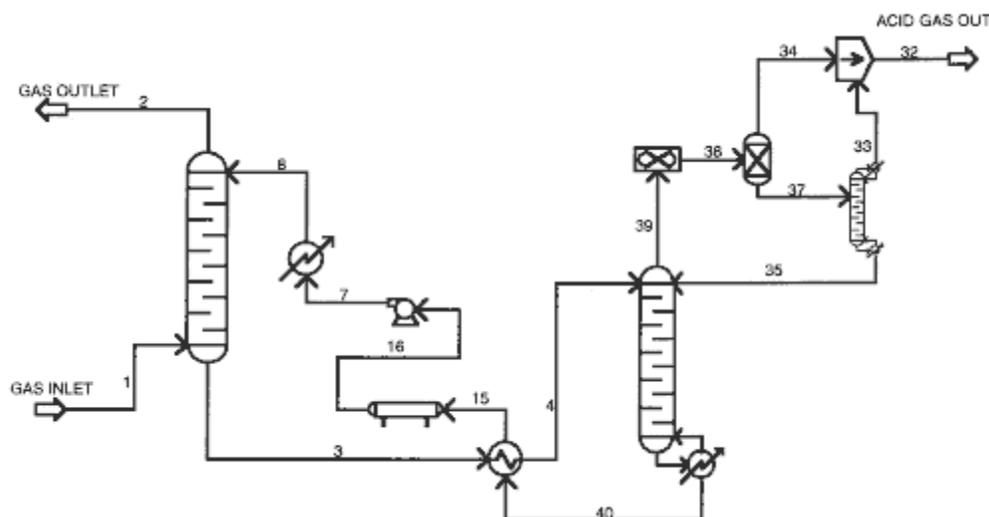


Figure 7. Amine unit with sour water stripper.

One other alternative may be considered. If neither high CO_2 concentrations in the sweet gas nor high water losses are acceptable and yet the unit must be operated, a sour water stripper can be added to the reflux. As shown in Figure 7, the stripper overheads are condensed to 120°F in the standard condenser. However, the liquid from the reflux accumulator is not returned directly to the column. Instead, the reflux is fed to a short stripper where the ammonia and remaining acid gases are separated from the water. Because a large fraction of the vapors have already been removed from the stream in the main reflux accumulator, the condenser on this column may be operated at 180 to 200°F , preventing ammonia recycle, and thus allowing almost total ammonia removal from the liquid returned to the main stripper as reflux, or alternatively simply added to the reboiler. In the case of 0.3% NH_3 in the feed gas, the main reboiler requires a 37 MMBTU/hr heat rate and the main condenser requires a 15.9 MMBTU cooling rate. In addition, the sour water stripper requires roughly 4 MMBTU and the condenser runs at about 1.6 MMBTU/hr. Water losses and CO_2 in the sweet gas have actually decreased compared to the no ammonia case. Clearly, this is the most economical from a utilities point of view. However, the increased capital cost of an additional column with its attendant controls and exchangers are a consideration. Figure 8 shows the CO_2 levels in the sweet gas and Figure 9 shows water losses for each operational option.

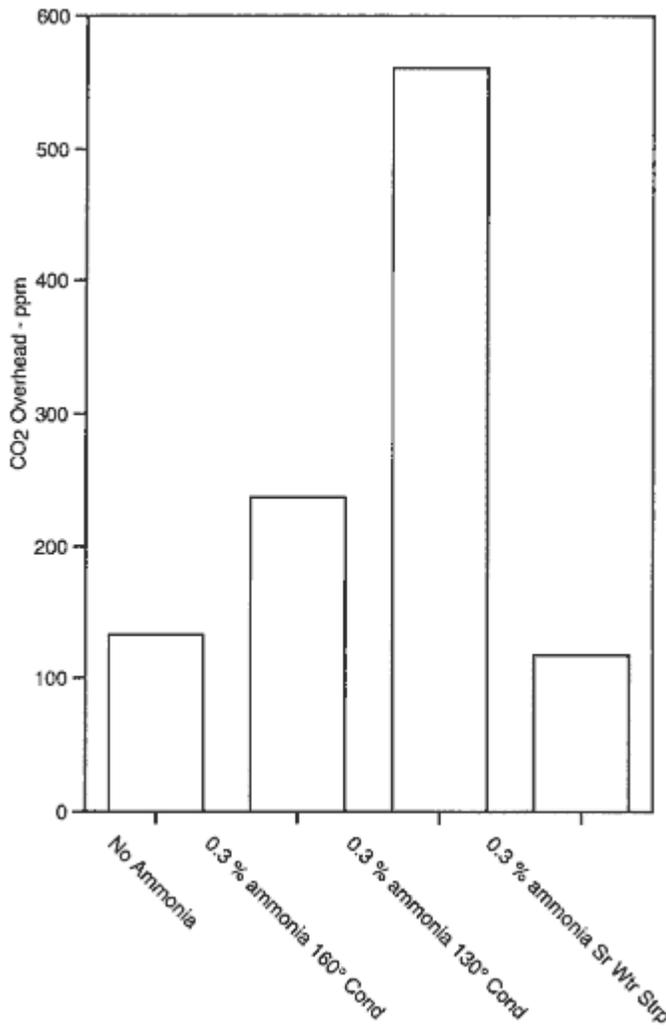


Figure 8. Effect of operating parameters on CO2 overhead in Case 1 -- MEA plant.

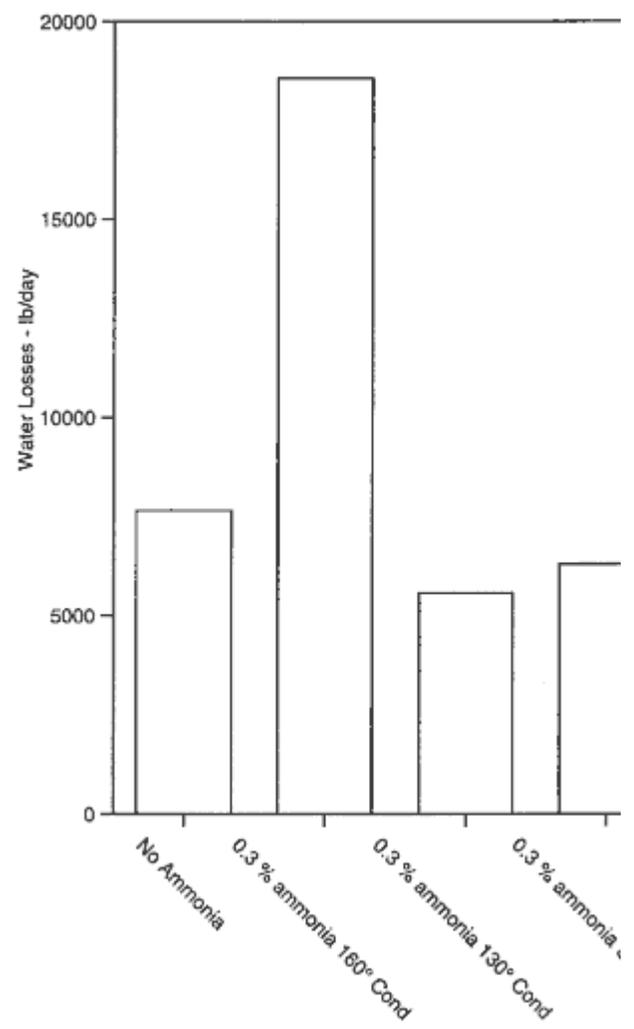


Figure 9. Effect of operating parameters on water losses in Case 1 MEA unit.

CASE 2: 15 Wt % MEA, 30 MMSCFD, 4% H₂S, 0.25% CO₂ at 1100 psia

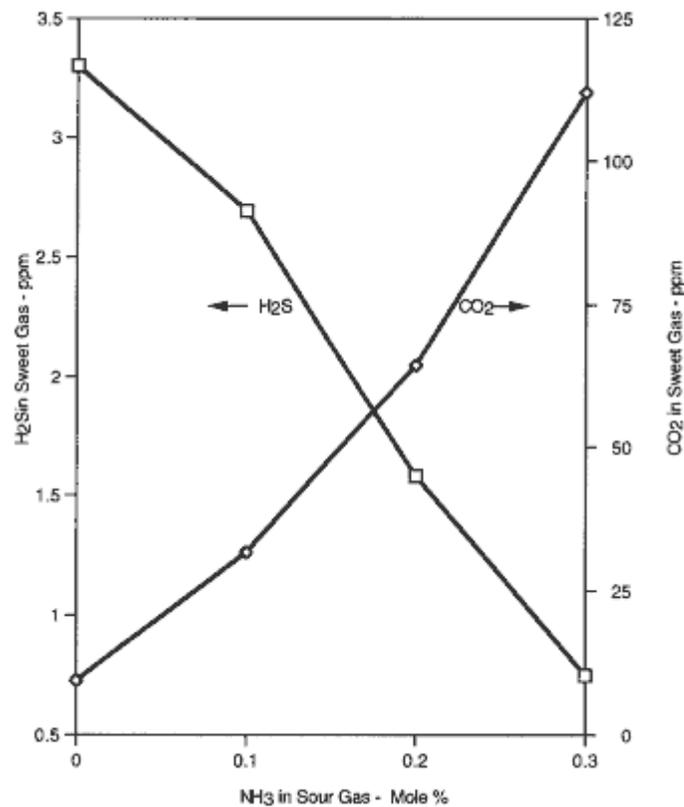


Figure 10. Effect of NH₃ on sweet gas for Case 2 -- MEA unit.

This case, which is more likely to be seen in a refinery application, requires 650 gpm to process 30 MMSCFD of gas. Because of the high H₂S concentration, very high stripping steam rates must be used. This leads to the results shown in Figure 10. As ammonia is introduced to the system, the CO₂ goes up as before. However, the numbers are much lower than in the previous case because there is so little CO₂ in the incoming rich amine. However, the interesting item to note is that the H₂S concentration actually goes down as the ammonia comes up. Figure 11 will show the reason for this. Even with a 0.3% ammonia feed, there is no significant ammonia buildup in the lean amine. However, the little ammonia which does get carried out the bottom of the stripper carries some CO₂ with it. This CO₂ in turn displaces H₂S in the bottom of the stripper, resulting in significantly lower H₂S residuals. This allows the amine to perform better in the absorber. Figure 12 is included to show that in this case, because there is no large ammonia load in the reboiler, the reboiler temperature remains essentially constant. In addition, the ammonia in the condenser is behaving more like water than in the previous case. The condenser duty rises only a few percent when the ammonia is introduced, meaning that in a temperature controlled system, the operator would probably not even notice. In general, this case requires no mitigating adjustments unless there is a very tight specification on CO₂, in which case an increase in steam rate would be the only viable alternative.

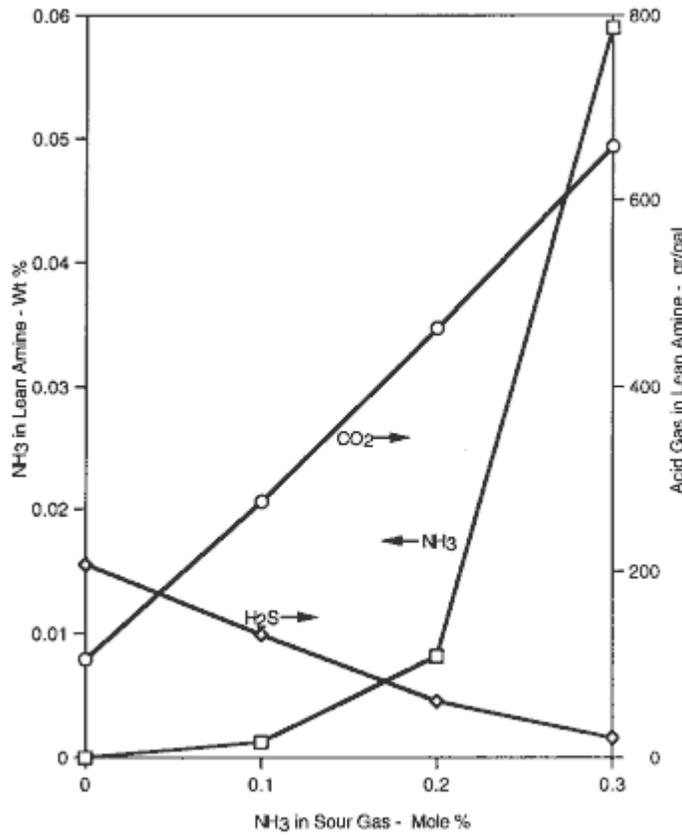


Figure 11. Effect of NH3 on lean amine for Case 2-- MEA unit.

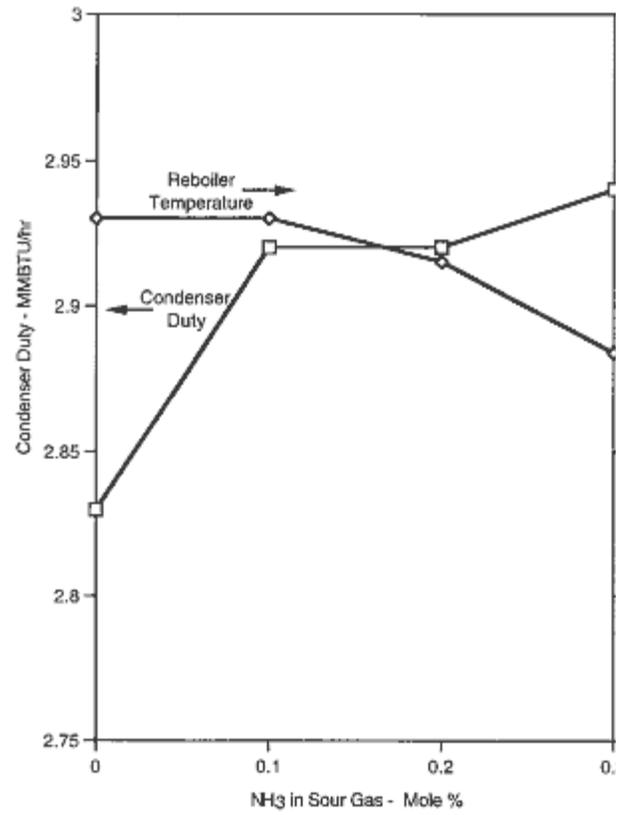


Figure 12. Effect of NH3 on condenser duty and reboiler temper. Case 2 -- MEA unit.

CASE 3 40 Wt % MDEA, 30 MMSCFD, 0.25% H₂S, 2.5% CO₂ at 300 psia

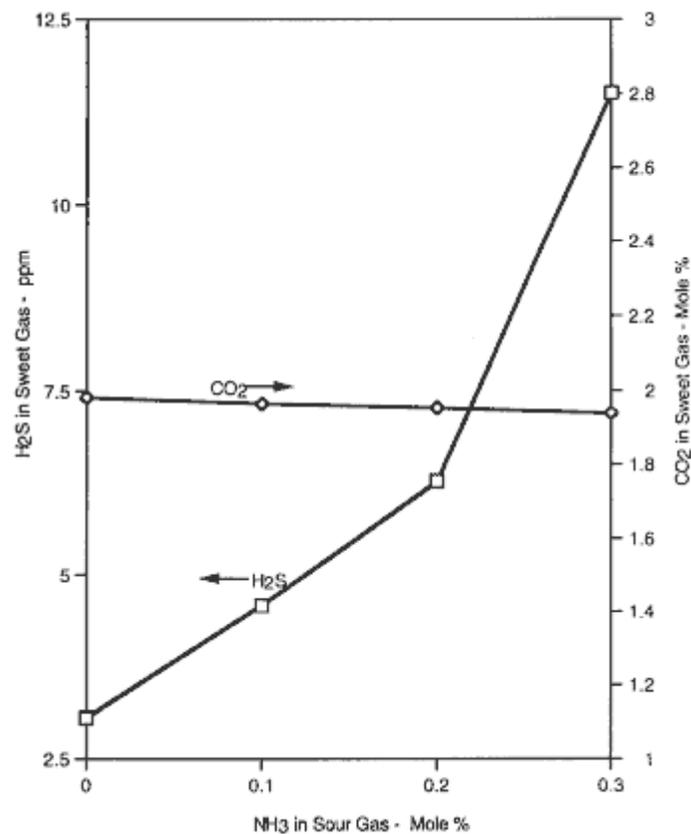


Figure 13. Effect of NH₃ on sweet gas for Case 3 -- MDEA unit.

The third case to be examined is a selective MDEA unit. It uses 200 gpm of 40% MDEA to treat 30 MMSCFD of gas at 300 psia. The unit rejects 70% of the CO₂ to produce a "pipeline" quality gas containing 2% CO₂ and 3 ppm H₂S. This type of unit shows a totally different set of problems when ammonia begins to infiltrate the system. As can be seen in Figure 13, the CO₂ in the sweet gas remains almost constant, irrespective of the ammonia level. However, as the ammonia level in the inlet gas increases, the H₂S in the sweet gas rapidly rises above 3.5 ppm. Figure 14 provides an explanation for this behavior. In a lightly loaded MDEA solution, it is easy to obtain almost total stripping of the amine. This causes large amounts of CO₂ to exit the stripper overhead. This CO₂ carries with it all of the ammonia, which in turn makes it a bit easier for the CO₂ to be carried out the top of the unit. CO₂ concentrations in the lean amine therefore go down and are no longer present to displace H₂S. The H₂S residuals, unlike the MEA cases above, begin to increase, hampering the absorber performance. The lower CO₂ residual in the lean amine does not have a large effect on the CO₂ pickup in the absorber, because this process is kinetically limited.

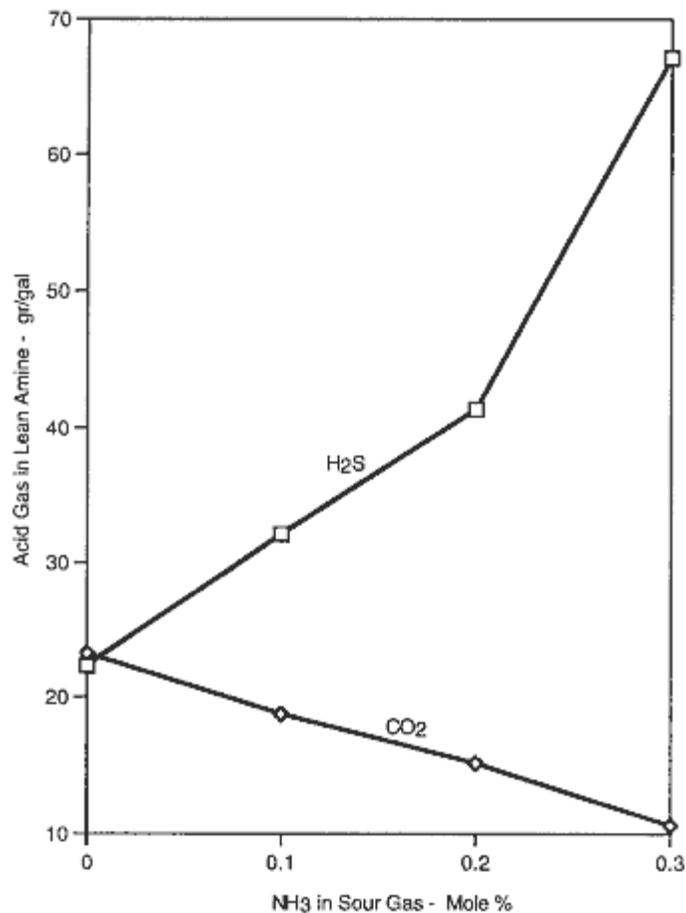


Figure 14. Effect of NH₃ on lean amine for Case 3 -- MDEA unit.

Because there is little buildup of ammonia, there is no measurable change in the condenser duty or reboiler temperature as the ammonia increases. Water losses decline slightly, as they did in Case 2, because some of the ammonia overhead in the condenser is displacing water. Accordingly, the only problem with this type of unit is the higher H₂S concentration in the sweet gas.

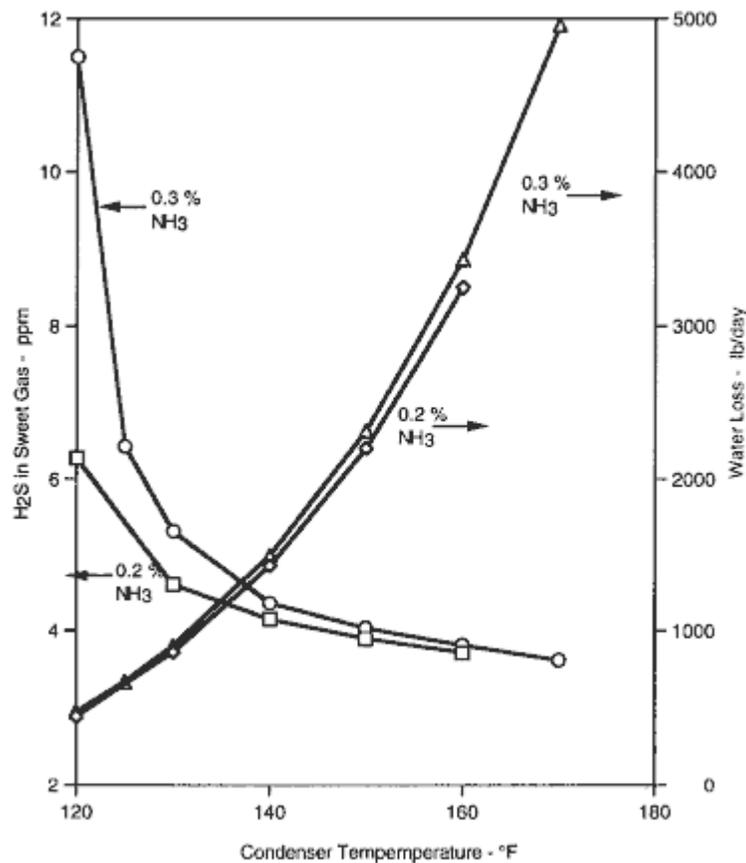


Figure 15. Effect of condenser temperature on H₂S in sweet gas and water losses for Case 3 - MDEA unit.

There are two possible mitigating actions which may be taken. Allowing the condenser temperature to rise, as was done earlier in the MEA case, is effective to some degree. However, as shown in Figure 15, these effects are limited above about 140°F, and can cause an order of magnitude increase in the water losses. If the unit has excess reboiler capacity, a much better alternative is to increase the stripping steam rate. As can be seen in Figure 16, even an increase from 11 to 13 MMBTU/hr can have a major effect on the H₂S in the sweet gas.

However, it should be remembered that each BTU put into the plant in the reboiler must be removed in the condenser. However, as long as the condenser is maintained at a constant temperature, water losses will remain constant. Because of the failure mode in this case, attempting to install a sour water stripper in the reflux would actually make the problem worse, since in addition to removing the ammonia, such a unit would also remove CO₂ which is useful in displacing the H₂S in the lower portion of the column.

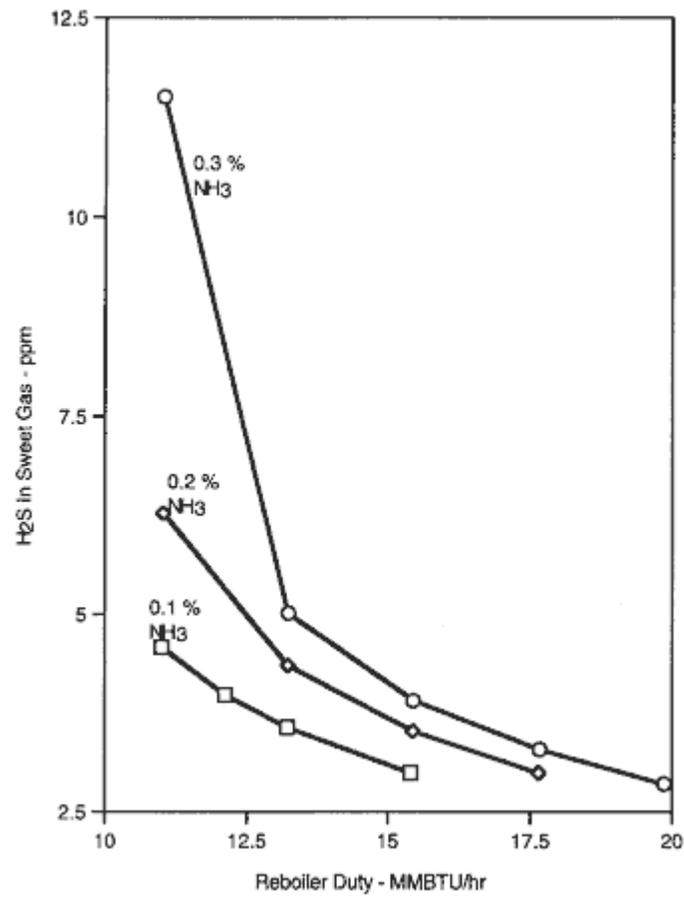


Figure 16. Effect of stripping rate on H₂S in sweet gas for Case 3 -- MDEA unit.

CASE 4: 45 Wt % MDEA, 2.5 MMSCFD, 0.8% H₂S, 51% CO₂ at 21 psi

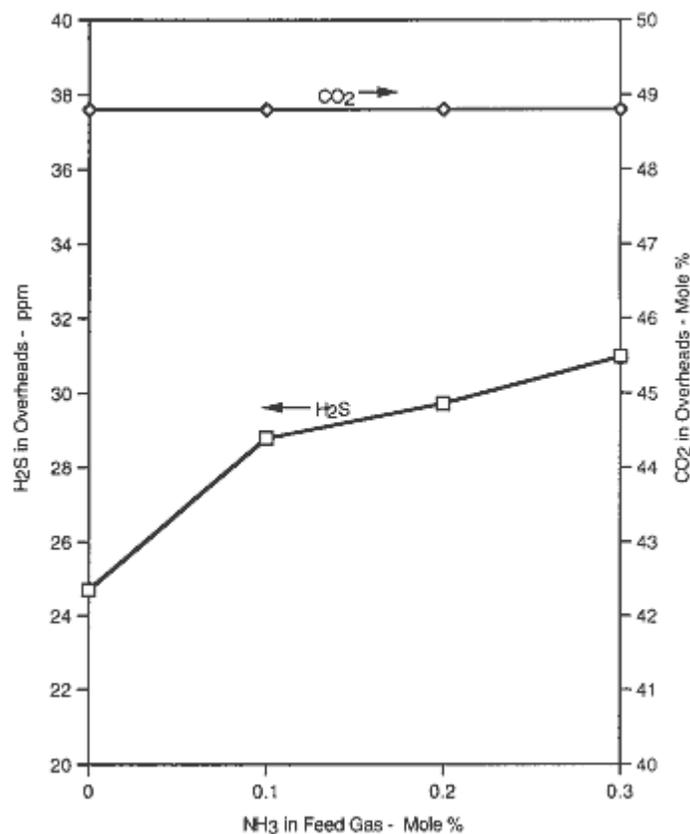


Figure 17. Effect of NH₃ on acid gas in overheads for Case 4 -- MDEA unit.

This case is typical of the conditions found in TGCU selective absorbers. The unit uses 120 gpm to remove virtually all of the H₂S, while leaving 75 to 95% of the CO₂ in place. From a process point of view, this unit is even less susceptible to ammonia problems than the Case 2 MEA unit. As can be seen in Figure 17, the CO₂ remains constant, while the H₂S shows a minor increase from 25 ppm to 31 ppm. If problems are encountered in this unit they will probably be equipment related. (The simulation does not predict the formation of insoluble ammonia salts or the corrosiveness of the mixture.) Because of the nature of the problems which might occur in the unit, there is no mitigating action which could be taken within the unit in any case. If the ammonia is going to cause problems in the TGCU absorption system, the corrective action must be taken either in the reactor to prevent the formation of ammonia, or in the spray tower which pre-cools the reactor output and can be used to remove most, if not all, of the formed ammonia.

CONCLUSIONS AND RECOMMENDATIONS

Small amounts of ammonia can cause large problems in amine sweetening units under certain conditions. These problems are usually traceable to a complex of ammonia with CO₂. If large amounts of CO₂ are present, this effect may either cause a build up of CO₂ and ammonia in the circulating amine or rob the lower section of the stripper of CO₂ which is needed to displace H₂S in the lean amine. In MEA, and it is to be expected with DEA and DGA as well, ammonia tends to push CO₂ into the reboiler, increasing the CO₂ residuals and ammonia in the lean amine. In MDEA, the ammonia appears to help drive CO₂ overhead, decreasing CO₂ residuals and by inference increasing the H₂S in the stripper bottoms. The secondary symptoms of ammonia contamination may be excessive water loss, high condenser temperature, low reboiler temperature or high acid gas residuals in the lean amine. Depending on the operational problem observed, ammonia contamination can possibly be corrected by increasing the reboiler duty, decreasing the condenser duty, or using a sour water stripper on the reflux water.

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