

Contaminants and Their Effects on Operations – Yes! You can have better operating amine and glycol systems!

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ABSTRACT

Gas processing plants encounter a variety of operational problems in their amine and glycol units. Some of these problems are caused by or exacerbated by contaminants – solids, hydrocarbons, salts and degradation products – that accumulate in the system. Drawing from multi-plant experience analyzing and controlling these contaminants, this paper addresses commonly posed questions such as:

- What contaminants accumulate in gas processing amine and glycol systems?
- Why do these contaminants accumulate in the amine and glycol systems?
- What are Heat Stable Salts and Degradation Products?
- What effects do contaminants have on amine and glycol operations?
- What do analytical reports really say about solvent condition?
- How can the contaminants – hydrocarbons, solids, salts and degradation products – be reduced, removed and controlled?
- How can lower sulfur emission specifications be met by sour gas plants and SRUs with and without SCOT units?

INTRODUCTION

Gas treating applications utilizing solvents such as alkanolamines and glycols rarely work trouble-free. Yet their design is based on a simple concept: the solvent absorbs undesirable substances from the natural gas, circulates to the regeneration or stripping section of the process, releasing the absorbed substances such that they can be collected for further processing or disposal, then circulates the regenerated solvent back to absorbing section. The regenerative recycle principle is wonderful. The solvent can be circulated indefinitely, performing its function flawlessly. The reality is, however, that over the long-term the solvent becomes contaminated and these contaminants cause operational problems.

When operational problems arise, a common response is to add something: anti-foam, corrosion inhibitor, neutralizer, fresh solvent, etc. However, additives can change the solvents properties and eventually contribute to the very operational problems they are intended to solve. For example, it is well accepted that excessive anti-foam can cause foaming in amine systems. The viscosity, surface tension, thermal conductivity, electrical conductivity, and water content of the solvent solution, are important characteristics of the solution that can be altered by accumulated additives and contaminants. Operators become accustomed to gas treating systems with operational problems because the composition of the solvent (amine or glycol) is much different than the pure solvent solution due to contamination and excessive additive issues.

This paper looks at methods of eliminating operational problems by removing solvent contaminants and minimizing additives. We propose that solvent based corrosion is best controlled by removing corrosion enhancers and corrosion products; solvent foaming is best controlled by removing hydrocarbons and corrosion products; solvent degradation is best controlled by minimizing contaminants so that degradation rates are minimized. Also, low sulfur specs are best achieved with clean amine solvent that can be made “ultraclean”. Removing the common contaminants allows the gas treating application to operate with a solvent solution that approaches the theoretical design. Plants can best approach goal of trouble-free operation by maintaining chemically and physically clean solvents. In simple terms, a clean gas treating solvent is a good gas treating solvent!

AMINES

Alkanolamine solvents are used in Gas Plants and Petroleum Refineries for removing acid gases from various gas and liquid hydrocarbon streams. The acid gases removed are H₂S and CO₂. The low sulfur specification of the products requires that the amine solvent work continuously and efficiently. The amine solvents have proven to be very predictable in removing acid gases until they become contaminated. Contaminated amines usually result in unstable operations and poor performance, which frequently becomes a limiting factor in the operation of the gas plant. More stringent sulfur emissions specifications increase the need for smoothly operating amine systems and may also require enhanced amine performance.

The principle contaminants of an amine solvent include:

1. Hydrocarbons
2. Iron Sulfide
3. Heat Stable Salts
4. Amine Degradation Products
5. H₂S

Hydrocarbons

Hydrocarbons enter the amine system due to their natural solubility in the amine solvent, by mechanical entrainment, by condensation into the cooler amine solution, and by upset conditions within the amine contactor. The foaming episodes, process upsets, and poor treating that result from hydrocarbon contamination are well known to amine system operators. While it is well known that hydrocarbons are related to foaming, the relationship has not really been well understood.

Surface tension effect

The function of amine contactors is essentially to generate surface area between the liquid amine phase and the hydrocarbon stream being treated to facilitate mass transport of acid gas components across the surface interface. Contactors can do this either by providing a large surface area for one phase to cling to while the other phase passes by the surface (packing, FiberFilmTM), by generating the surface area by agitation (trays), or by creating droplets that pass through the other phase (spray towers). Regardless of the device, energy is expended in the formation of the surface area. The amount of energy required per unit of surface area generated is proportional to the surface tension of the liquid. Therefore as the surface tension of the fluid decreases, the greater the amount of liquid surface area generated by doing work on the system.^{R-1}

Foam and emulsions

Foam is generally associated with the use of detergents, i.e. soaps which generates the familiar head of suds during a shampoo or while doing the dishes. Foam is simply a structure of expanded liquid surface area containing the gas. The energy from agitation generates the surface area in the liquid; the low surface tension of the liquid makes the energy more efficient in the generation of the surface area; and the liquid surface stays stable because it cannot drain effectively from the structure. The soap or detergent generates a stable foam by lowering the surface tension and increasing the liquid viscosity in the bubble film. Dissolved heavy hydrocarbons influence amine solutions to foam in a similar fashion.

Emulsions in liquid/liquid treating applications are analogous to foaming. The significant difference is that emulsions involve generating large surface areas between two liquid phases. Liquid-liquid treaters generate emulsions through agitation the same way gas treaters generate foam.

The amine solution is considered aqueous. Common sense tells us that oil and water don't mix, so it is understood hydrocarbons will separate easily from the amine solution. This is the premise behind the use of a rich amine flash drum to reduce hydrocarbon contamination. If you build it large enough, the oil will be separated. If any slips out, an activated carbon filter will get the little bit that did not separate.

There are two regimes of hydrocarbon contamination. The very familiar one is the rapid deterioration of the amine system performance usually concurrent with a large scale upset in a process unit tied to the amine system. A large amount of oil accumulates quickly in the amine system causing a large upset episode somewhere in the system. Much of the time the entry point of the oil and the place where the upset in the amine system occurs is not the same. The flash drum is essential for combating this situation as bulk hydrocarbons can be skimmed easily. Operators typically work out of this regime with better control of the upstream units, or installation of preventative measures at the contactors such as inlet knock-out drums, filter/coalescers, and sour gas lean amine differential temperature controllers to make them resistant to large incursions.

The more subtle and troublesome hydrocarbon contamination regime occurs when the large-scale contamination measures listed above are in place, but small amounts of hydrocarbon accumulate in the solution by contacting a stream containing low levels of oil. This is particularly true when treating streams such as recycle hydrogen from a diesel or gas oil hydrotreater or from a lean oil absorption LPG recovery system following a cracking unit or gas that contains well additives. In this regime, the oil contamination accumulates in small increments. At low levels, the oil is dispersed throughout the entire solution. It has been shown that olefinic/aromatic hydrocarbons are more soluble in amine than paraffinic hydrocarbons. As the amount of oil increases toward saturation, the natural tendency is for the oil to migrate to the surface and to break out in a free oil phase once the saturation point is reached. With oil accumulating near the surface of the amine, the surface chemistry of the amine will change; a lowering of the surface tension and increase in the liquid viscosity occurs. So as surface area is generated in the contactor, and even in the regenerator, the bubbles that were once easily broken by removing the agitation energy now stay stable because the hydrocarbon contamination changed the surface chemistry of the amine in a manner similar to the changes soaps cause in water. Foam forms when the heavy liquid hydrocarbons alter the surface chemistry.

Similarly, emulsions form in a liquid/liquid contactor as a surface layer of oil-contaminated amine stabilizes tiny droplets of amine. The NGL or LPG stream being treated carries these emulsions away causing significant amine losses.

The flash drum is ineffective at dealing with this regime because no oil separation takes place until the amine is saturated with the contaminant. Activated carbon filters are effective at removing the dissolved oil, until the surface of the carbon becomes saturated with adsorbed oil. After that, an amine system will cycle through periods of foaming or emulsions which purge some of the oil accumulation, then settle down and accumulate more until the amine surface chemistry is altered again through the hydrocarbon contamination.

One effective method of dealing with both dissolved and entrained hydrocarbons in amine solvents is the HCX™ process, as illustrated in the following table.

Hydrocarbon at HCX inlet ppm	Hydrocarbon at HCX outlet ppm	Removal %
6480	420	94%
226	27	88%
44	7	84%
5	1	80%

Anti-foam

Most amine operators don't consider anti-foam a contaminant. If used properly, it isn't. However, anti-foam is a contaminant when used improperly.

Anti-foam works in small quantities by making big changes in the surface chemistry of the amine solution trapped in a foam structure. This allows effective drainage of the liquid from the foam structure. Anti-foam is more properly described as an anti foam-stabilizer because it doesn't really prevent foam; rather, it acts to destroy stable foam structures.

To some degree, anti-foam works against the amine system operator because anti-foam disperses over the surface of activated carbon, stealing activated carbon capacity. The surface available on the activated carbon for hydrocarbon removal diminishes. Antifoam, heavy liquid hydrocarbon, and iron sulfide can combine into tight emulsions with the amine solution causing large LPG treater carryover. This is particularly true when anti-foam is added to liquid/liquid treaters to reduce "foaming". The problem is that liquid-liquid treaters don't form "foams", so anti-foam technically is misapplied in this circumstance.

Anti-foam contaminated amine accumulates hydrocarbon contamination because the carbon filter is disabled by the anti-foam removal as described above. Hydrocarbon will cause changes in surface chemistry as it builds in the system. Operators will typically fight the foaming episode with more injections of anti-foam. After so many injections, the amount of anti-foam in the foam liquid structure will be great enough that small dosages of antifoam will not change the concentration of anti-foam in the structure. At that point, anti-foam becomes totally ineffective. One refinery added enough antifoam to have a two-inch layer of anti-foam break out on the surface of the lean amine sample. The main operations complaint at the time of the incident was foaming!

Iron Sulfide – Corrosion Products

Iron Sulfide (FeS) is a common contaminant in amine systems processing gas containing H₂S. The H₂S reacts with carbon steel and forms FeS. Under the proper conditions, this FeS adheres to the carbon steel and forms a protective barrier to retard continuing H₂S attack. It is this protection (or passivation) that makes it possible to use carbon steel as a material of construction.

FeS suspended in the amine solution will cause many problems in the amine system operation. FeS plugs exchanger tubes, stripper and absorber trays, and piping, leading to fouling, channeling, and a reduction in heat and mass transfer efficiencies. Suspended FeS is abrasive, so it contributes to erosion of the protective FeS layers, leading to a cycle of corrosion, erosion, corrosion, and erosion. ConocoPhillips conducted lab tests that indicate that FeS particles tend to migrate to oil/water interfaces. The combination of high levels of hydrocarbon and FeS particles at the surface of amine solutions contributes to more frequent or severe foaming incidents. FeS will also stabilize foam and emulsions by not allowing the liquid in the foam structure to drain.

There are conditions in the amine system that interfere with FeS passivation and, thus, cause increased corrosion and FeS formation. These conditions can be mechanical, thermal, or chemical. Mechanical conditions include vibrations, erosion in high velocity areas, and mechanical shocks during shut down and start-up. These remove the FeS layer, sending particles into the circulating amine. Rapid thermal changes can cause FeS to come loose from the carbon steel and then become an abrasive material as it is circulated in suspension. This suspended FeS mechanically removes more FeS, exposing more carbon steel to H₂S and accelerates the deterioration of the amine system. Chemical factors that affect the passivation nature of FeS include high levels of Heat Stable Salts and amine degradation products.^{R-2} These contaminants must be kept as low as possible at all times to prevent the FeS corrosion, more FeS, more corrosion cycle.

One effective method of dealing with suspended solids in amine is the SSX™ process, as illustrated in the following table.

Suspended Solids at SSX inlet ppm	Suspended Solids at SSX outlet ppm	Removal %
1050	315	70%
550	117	79%
624	27	96%
27	3	89%

A distinguishing characteristic of the SSX process is the open fiber construction of the filtration media. Iron sulfide particles large and small (even sub-micron) adhere to the fibrous media without occluding passages or restricting flow. In one pass of the amine solution through the filtering media, most particles are retained on the media, but some particles may pass through. As the amine circulates and re-circulates, the number and average size of particles remaining in solution decreases, until only the green color caused by colloidal iron sulfide is visible. Eventually even the green disappears.

Heat Stable Salts – Corrosion Contributors

Heat Stable Salts (HSS) are any ionic substances that are not removed from the amine solution by heat (as in the regenerator or “stripper”). This definition is not restricted to salts that arise from reactions with contaminants absorbed in the contactor. It includes as well salts arising from

addition of “neutralizers” and other special additives, and salts that enter the amine from cooling water leaks, etc.

When the cation of the salt is the protonated amine, the salts are often termed Heat Stable Amine Salts (HSAS). There has been a tendency to ignore heat stable salt anions where the cation is something other than protonated amine, such as sodium or potassium. That leads to incorrect understanding of the amine solution. Tests conducted by MPR Services and ConocoPhillips show that negatively charged HSS anions have a pronounced affect on corrosion rates regardless of the cations they are associated with (whether protonated amine or sodium or potassium) because the anions are the same as they were when paired with a protonated amine.^{R-2,R-4} It is believed that the negatively charged anions compete with sulfide ion in the passivation layer for ionic iron in the layer by forming stable complexes.

Caustic “neutralization” is the main source of sodium and potassium HSS in amine systems. Cooling water leaks may also bring sodium and potassium salts into the amine.

The HSS are generally identified by the name of the anion of the ion pair, such as acetates, formates, thiosulfates, sulfates, thiocyanates, oxalates, butyrates, propionates, chlorides, phosphates, and nitrates, etc. Heat Stable Salts are termed “heat stable”, because they do not leave the solution or release the "bound" amine as the solution passes through the regenerator. This means every mole of Heat Stable Salt removes a mole of amine from being "free" or available for removing acid gas. This reduces the amine system capacity, and can result in increased amine circulation rates, increased steam usage to the amine stripper reboiler, lower sulfur removal from the feed gas, or reduced production capacity.

In addition to the effect of Heat Stable Salts on capacity, they also increase corrosion, increase iron sulfide production, increase filtration requirements, and increase hydrocarbon entrainment. All of these combine to increase foaming, system instability, and reduce production rates. An amine system in an upset condition results in more flaring incidents, excess sulfur in fuel gas and tail gas incinerators, amine in flare knockout drums, and amine in waste water. Elevated levels of amine in waste water treatment systems can kill microbes and will result in reduced waste water treatment capacity.

Degradation Products

Degradation Products are molecules formed that include the amine as part of the molecule. These degradation products are usually inert, but can be polar and strong chelators of iron and thereby contributors to corrosion. They also cause increased solution viscosity and density, reduced surface tension, reduced water content and reduced available amine which can lead to increased foaming, fouling, and high flash gas production. Many amine degradation products have been known for years, but higher demands on amine system performance and analytical advances have resulted in a resurgence of interest.^{R-5, R-6, R-3, R-7}

Examples of Degradation Products in a primary or secondary amine include **amides**, such as Formyl-MEA, Formyl-DEA, and Formyl-DIPA (alternatively referred to as MEAF, DEAF,

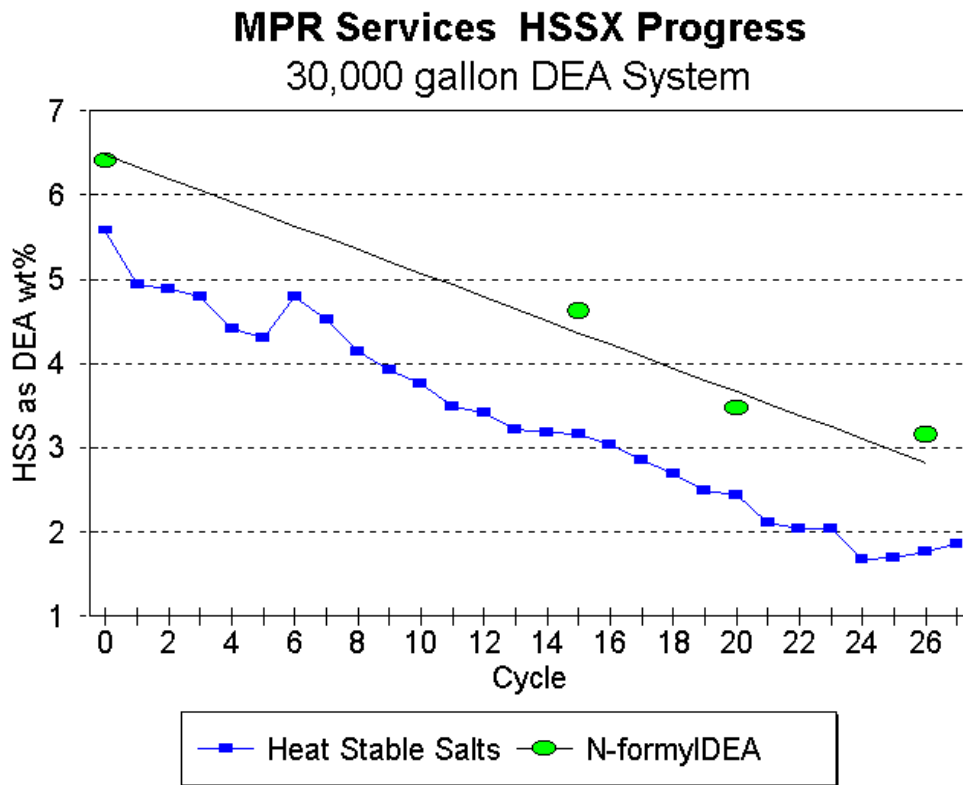
DIPAF). Formation of formamides results in a loss of one mole of useful amine per mole of formamide. The formation of these formamides may be depicted as follows:



Other amides, such as acetamides (e.g., Acetyl-DEA from DEA and acetate) may also form. Temperature, time, pH and concentration affect the formation of amides. Since the first two factors are usually fixed in the amine system, attention must be focused on concentration. There is a molar relationship between the presence of the formate heat stable salt in primary or secondary amines and the presence of the formamides. The molar ratio of formamides to formates varies with amine type and degree of contamination, with higher ratios typically seen at higher contaminant concentrations. Formamides have been seen in operating amine systems from less than 1 wt% to 15 wt% and higher. Fortunately, experience has shown, that formamides may be converted back to useful free amine, while using the HSSX® process (see Table 1 and Figure 1).

Table 1			
Formamides converted to useable Amine while using MPR's HSSX® process			
System	AMINE	AMIDES Start wt%	AMIDES End wt%
A	DEA	6.1	1.0
B	DEA	6.4	3.1
C	DEA	2.2	1.2
D	DEA	11.0	3.0
E	DEA	16.0	2.0
F	DIPA	6.0	1.9
G	DIPA	4.1	2.5

FIGURE 1



Another family of degradation products commonly found in primary and secondary amine systems are **oxazolidones**. These compounds may accumulate in CO₂ service, as suggest by the following:



Formation of oxazolidones results in a loss of one mole of useful amine per mole of oxazolidone formed. Accumulation of oxazolidones will reduce water content and lower treat effectiveness. A process called the Oxex™ Process can be used to reverse this formation and recover the amine on-line, while the amine system is operating (see Table 2, Figure 2 and Figure 3).

Table 2			
Oxazolidones converted to useable Amine using MPR's OXEX™ process			
System	AMINE	OXAZ. Start wt%	OXAZ. End wt%
A	DIPA	7.2	2.3
B	DIPA	2.2	0.5
C	DIPA	15.7	4.4
D	DIPA	10.2	5.1

FIGURE 2

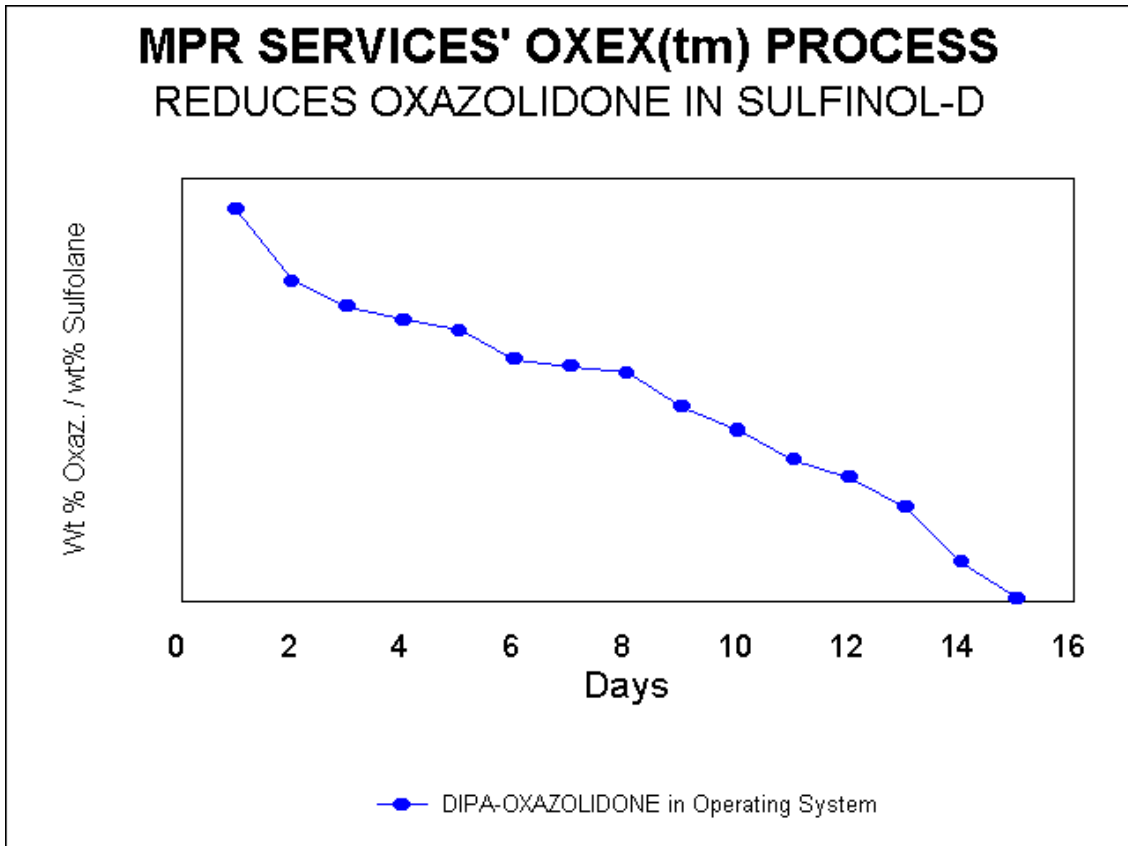
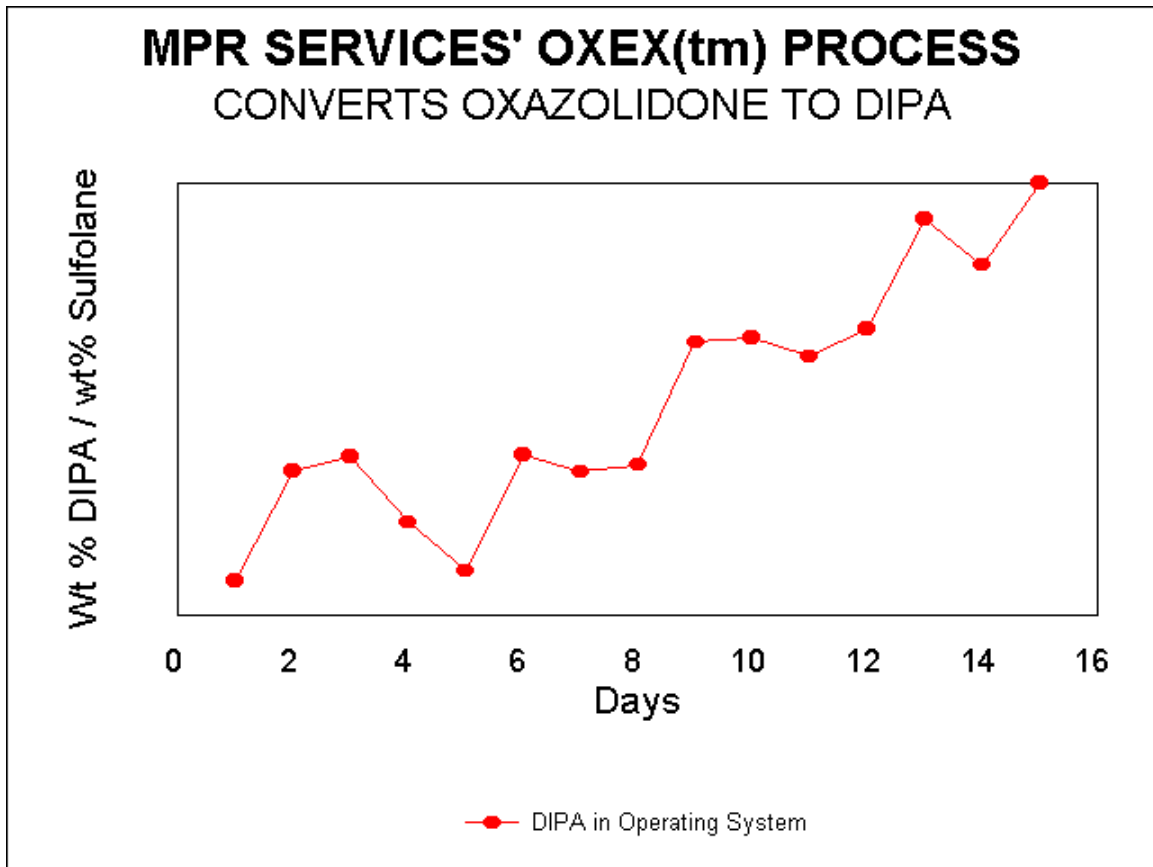


FIGURE 3



Amino acids, such as **bicine**, are degradation products found in systems using tertiary amines such as MDEA, as well as secondary amines, such as DEA.^{R-3, R-8} Bicine has been shown to contribute to corrosion^{R-2, R-4, R-9} and should be monitored closely. One amine vendor recommends that Bicine not exceed 250 ppm.^{R-9} Amino acids form after oxygen and SO₂ ingress to Tail Gas Treating systems. Serious increases in bicine and secondary amines occur in tail gas units in the weeks following Claus plant upsets.^{R-3} Bicine formation can be interrupted by immediate removal of the Heat Stable Salts (primarily thiosulfate) caused by the upset. Bicine has been successfully removed by MPR's HSSX® Process (see Table 3).^{R-8}

Table 3 – Examples of Bicine Removal Projects

System	Amine	Initial Bicine, Wt. % or ppm	Removal End Point, Wt % or ppm
A	MDEA	4.9	1.8
B	MDEA	3.9	1,200 ppm
C	MDEA	2.1	3,200 ppm
D	MDEA	3.1	0.7
E	MDEA	2.0	0.6
F	DEA	1.2	0.6
G	MDEA	1.0	2,300 ppm
H	MDEA	2.1	1,400 ppm
I	MDEA	3,000 ppm	200 ppm
J	MDEA	4,000 ppm	500 ppm
K	MDEA	1,825 ppm	24 ppm
L	MDEA	500 ppm	40 ppm

Hydrogen Sulfide (H₂S)

When an amine system is unable to meet desired treatment levels or final emissions specifications, then hydrogen sulfide can play the role of a contaminant that affects the effectiveness of the amine system. It has long been recognized, particularly in tail gas systems, that increased H₂S removal can be obtained by reducing the H₂S concentration (the lean loading) in the lean amine that is directed to the top of the absorber. Thus, in this instance, H₂S is not only the target of the amine absorber, but it also acts as a contaminant in the lean amine.

New sulfur emission regulations are requiring reduced emission levels, so the topic of increased H₂S absorption has new life. For example, Shell recently introduced SCOT modifications to address the issue^{R-11} and MPR has introduced the UltraLean™ Amine (ULA) process.^{R-12} The UltraLean process addresses the problem without affecting the design and operation of the existing amine system. By taking a small slipstream of the lean amine that was previously flowing to the existing absorber, and removing essentially all of the residual acid gas that was not removed during the normal stripping operation (zero H₂S lean loading), an amine is produced with enhanced absorption capability. The result is that the vapor/liquid equilibrium on the top tray of a ULA Absorber will be markedly shifted in favor of increased acid gas absorption.

Typical improvements would be reductions in the H₂S content in the Sweet Fuel Gas from 300 ppmv to 30 ppmv, 150 ppmv to 15 ppmv, and 30 ppmv to 3 ppmv.

Figures 4 and 5 illustrate a implementation of the UltraLean process on typical amine systems.

The UltraLean Process does more than just remove the residual lean loading from the amine. It simultaneously removes Heat Stable Salts and can be packaged with processes for the removal of Suspended Solids and Hydrocarbons. If desired, the UltraLean process can slip CO₂. Impurities are removed from the entire amine system. Even though only a slipstream of the amine system is being processed, over a short period of time the entire amine system will be treated. The HSS incursion rate, the HSS concentration, and the HSS removal rate will come into balance such that the entire amine system solution will be maintained in nearly new condition.

Major emissions reductions are also possible in TGUs utilizing SCOT type treaters. As described above, the ULA will shift the vapor/liquid equilibrium markedly towards the absorption of H₂S thereby reducing TGU emissions. Emission level reductions from 200 ppmv H₂S to less than 20 ppmv can be accomplished.

For smaller SRUs that do not currently have a TGU, the addition of a single ULA Absorber will meet the required emission levels without the necessity of a “full blown” TGU. Quenching and cooling is all accomplished in a single tower. The SO₂ salts are a small quantity and are removed simultaneously with the other HSS.

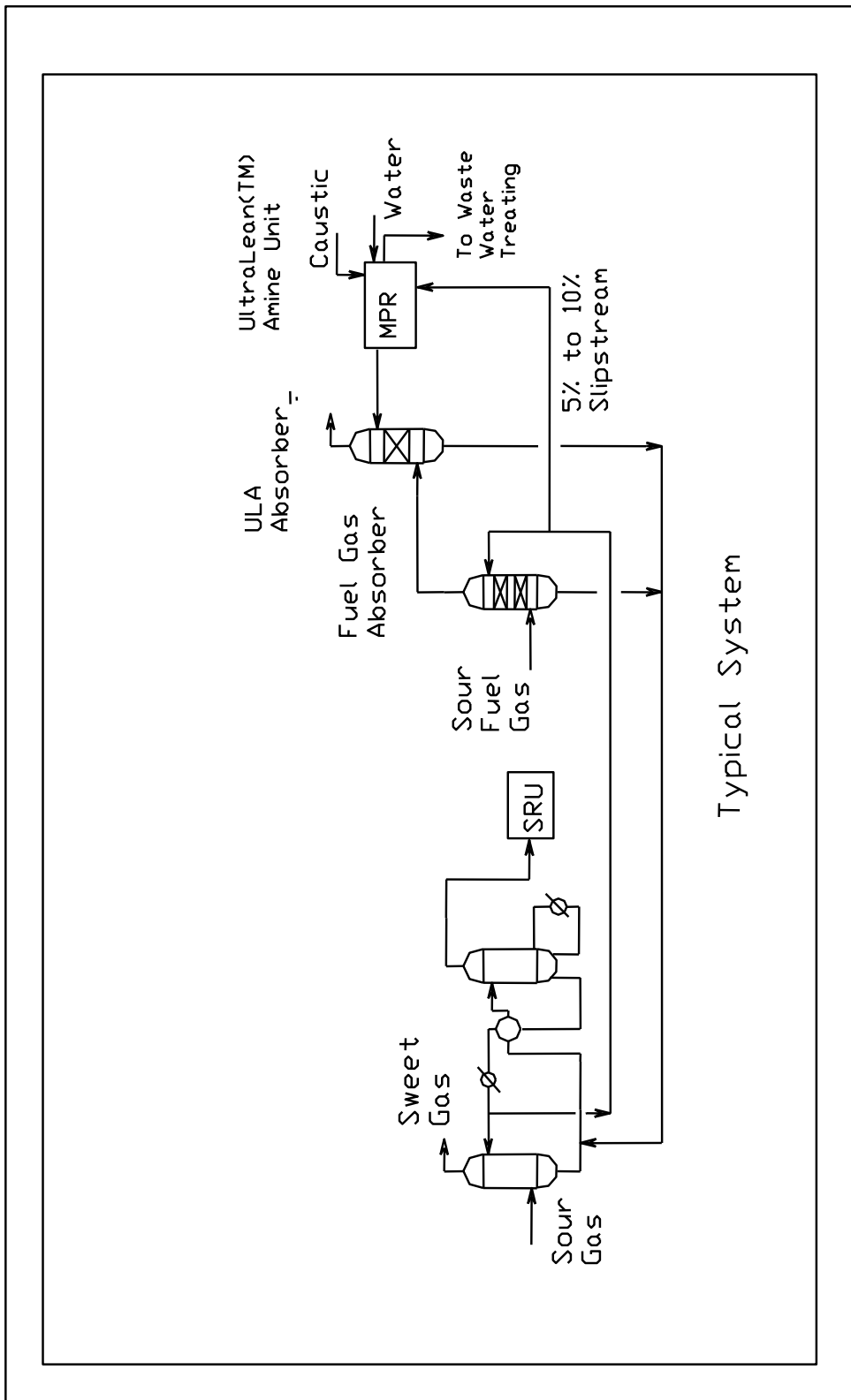
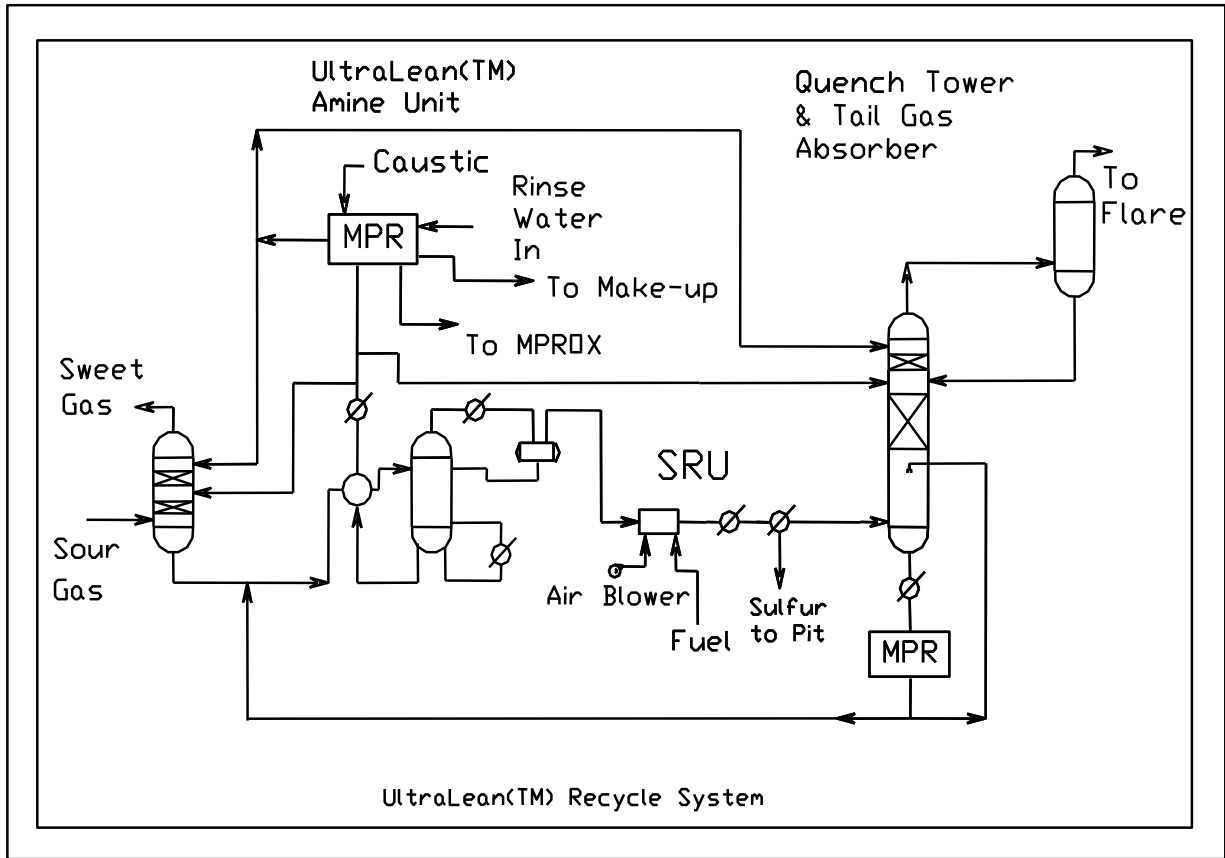


FIGURE 4

FIGURE 5



GLYCOLS

Glycols are typically used for natural gas dehydration, oil and gas production hydrate inhibition, and aromatics extraction. Primary contaminants are salt (chlorides) from seawater and salt domes and glycol degradation products. The typical range of salt concentrations in operating glycol systems may run from hundreds of ppm to several percent. MPR's Glycolex™ process, based on MPR's ion exchange technology, has successfully reduced salt concentrations from several percent to the low ppm levels. Permanent Glycolex installations maintain salt levels continually below 100 ppm.

ANALYTICAL REPORTS

Knowledge of the concentration of the active solvent (e.g., free amine or glycol) and of the target compounds (e.g., acid gases or water) is clearly necessary for proper operation of a amine or glycol system. Contaminant concentrations are also important to know, but there exist a variety of attitudes as to what degree of analysis is necessary. An amine analysis report, for example, might contain only free amine, lean loading, water, with the "residue" left to the imagination of the reader. If an amine or glycol system is to be properly managed, however, one must know the quantity and distribution of contaminants (hydrocarbons, solids, salts, degradation products) in the residue.

Currently there is great need for definition and standardization of terms used in the reports of analysis of amine and glycol solutions. Significant confusion and misinterpretation occurs because different analytical laboratories report results in similar sounding, but much different units. A thorough discussion of the problem is beyond the scope of the present paper, but all amine and glycol uses should be aware fo the current confusion in the industry.

METHODS OF CONTAMINANT REMOVAL

Observation of amine and glycol system operations both clean and dirty, leads to the conclusion that systems operate much better and contribute more to the 'bottom line' when the operating solvents are clean – as they were designed to be. In the foregoing text, mention has been made of hydrocarbon removal and solids removal by an on-site process that is regenerable (HCX and SSX processes) and of salts removal and degradation products removal or conversion by ion exchange based regenerable processes (HSSX, GLYCOLEX, and OXEX processes). All these are focused on the target impurities and are well suited to achieving and maintaining low concentrations of the contaminants.

Other means for the removal of hydrocarbons (activated carbon) and solids (varieties of filters) are well known. Other available means of removing salts include distillation, electrodialysis, and bleed-and-feed. These methods are efficient at high contaminant concentrations, but, as discussed above, high contaminant concentration is not a desirable amine system operating condition. Furthermore, they suffer disadvantage from high solvent loss rates. Bleed-and-feed – removing contaminants by removing contaminating amine and feeding in new amine – requires disposal of large amounts of amine and is environmentally unfriendly.

GAS PLANT EXAMPLES

AMINES

Case History 1 – Bicine (degradation product)

A Texas gas plant utilizing a specialty MDEA solvent was experiencing significant corrosion shortly after plant start-up in the carbon steel sections of the amine plant. With the assistance of their amine supplier, the plant determined that the corrosion was being caused by the presence of Bicine generated due to O₂ in the sour gas feed. The incoming oxygen incursion into the amine system could not be eliminated. A combination corrosion inhibitor/oxygen scavenger was added to the amine to scavenge the O₂ and to prevent further degradation of the MDEA to Bicine. The implementation of the O₂ scavenger program did decrease the Bicine formation rate. However, this action was not totally adequate to control the corrosion. MPR was requested to provide their mobile ion exchange equipment to reduce the Bicine. The Bicine level was reduced from 3,929 ppmw to 471 ppmw in the operating amine system.^{R-13} Figure 3 depicts the Bicine reduction during the mobile cleaning period. The corrosion was reduced by the mobile cleaning service but returned when the mobile cleaning equipment was removed.

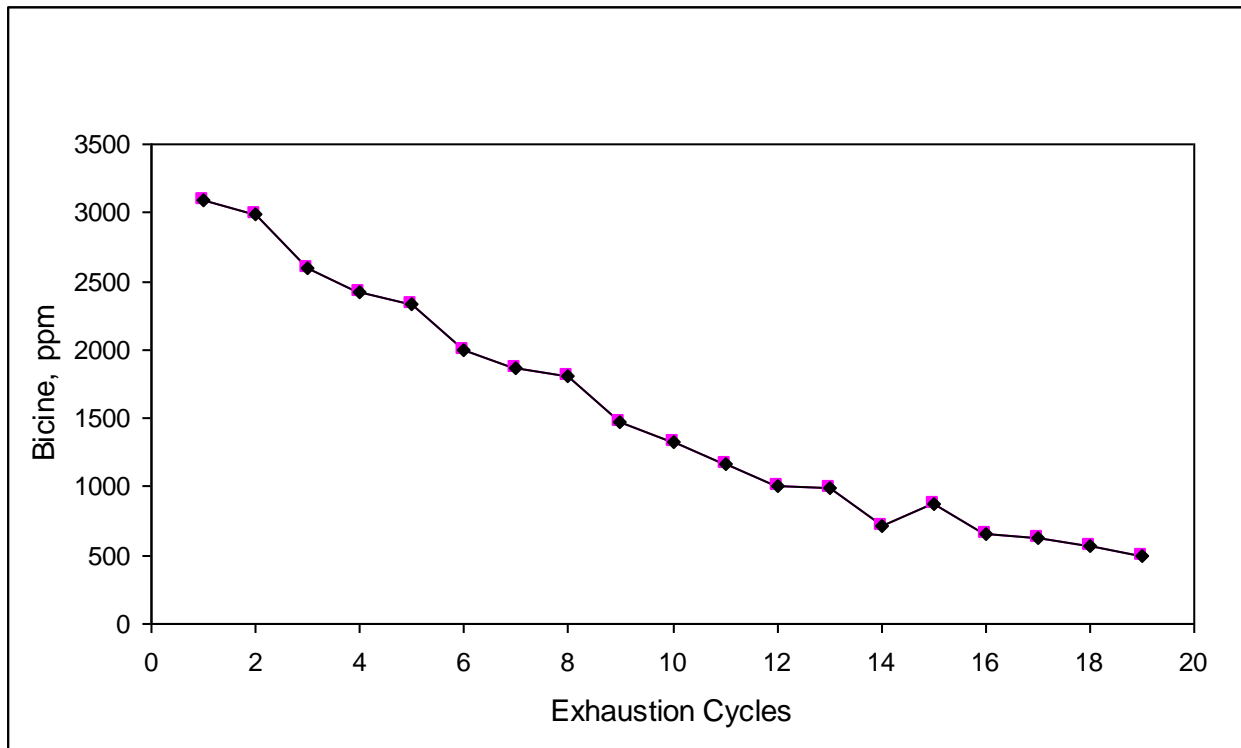
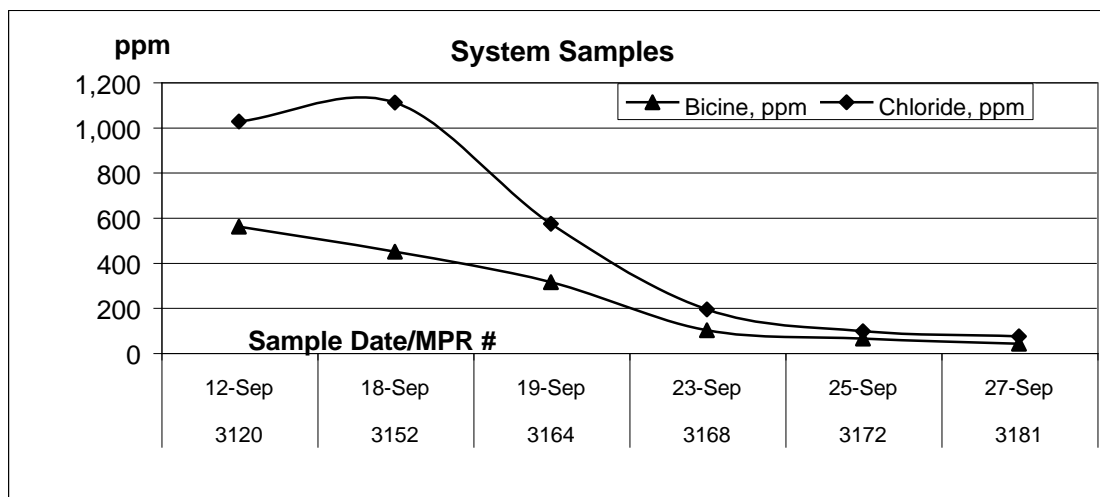


Figure 3 – Bicine Removal

Case History 2 – Bicine and Salt

In 2002, Pinnacle Gas Treating Inc. (a subsidiary of Anadarko Petroleum) at the Bethel Gas Plant at Tennessee Colony, Texas became concerned when their Bicine level reached the 500 ppm level in their specialty formulated MDEA solvent. The plant began experiencing high corrosion rates, excessive foaming, equipment fouling and unstable plant operations. Chlorides were also elevated and were an additional concern. A mobile ion exchange project successfully reduced the Bicine to less than 40 ppm. Figure 4 shows the Bicine reduction during the mobile cleaning job.

Figure 4 – Bicine and Chloride Removal



Case History 3 -- Hydrocarbons

A large refinery struggled with continual large amounts of hydrocarbons in the amine system, even up to several thousand ppm. An HCX unit was installed for continual removal of hydrocarbons on a slip stream that draws about 1 system-volume per day (about 16% of circulation rate). As the unit began operations, hydrocarbons in the system were seen fluctuating greatly, up to 6500 ppm. During the 3 and 4th months of HCX operation, hydrocarbons in the system were more consistently under 100 ppm. In the 5th month, the hydrocarbons in the amine were being held under 10 ppm.

Case History 4 – Solids, Corrosion, Salts, Hydrocarbons

A refiner experienced severe corrosion problems evidenced by the need to change filter elements 1 to 3 times a day. To minimize filter change-out frequency, larger pore size elements were employed. Amine system upsets frequently curtailed production and caused flaring. Heat Stable Salt contamination was up to about 5 wt% as MDEA in solution. The patented HSSX® Process (utilizing ion exchange) was contracted to remove heat stable salts. Salt levels were reduced to less than 1 wt% as MDEA. The next filter change out was performed a month later, not because

of need, but to inspect the filters, which were found to be in good condition. Corrosion had also been controlled by removing contaminants. Flaring incidents ceased for 6 months. Only after heat stable salt levels increased again did operational problems recur and filter change out frequency increase. Operational problems had been reduced by removing contaminants.

For several years this refinery repeated this cycle with regular periodic removal of HSS. As production demands became more severe, hydrocarbon incursions into the amine system and solids accumulations became more significant and frequent, resulting in operational difficulties and production curtailments. Trials of the SSX™ and HCX™ processes were conducted, producing clear proof of capacity and effectiveness of solids and hydrocarbon removal. A continuous Amine Shield™ Slip Stream Unit (SSU) [an automated unit comprising the SSX, HCX, and HSSX processes] was installed to continuously keep HSS, hydrocarbons and solids concentrations low. Immediate benefits to the refinery production were evident. In the first year of SSU operation, amine-related incidents at the wastewater treatment plant were reduced 98% and increased sour crude purchases attributable to smoother amine system operations were valued at \$2.6 million. After 2.5 years of continuous SSU operation, the refinery ascribes the following benefits to the use of the SSU:

- Reduced operational upsets
- Reduced amine losses
- Reduced corrosion – even the rich amine is clear (low corrosion rate; minimal dissolved iron in lean amine; erosion miniscule; any suspended FeS particles are much less than 1 micron in size)
- Estimated annual bottom line return \$3.5 million

Discussion – Hydrocarbons, Solids, Foaming in Gas Plants

Gas plants often experience operational problems with amine systems. Hydrocarbons and solids are well-known contributors to the problems. A recent presentation at the GPA convention detailed an example of what is all too typical. ^{R-10} A Texas cryogenic natural gas liquids recovery facility had experienced years of difficulties with their amine plants, resulting in high amine losses and off spec product. An engineering study found that filtration of the amine was inadequate as was downstream amine / product separation equipment. Operations were much improved after specific application of high-technology mechanical separation and filtration systems to address the contamination issues.

New tools are now available to address such gas plant problems – the onsite-regenerable SSX and HCX processes. These new processes, previously described, offer increased removal of solids and hydrocarbons over that now available by mechanical methods. The enhanced removal results in much cleaner amine solutions without the need to replace mechanical filter elements. The on-site regeneration is accomplished with the use of a combination of ambient temperature water and hot water or steam condensate.

GLYCOLS

Case History 5 – TEG

A gas plant utilizing salt dome storage periodically experienced carry over of sodium chloride into its TEG system during periods of heavy gas demand. The sodium chloride level exceeded its solubility level at some points in the system causing fouling of reboilers. A proprietary process (the Glycolex™ Process utilizing ion exchange) was contracted to remove the chloride. While the regenerators were off line, the glycol system was cleaned producing a product with less than 20 ppm chloride without glycol loss. Salt removal continued until precipitated salt was redissolved and the chloride level in the system was less than 200 ppm. Operational problems were eliminated by removal of contaminants.

Case History 6 – MEG

A MEG system at a gas plant associated with a pipeline was plagued by operations and maintenance problems because of the precipitation of iron carbonate in heat exchangers and regenerators. Additionally, the extremely fine particulate iron carbonate defied filtration, and added to the fouling in the heat exchangers and tower elements. Agglomerated particles formed during regeneration collected on filters in the regeneration trains necessitating 6 or more filter changes per day. The Glycolex™ process was utilized and dissolved iron and salts were removed. Glycol from the rich and lean storage tanks was cleaned of dissolved iron, agglomerated particulate iron, fine particulate iron, condensed hydrocarbon and sodium chloride. From black, particulate-laden glycol containing over 6000 ppm sodium chloride, dissolved and particulate iron ranging from hundreds to thousands of ppm, and condensed organics, a product was produced that was clear, colorless glycol containing consistently less than 1 ppm iron, 20 ppm chloride, and 20 ppm sodium, with the pH maintained at the desired level. As the plant circulated this cleaned glycol in their system, filter changes dropped to less than 1 per day and operational problems were greatly reduced.

Case History 7 – EG

An EG system at a gas plant associated with a pipeline contained over 4900 ppm sodium chloride. The Glycolex™ Process was employed to reduce the sodium and the chloride. The desired level of less than 350 ppm chloride and less than 300 ppm sodium was achieved by processing a slipstream of glycol while the system continued to treat gas. Corrosion concerns were eliminated by removal of contaminants.

Summary and Conclusions

The primary contaminants that cause trouble in amine and/or glycol systems are Heat Stable Salts, Hydrocarbons, Solids, degradation products, and Hydrogen Sulfide (H₂S). The relationship of these contaminants to operational problems was discussed and several means of reducing and maintaining low contaminant concentrations were presented.

Tremendous benefits to the gas plant operator result from controlling amine and glycol system contaminants at very low levels. Demonstrated benefits include reduced operational problems and increased plant throughput. These benefits have been experienced by some operators by employing a system for controlling contaminants that has the unique feature that all three processes – salt, hydrocarbon and solids removal – are all regenerable on site with water-based regenerants.

References

- R-1:** Pauley, C. R., Hashemi, R., and Caothien, S., "Analysis of Foaming Mechanisms in Amine Plants", paper presented at AIChE Summer Meeting, Denver, Colorado, August 22-24, 1988.
- R-2:** Cummings, A.L., Veatch, F.C., Keller, A.E., "Corrosion and Corrosion Control Methods in Amine Systems Containing H₂S", Paper 97341, NACE International (1997).
- R-3:** Critchfield, J.E., and Jenkins, J.L., "Evidence of MDEA Degradation in Tail Gas Treating Plants", *Petroleum Technology Quarterly*, Spring 1999, pp 87-95.
- R-4:** Mecum, S.M., Veatch, F.C., and Cummings, A.L., "Why Caustic Addition is Bad for Amine Systems", *Hydrocarbon Processing*, October 1997, pp. 115-19.
- R-5:** Blanc, C., Grall, M., and Demarais, G., "The Part Played by Degradation Products in the Corrosion and Gas Sweetening Plants using DEA and MDEA", Laurance Reid Gas Conditioning Conference, 1982.
- R-6:** Rooney, P.C., DuPart, M.S., and Bacon, T.R., "The Role of Oxygen in the Degradation of MEA, DGA, DEA, and MDEA", Laurance Reid Gas Conditioning Conference, 1998.
- R-7:** Smit, C.J., van Heeringen, G.J., and van Grinsven, P.F.A., "Degradation of Amine Solvents and the Relation with Operational Problems", Laurance Reid Gas Conditioning Conference, 2002.
- R-8:** Lawson, G.L., Cummings, A.L., and Mecum, S.M., "Amine Plant Corrosion Reduced by Removal of Bicine", Gas Processors Association, San Antonio, Texas, March 2003.
- R-9:** Rooney, P.C., Bacon, T.R., DuPart, M.S., "Effect of Heat Stable Salts on Solution Corrosivity of MDEA-based Alkanolamine Plants. Part III", Proceedings of the Laurance Reid Gas Conditioning Conference, March 1997.
- R-10:** Webb, T., Lopez, M., Miller, M., and McDowell, M., "Duke Entergy Field Services East Texas Gas plant Optimizes Productivity Through Implementation of Enhanced Separation and Filtration Technology", Gas Processors Association Annual Convention, San Antonio, TX, March 12, 2003.
- R-11:** van den Brand, Kees, "Shell's New Low Cost SCOT Process", 2002 Sulfur Recovery Symposium, Vail Colorado, September 2002.
- R-12:** Lawson, G., "UltraLean™ Amine Zero Residual Acid Gas Loading", Gas Processors Association 80th Annual Convention, San Antonio, TX, March 2001.

R-13: Howard, M. and Sargent, A., “Operating Experience at Duke Energy Field Services Wilcox Plant with Oxygen Contamination and Amine Degradation”, Proceedings of the Laurance Reid Gas Conditioning Conference, February 2001.

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