



HYDROCARBON REMOVAL FROM AMINES DEMONSTRATED EXPERIENCE

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ABSTRACT

Several large Operating Facilities are now using the latest Technology from MPR Services, Inc. for the removal of hydrocarbons from their amine systems. These HCXTM units have been installed and operating from six months to over five years. The measured results show that the new Technology maintains a hydrocarbon content of less than 10 ppm (the maintenance level) when the amine system is experiencing normal hydrocarbon incursion and a recovery period (return to maintenance level) of less than thirty days after a major operating system upset (large single event hydrocarbon incursion). Prior to installation of HCX, the amine systems had continuous hydrocarbon levels of 200 ppm to 6,000 ppm (at which point foaming created a purging of the system by amine carry-over with new amine then being introduced).

The amine removal media is fully “regenerable” using hot water (steam condensate) and is PLC or Timer Controlled for automatic switching between the absorption period, the rinse (amine displacement) step, and the hot water regeneration step. The removal media life is exceeding three years before replacement is required.

The demonstrated results after several years of operating experience show that maintaining a continuously low level of hydrocarbons reduces foaming, reduces amine losses, improves amine system performance and reliability, and greatly reduces carbon filter change-outs and the associated maintenance labor and solid waste disposal.

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INTRODUCTION

Hydrocarbons are second only to Heat Stable Salts as a major contaminant in amine systems. If there is a steady incursion and accumulation of hydrocarbons in the amine treating solution, then ultimately the amine solution will begin to foam. Foaming in turn leads to amine loss through carry-over and reduced amine system performance. The MPR HCX™ Hydrocarbon Removal Process has now been installed and operating in four major refineries for periods ranging from several months to several years. These units produce a continuously clean amine solution containing less than 10 ppm of hydrocarbons. The important result is that the stability and performance of these amine systems has been greatly improved with much lower loss of amine.

Table I - Hydrocarbon Content of Amine – Before and After HCX Process Installation

Refinery Location	Before HCX HC ppm	After HCX HC ppm	Operation Time	Operator Comments
Midwest	100 - 3000	1 to 10	> 5 years	Smoother operations; Sulfur plant happy
Midwest	200 to 400	2 to 30	> 4 years	2.6 MM\$ to bottom line in first year
Gulf Coast	2000 - 6500	1 to 30	> 2 years	Amine losses greatly reduced
Middle East	700	2 to 15	> 2 years	More efficient than prior installation

GENERAL OPERATIONS

The performance numbers presented in Table I above are maintained by periodic regeneration of the HCX hydrocarbon removal beds. Regeneration occurs typically once per week when operating at the maintenance level and once per day during those periods when recovering from a massive instantaneous influx of hydrocarbons.

The hydrocarbons are removed from the absorption media by flushing with hot water (typically steam condensate). The oil-water mixture is routed to the oily water sewer, an API separator, or a slop tank. There is a rinse step (for amine displacement) between the amine absorption and the hot water regeneration, this rinse reduces the amine lost to the oily water to less than 500 ppm. The rinse water is returned to the amine system thus reducing the normal water makeup requirement.

The hydrocarbon removal capacity of the HCX absorption media is approximately seventeen times the equivalent volume of charcoal. Full absorption capacity is regained upon each regeneration. The actual lifetime of the media in the operating plants has been over three years.

SLIPSTREAM OPERATION

Full flow is not required. The above units are installed and operating on a 5% to 15% slipstream taken from the cool lean amine solution prior to its entering the amine contactor. This smaller flow reduces equipment size and cost but will still effectively remove the contained hydrocarbons. In a typical operation mode the slipstream flow will turnover the amine system volume approximately once per day. The daily treatment of the entire amine system volume will remove the typical daily incursion of hydrocarbons and maintain less than 10 ppm in the entire system.

But, what about the periodic incursion that occurs from an operating up-set that dumps many gallons of hydrocarbons into the amine system and floods the amine Flash Drum? This is actually handled by the amine system “carrying capacity” for hydrocarbons, if the amine is routinely kept clean. Most amine systems currently operate with some contained hydrocarbon (anywhere from a hundred to several thousand ppm). If an amine system has minimal initial hydrocarbon content, it is well positioned to absorb the shock of an instantaneous influx of hydrocarbons. While there is a quantity of hydrocarbons that can overwhelm any system, there is a large potential “carrying capacity” in a clean system that will handle up-sets that would normally destabilize an amine system already containing significant amount of hydrocarbons. For example, a 100,000 gallon amine system carrying 3,000 ppm of hydrocarbon would have 440 gallons of dispersed and/or dissolved hydrocarbons. If this system contained essentially no hydrocarbons, then an upset that results in less than 440 gallons of hydrocarbons passing through the Flash Drum and into the amine system will be much less likely to become unstable.

FOAMING

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 and/or CO₂ 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 facility.

Hydrocarbons will remain in the amine system due to their natural solubility in the amine solution even after the amine regenerator. The foaming episodes, process upsets, and poor treating that result from hydrocarbon contamination are well known in the Industry.

The function of amine contactors is essentially to generate surface area between the liquid amine phase and the sour gas 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 (i.e. packing), 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 [1].

Foam is generally associated with the use of detergents, i.e. soaps which generates the familiar head of suds. 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 stable foam by lowering the surface tension and increasing the liquid viscosity in the bubble film. Dissolved

hydrocarbons influence amine solutions in a similar fashion.

The amine solution is considered aqueous and common sense tells us that oil and water don't mix, so it is understood that hydrocarbons will separate 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.

However, there are two modes of hydrocarbon contamination. The very familiar one is the rapid deterioration of the amine system performance resulting from a large scale upset in a process unit upstream of the amine system. A large amount of oil accumulates quickly in the amine system causing it to become unstable. The flash drum is essential for combating this situation.

The more subtle, and often more troublesome, hydrocarbon contamination mode occurs when small amounts of hydrocarbon accumulate in the solution by contacting a stream containing low levels of oil. In this mode the oil contamination accumulates in small increments. At low levels the oil is dispersed throughout the entire solution. 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 now remain 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.

The flash drum is ineffective at dealing with the dispersed oil mode 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 which purge some of the oil accumulation, then settle down and accumulate more oil until the amine surface chemistry is altered again through the hydrocarbon contamination.

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.

Amine contaminated with anti-foam can promote hydrocarbon contamination because the carbon filter is disabled by the anti-foam removal. 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 many injections the amount of anti-foam in the foam liquid structure will be so great that small dosages of antifoam will not change the concentration of anti-foam in the structure. At that point, anti-foam becomes totally ineffective.

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. [2] 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 HCX process for control of hydrocarbons and its companion regenerable SSX process for control of solids. As shown above, the HCX process offers increased hydrocarbons removal capacity relative to common current methods. The enhanced removal results in much cleaner amine solutions without the need to replace filter media. The on-site regeneration is accomplished with the use of a combination of ambient temperature water and hot water or steam condensate.

SUMMARY

As expected and as demonstrated, the reduced hydrocarbon content of the circulating amine has resulted in less foaming and less amine loss through carryover. In addition, the operating amine systems are more stable providing consistently improved sour gas removal.

REFERENCES CITED

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