Increasing Profitability And Improving Environmental Performance by Maintaining Amine Solvent Purity

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Abstract

By aggressively managing amine solvent purity, many Refineries have experienced significant improvement in Refinery profitability with higher throughput, fewer upsets, and consistent quality product. Refineries with a continuous process for maintaining amine purity have also experienced improved environmental performance. This paper will discuss why continuous solvent purity is important and review some case histories.

Introduction

Amine solvent is used in Petroleum Refineries for removing acid gases from various gas and liquid streams. The acid gases removed are H_2S and CO_2. The low sulfur requirements of the Refinery's products require that the amine systems work effectively and continuously. The amine solvents have proven to be very predictable in removing acid gases until they become contaminated. Contaminated amines usually result in unstable performance and frequently become a limiting factor in the operation of a refinery.

This paper discusses some of the sources of contamination of amine solvents, how to remove the contamination and how to minimize the amount of contamination. Case histories will be reviewed to illustrate the opportunity for increased refinery profitability and improved environmental performance.

Contamination

The principle contaminants for an amine solvent include:

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

This paper will show that the effects of these contaminants are interrelated and that an integrated approach must be considered to obtain the maximum benefit of a stable, effective, amine system.

Heat Stable Salts

Heat Stable Salts are a result of carryover from the gas or liquids being treated. They are generally formed as a reaction between various components of the gas or liquid stream being treated by the amine solvent including; hydrogen cyanide, hydrogen sulfide, carbon monoxide, sulfur, chlorides. These reactions result in various organic salts, such as acetates, formates, thiosulfates, sulfates, thiocyanates, oxalates, butyrates, propionates, etc. Cooling water leaks, impurities in catalysts, and poor water treating can result in inorganic salt contamination (such as chlorides, phosphates, and nitrates).

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 thermal 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 the necessity to increase circulation rate, increase steam to the amine stripper reboiler, accept lower sulfur removal from the feed gas, or cut back production rates.

In addition to the effect of Heat Stable Salts on capacity, they also increase corrosion, increase iron sulfide production, increase the filtration requirements, and increase hydrocarbon entrainment. All of these increase foaming, system instability, and reduce production rates and quality.

An amine system in an upset condition results in more flaring incidents, excess sulfur in fuel gas and tail gas incinerators, amine in flare knock-out drums, and amine in waste water treatment systems. Amine in waste water treatment systems usually results in microbe kills and reduced waste water treatment capacity. All of these add up to a significant event to be avoided.

Degradation Products

Degradation Products are defined as molecules formed that include the amine as part of the molecule. These degradation products are usually inert, but can be polar and strong chelators and a cause of corrosion. They also can cause increased viscosity, density, reduced surface tension and reduced available amine.

Examples of Degradation Products in a primary or secondary amine include formamides, 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:

$$\textbf{AmineH}^{+} + \textbf{Formate}^{-} \rightarrow \textbf{Formyl-amine} + \textbf{H}_2\textbf{O}$$

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 system, attention must be given to concentration. There is a molar relationship between the presence of formate in primary or secondary amines and the presence of these 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 on a slip stream of operating amine systems (see Table 1).

Table 1

Formamides converted to useable Amine while using MPR Services, Inc. HSSX® process on operating Amine Systems

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

Another family of degradation products commonly found in primary and secondary amine systems are oxazolidones. These compounds may accumulate in CO_2 service, as suggest by the following:

$$\textbf{Amine} + CO_2 \rightarrow \textbf{Amine-oxazolidone} + H_2O$$

Formation of oxazolidones result in a loss of one mole of useful amine per mole of oxazolidone and can accumulate to a level to reduce water content and affect treat effectiveness. A process called the Oxex™ Process can be used to reverse this formation and recover the amine while the amine system is operating (see Table 2).

Table 2

Oxazolidones converted to useable Amine using MPR Services, Inc. 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

Amino acids, such as bicine, are degradation products found in tail gas systems using tertiary amines such as MDEA.[1] Bicine has been shown to contribute to corrosion [2, 3, 4] and are to be monitored closely. One recommendation is that Bicine not exceed 250 ppm.[4] Amino acids seem to form slowly after oxygen and SO_2 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,[1] but should be preventable by immediate removal of the Heat Stable Salts (primarily thiosulfate) caused by the upset. Bicines can not be removed by distillation because of their close physical chemistry relationship to amine. Bicines have been successfully removed by MPR's HSSX® Process utilizing Versalt® Resin (see Table 3).

Table 3

Bicines (amino acids) Removed while using MPR Services, Inc. HSSX® process on operating Tail Gas Systems

System	AMINE	BICINES Start wt%	BICINES End wt%
A	MDEA	4.9	1.8
B	MDEA	3.9	0.1
C	MDEA	2.1	0.3
D	MDEA	3.1	0.7
E	MDEA	2.0	0.6
F	MDEA	1.0	0.2

Iron Sulfide (FeS)

Iron Sulfide (FeS) is a common contaminant in amine systems when one of the acid gases is H_2S. The H_2S reacts with carbon steel and forms FeS. Under the proper conditions, this FeS adheres tightly to the carbon steel and forms a protective barrier to retard continuing H_2S 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 system causes many problems in amine system operation. FeS plugs exchanger tubes, stripper and absorber trays, and pipes.

FeS is also known to interfere with oil / water separation and cause high levels of hydrocarbon in amine solutions and result in foaming incidents.

FeS is also known to stabilize foam and not allow it to dissipate in a timely manner. This results in high amine losses.

Thus, FeS and hydrocarbons together create a cycle of increasing amine system operating problems.[5]

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, exposes more carbon steel to H_2S and accelerates the deterioration of the amine system operations. High levels of suspended FeS must be avoided.

Chemical factors that affect the passivation nature of FeS include high levels of Heat Stable Salts and amine degradation products.[2] These contaminants must be kept as low as possible at all times to prevent the FeS, Hydrocarbon, more FeS, more hydrocarbon cycle. Table 4 illustrates the affect of Heat Stable Salts on corrosion in an amine system.

TABLE 4

CORROSION RATES OF LEAN AMINES FROM OPERATING SYSTEMS REDUCED BY REMOVING HEAT STABLE SALTS (HSS)

Amine	Total Amine wt%	HSS as Amine wt%	Caustic Added as Amine wt %	CORROSION RATE at T=150 F mpy	at T=200 F mpy	at T=250 F mpy
MDEA, Sys 1	34	4.0	0	18	50	115
MDEA, Sys 1 HSS reduced		1.5		5	15	35
MDEA, Sys 1 HSS reduced		0.7		5	10	18
MDEA, Sys 2	30	3.6	0	20	65	190
MDEA, Sys 2 HSS reduced		2.6		18	30	65
MDEA, Sys 2 HSS reduced		0.9		10	12	15
MDEA, Sys 3	40	12.8	8.9	20	50	140
MDEA, Sys 3 HSS removed		<0.2	<0.2	<5	<5	<5
MDEA, Sys 4	35	4.9	0	10	25	70
MDEA, Sys 4 + Caustic		4.9	3.9	10	30	130
DEA, Sys 5	24	3.6	1.6	14	32	62
DEA, Sys 5, + Caustic		3.6	3.6	13	18	30
DEA, Sys 5, HSS removed		<0.2	<0.2	3	4	5
MEA, Sys 6,	19	2.1	0	80	200	>350
MEA, Sys 6, HSS removed	19	0		30	55	100
MEA, Sys 6, no HSS, no LL	19	0		20	22	25

Hydrocarbons

Hydrocarbons enter the amine system due to their natural solubility and in some cases due to condensation in the cooler amine solution. They are normally effectively separated in the flash drum. In addition to high levels of FeS discussed above, several factors can affect the separation. High amine concentration (or low water concentration) can result in a higher solubility of hydrocarbons in the solution. The low water concentration of the solution can be caused by high heat stable salts, high amounts of amine degradation products, and high quantities of sodium or potassium. Hydrocarbons cause foaming in amine systems and foams are stabilized by other impurities, such as heat stable salts, particulates (FeS), well treating fluids, corrosion inhibitors, lubricants, and anti-foams.[5]

Removal of hydrocarbons by Activated Carbon has been helpful, but has often been inadequate due to the low capacity of the activated carbon, lack of good quantification methods, lack of monitoring capabilities, or lack of operator attention.

Water Content and Amine Strength

Contaminant buildup, and some additives used to combat contaminants, have an insidious effect on amine system operations: reducing the water content of the solution. The water content of an amine solution is a significant contributor to the physical and chemical properties of the solution, which affect contactor efficiency and stripping. How one deals with contaminants can greatly affect the water content.

For example, as free amine content is reduced by increasing Heat Stable Salts or amide formation, an operator may add fresh amine to bring back capacity. To maintain level, however, water must be flashed off. The result is a reduction in water content. The greater the salts and degradation products, the lower the water content.

Continuous Purification:

As shown before, high Heat Stable Salts increase corrosion, leading to higher levels of FeS, leading to higher levels of hydrocarbon, and resulting in an unstable amine system and high amine losses. The unstable amine system causes production cut-backs, poor product quality, discharge exceedance and waste water upsets.

The relationships between all the common contaminants to an amine system dictate an integrated approach.

Maintaining at all times low Heat Stable Salts levels, will:

- reduce corrosion,
- reduce FeS contamination,
- reduce hydrocarbon retention and build-up
- reduce amine degradation products
- reduce air emission exceedance
- reduce waste water upsets.

Case Histories:

Case 1: Mid-West Refinery with two large DEA systems traditionally experienced continuous accumulation of Formyl-DEA (DEA-Formamide). Installation of an MPR HSSX® Kidney for continuous Heat Stable Salt removal has reduced the Formyl-DEA to low levels and has resulted in recovery of so much DEA previously tied up as the Formamide, that they were able to inventory substantial quantities of DEA for future amine make-up, as shown in Table 5.

Table 5

Formamides Converted to Amine In Refinery DEA Systems by Continuous HSSX® process

	System 1 HSS wt%	System 1 Amides wt%	System 2 HSS wt%	System 2 Amides wt%	Total
At Start of HSSX®	6.0	11.1	6.0	16.2	
After months of HSSX®	3.9	3.0	3.0	2.0	
Verifiable excess DEA generated by HSSX®					90,000 lbs

Case 2: A large refinery in the Gulf Coast had difficulty meeting production targets due to frequent amine system foaming incidents. Heat stable salts were high, corrosion was high, filter change-out frequency was high, amine losses were high, and caustic was frequently added to meet acid gas scrubbing demand, resulting in high sodium salt levels.[6] Contamination caused such problems that amine loss control measures were impractical because contamination would increase more rapidly. Finally, the HSSX® process was employed to systematically remove heat stable salts and sodium. In the first phase, HSS levels were reduced from 5 wt% to about 1 wt% as anions (2.3 wt% as MDEA) and sodium was reduced from 2.5 to about 0.5 wt% sodium. Immediately after the initial cleanup, heat exchanger fouling problems were eliminated. Filtration costs were cut

in half. Antifoam usage dropped by 90%. The system stabilized enough to allow record crude, coker and cat cracker runs simultaneously, while amine consumption was cut in half.

Thereafter, a continuous HSSX® kidney with MPR Versalt® Resin was installed to maintain salts at a very low level. As the ion exchange removal process reduced the contaminant levels to about 0.5-0.8 wt% anions (~1-2 wt% as MDEA) and sodium less than 1000 ppm, even greater operational benefits have resulted. Filtration costs have been cut by 80%. All the heat exchangers show little, if any, fouling. Amine losses have been reduced by 90% without detrimental build-up of HSS.

Further improvements have come from installation of regenerable hydrocarbon filtration (HCX™), regenerable particle filters (SSX™) that trap FeS particles down to sub-micron size, and amine loss control measures. Combined, the maintenance of low impurity levels in the amine system has netted the bottom line of this refinery more than $30 million per year from reduction in amine unit operations costs and increased production.

Case 3: A Mid-West Refinery had continual amine losses and production curtailments due to severe hydrocarbon carryover into the amine. Continual slipstream hydrocarbon filtration with the regenerable HCX™ filter netted this refinery about $1 million per year through increased production.

Case 4: A Mid-West Refinery had over 50 incidents of waste water treatment plant (WWTP) upsets because of amine contamination. Maintaining amine solvent purity with HSSX® salt removal, HCX™ hydrocarbon removal, and SSX™ solids removal reduced amine-related WWTP incidents to one in a twelve-month period. This, and attendant fewer production curtailments, netted this refinery's bottom line over $6 million in one year.

Case 5: An upper mid-west refinery suffered from amine-related environmental concerns and production curtailments when amine contaminants were elevated. Contaminant control measures have netted this refinery nearly $2 million annually.

Table 6

Annual Benefit to Bottom Line of Maintaining Low Impurity Level in Amine Systems

Refinery	Annual Benefit
Case 2	$30 million
Case 3	$1 million
Case 4	$6 million
Case 5	$2 million

CONCLUSION

Contaminated amines usually result in unstable performance and frequently become a limiting factor in the operation of a refinery. Heat stable salts, amine formamides, suspended solids (FeS), and hydrocarbons are synergistic contributors to amine system instability. Continual maintenance of low levels of all these contaminants is now possible. Major environmental and financial benefit can be realized by doing so.

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