



Contaminants in Amine Gas Treating

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ABSTRACT

Amines have been used for many years to remove acid gases from natural gas, and there is a large volume of technical information on their performance capabilities. It is also common knowledge that performance-limiting contaminants can build up in amine solutions over an extended period of operation. However, because of the complicated chemistry and the various ways of reporting these contaminants, there is still a considerable amount of confusion over their exact nature. What are they? Where do they come from? How are they measured? Why should operators be concerned? Should they be neutralized or removed? Are there industry-recommended quality standards? Recent studies and improved analytical procedures have added more knowledge about these contaminants, but may have also added to the confusion. This paper reviews the latest developments and simplifies the What, Where, How, and Why of amine contaminants in gas treating service.

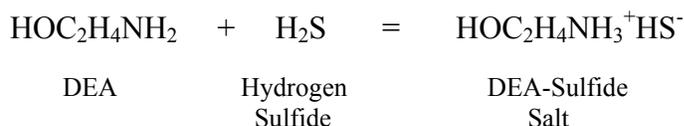
INTRODUCTION

As environmental regulations pertaining to “clean fuels” become more stringent in the next few years, additional burdens will be placed on sour gas processors. Amine systems have been the workhorse of the gas treating industry for many years, and will be pushed harder than ever for optimum performance and reliability in the future.

Although maintenance of mechanical equipment is of prime importance, proper care of the chemical solvent can do even more to improve plant throughput and lower operating costs. Paying attention to “amine hygiene” is becoming essential for optimum performance. Excessive corrosion and amine solvent loss from foaming upsets are two of the most expensive costs in operating an amine system. Each year more plants instigate a simple amine hygiene program and (1) monitor amine contaminants with regular lab analysis, (2) reduce amine losses by locating and correcting system leaks, and, (3) periodically remove objectionable contaminants to meet industry recommended amine quality standards. This will insure that gas is treated to specification quality at optimum throughput without excessive corrosion or energy costs.

AMINE USE IN GAS TREATING SERVICE

For over seventy years the alkanolamine process has been considered the best approach in removing H₂S and CO₂ acid gases from natural gas. It is based on the reaction of a weak base (alkanolamine) and a weak acid (H₂S and/or CO₂) to give a water-soluble amine acid gas salt. For diethanolamine, the reaction can be stated as:



This reaction creating the weak amine-sulfide salt is reversible at elevated temperatures, which allows the amine to be regenerated and recycled to the contactor for additional acid gas removal.

There is a substantial amount of literature available on the selection and performance of amines in the removal of acid gas. There is also a wealth of information on the performance limiting contaminants that occur in amine solutions, and continuing research adds to this knowledge every year. However, there is still a considerable amount of confusion over the exact nature of amine contaminants.

AMINE CONTAMINANTS – WHAT ARE THEY?

Amine contaminants can be grouped into five distinct categories; (1) heat stable salts, (2) degradation, (3) injection chemicals, (4) hydrocarbons and (5) particulates. All of these contaminant categories can typically be present in any given amine system at the same time, although the amount of each one can vary from insignificant to several per cent.

Heat Stable Salts: Strong acid anions such as formate, acetate, thiosulfate, thiocyanate, and chloride can tie up an amine molecule to form a salt that is not capable of being regenerated by the addition of heat, and are thus referred to as Heat Stable Salts. Not only do they tie up the amine and thereby reduce the acid gas carrying capacity, but they are also considered corrosive.

However, there is still a considerable amount of confusion in the industry over the term “Heat Stable Salt”. Many times the term is used in a generic sense to mean “contaminant”, while in fact it is only one type of amine contaminant, and may not even be the most offensive contaminant. New engineers assigned to amine and sulfur plant areas, then often assume that the only contaminants in their amine system are the Heat Stable Salts. This idea can be reinforced when lab analyses show only Heat Stable Salt contaminants, but do not report other types of contaminants such as degradation products.

Degradation: Degradation products are contaminants in solution that are derived from the breakdown of the base amine molecule itself, often irreversibly,

to form totally different chemical species. Examples of degradation products are the ethylenediamine derivatives (THEED in the case of DEA), which can form when CO₂, COS or O₂ are in an amine system.

The loss of amine to degradation can be deceiving because these products can still have base strength and will show up as amine under normal titration, but they no longer have any acid gas removal capability. Degradation products continue to be the target of ongoing research as to any negative effects on amine solutions (corrosivity and other physical properties). Because they have only recently been considered important to measure, degradation products, such as bicine, are difficult for labs to consistently measure in small quantities, and can add to analysis expense.

Injection Chemicals: Corrosion inhibitors from upstream pipeline operations and amine system injections, such as anti-foam chemicals can concentrate in amine systems. While these chemicals are excellent in controlling operating problems, their injection into an amine system over the months and years between turnarounds can build up to a substantial percentage of the amine concentration. A large buildup of injection chemicals can eventually lead to fouling and can cause changes in solution physical properties, such as viscosity and mass transfer.

Hydrocarbons: Heavy hydrocarbons from natural gas streams can condense in the contactor, and lubrication oil from upstream reciprocating compression can build up in amine systems over time. These hydrocarbons can cause foaming, and at high enough concentrations can change amine solvent physical properties.

Particulates: Typical insoluble particulates include iron sulfides, metals from equipment corrosion, charcoal from amine filters, and catalyst fines from upstream units.

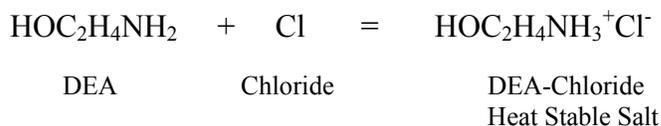
Amine manufacturers and suppliers stress overall solvent quality. When thinking about overall amine hygiene, it should be kept in mind that any compounds in an amine system that are not either (1) amine or (2) water are considered contaminants, and should be removed when they exceed recommended levels.

WHERE DO THEY COME FROM?

Contaminants found in amine systems come from three sources: (1) makeup water, (2) feed gas and (3) derived contaminants formed by reactions of amine with contaminants from sources (1) and (2).

Makeup Water Contaminants: Pure water, either de-ionized or distilled, is recommended as make up for amine systems. Otherwise a number of

contaminants such as sodium, potassium, calcium, magnesium, chloride, sulfate and bicarbonate ions can enter the system with impure make up water. These strong anions will react to tie up the amine cation to form Heat Stable Salts, as shown.



Feed Gas Contaminants: In natural gas service, contaminants entering with the feed gas are generally less troublesome than refinery feed gas contaminants. Contaminants in natural gas feeds that typically cause the most problems in amine systems are oxygen, carbonyl sulfide, and carbon dioxide, and hydrocarbons.

It is not uncommon for small amounts of oxygen to be drawn into the suction side of low-pressure field compressors in natural gas gathering systems. The oxygen molecule will then react to provide a number of contaminants in amine solutions. For instance, oxygen will react with hydrogen sulfide to eventually form thiosulfate and sulfate salts, which are heat stable. Oxygen will also react with amines to form formic, glycolic and oxalic acids, the ions of which form Heat Stable Salts.

Derived Contaminants: Carbon dioxide, which is often a component of sour natural gas feeds, will also react to form contaminants that can then react with the amine molecule to form degradation compounds. Amine degradation chemistry is more complex than salt formation, because a series of intermediate compounds are formed that continue to react to eventually form ethylenediamines. Typical degradation compounds are listed below.

Amine Degradation Products

Amine	+O ₂	carboxylic acids	heat stable salts
		imidazolidone	
MEA	+CO ₂	oxazolidone	OZD
		hydroxyethyl imidazolidone	HEI
		hydroxyethyl ethylenediamine	HEED
	+COS	diethanolurea	
DGA	+CO ₂	bis hydroxyethyl ethoxy urea	BHEEU
	+COS	bis hydroxyethyl ethoxy thiourea	
DEA	+CO ₂	hydroxyethyl oxazolidone	HEOD
		bis hydroxyethyl piperzine	BHEP
		tris hydroxyethyl ethylenediamine	THEED
	+COS	monoethanolamine	MEA
		hydroxyethyl imidazolidone	HEI
		bis hydroxyethyl ethylenediamine	BHEED
DIPA	+CO ₂	hydroxymethyl propyl oxazolidone	HMPO

MDEA	ethylene glycol	EG
	hydroxymethyl piperzine	HMP
	diethanolamine	DEA
	triethanolamine	TEA
	bis hydroxyethyl piperzine	BHEP

WHY SHOULD OPERATORS BE CONCERNED?

When processing with new or recently reclaimed amines, contaminant quantities should be low and the system should not exhibit any operating problems. However, as contaminant levels build up, amine systems may show increased signs of foaming, fouling and corrosion, which will eventually lead to loss of amine, high energy use and limited equipment life. And, of course the worst-case scenario occurs when excessive contamination prevents specification gas from being attained

Foaming is usually the first sign of contamination problems, and can occur with relatively small amounts of heavy hydrocarbons, particulates or injection chemicals. Continually adding fresh amine after foaming losses (bleed and feed) is a very expensive way to operate a system.

Fouling occurs from excessive particulate concentrations and can eventually lead to poor amine/feed gas contacting and off-spec gas. Proper filtration can remove suspended solids, unless they become excessive, and in this event, system corrosion is the real problem.

It has been said that unchecked corrosion is the single largest cost element in operating an amine system. Heat stable salts or degradation products are the usual culprits, and should be either neutralized or removed when they exceed the maximum levels listed in the Amine Quality Guidelines. Heat stable salts and degradation products can also change the amine strength and will eventually reduce the treating capacity of a system.

Seldom is a single contaminant responsible for amine system operating problems. System operating problems can be difficult to solve, and it is not unusual to trace a problem to several suspected contaminants.

HOW ARE THEY MEASURED?

Although many operators determine amine strength by running a simple titration in their own labs, they typically rely on their amine suppliers for periodic analysis of the contaminants in their amines. Amine supplier analyses are an excellent way to catch any increase in contaminants, particularly heat stable salts, so that corrective measures can be planned ahead of time. However, a huge amount of confusion can occur if an analysis from one lab is compared with an analysis from another lab, or with published guidelines for maximum contaminant levels. This is because labs use different ways to report contaminants and are not consistent with each other.

Even the term “Heat Stable Salt” can have different meanings to different labs. Heat Stable Salts can be reported as HSS Anions (not connected to any specific cation), HSAS (heat stable amine salt, with the anion connected to an amine cation), or simply as HSS (measured as a heat stable salt anion connected to a sodium cation). Some contaminants may be reported in terms specific to that lab only, and are not easily converted into a basis used by another lab or quality guidelines found in technical literature. Examples of these terms are: HSS, HSS Anions, HSAS, ash, bound amine, and fragments.

The units of measurement can also vary in different lab reports. HSS can be reported at least three different ways, and it is important to understand the differences:

HSS Anions – Weight Percent of Solution

HSS Anions measured as weight percent of the total solution.

HSS – Expressed as Weight Percent as Amine

This unit of measurement assumes that the HSS anions are bound to an amine cation (also reported as HSAS, Heat Stable Amine Salt). This number is determined by calculating the equivalent amount of amine cations that are tied up with the HSS anion, and is expressed as weight percent of the total solution.

HSS – Expressed As Percent of Amine Capacity

Amine HSS (or HSAS) expressed as weight percent amine, divided by the amine strength.

As an example, the same MDEA sample could be reported three different ways, with a substantial difference in the percentage depending on what measurement units are used.

Amine Strength wt%	30.5
HSS anions wt%	5.33
HSS expressed as wt% as MDEA	13.13
HSS as Percent Amine Capacity	43.05

MDEA MW = 119

HSS Anion MW = 48.2

As a matter of clarification, there is absolutely nothing wrong with these specific contaminant terms and measurement units. On the contrary, they provide an excellent way of keeping up with amine contaminant trends when the same lab analysis is used consistently. However, caution should be used when two separate labs analyze your amine for comparison purposes. Likewise, care should be taken when a lab analysis is compared to quality guidelines. Make sure to use the same basis when comparing two analyses.

HOW ARE CONTAMINANTS REMOVED?

There are several methods of handling contaminated amine systems. Depending on the type of contaminant, one or more of the following methods can be used for cleaning an amine system.

- Disposal and Replace
- Continuous Disposal and Replace (Bleed & Feed)
- Filtration of Particulates
- Neutralization of Heat Stable Salts
- Electrodialysis
- Ion exchange
- Vacuum Distillation Reclaiming.

Until recently, both Dispose/Replace, and Bleed/Feed were commonly used for controlling contaminants. However, increased costs of amine and disposal have made these methods more uneconomical. These methods of purification should now only be considered as a last resort.

Filtration is the preferred method if suspended solids are the only contaminant, and charcoal filtration can be used to control hydrocarbons and injection chemicals.

Heat Stable Salts can be neutralized, usually with sodium hydroxide, which will free up the amine bound to the HSS anion. However, neutralization only changes the HSS from an amine HSS to a sodium HSS, but does not remove any contaminants from the system. It is a band-aide approach that will free up amine and may allow some additional time before reclaiming can be done.

Electrodialysis and Ion exchange can remove ionic contaminants like Heat Stable Salts, but will not remove all of the various neutral degradation products, particulates, hydrocarbons and injection chemicals that can exist in an amine system.

Vacuum Distillation Reclaiming is considered the only process that can remove essentially all contaminants from an amine solution. This process produces distilled amine and distilled water. Any contaminant that does not boil near the same temperature and pressure as the amine or water will not distill, and will thereby be separated and removed from the solution.

ARE THERE INDUSTRY-RECOMMENDED QUALITY STANDARDS?

Amine manufacturers provide quality standards for their amines, with recommendations of maximum levels for specific contaminants for each type of amine that they produce. For corrosive contaminants like Heat Stable Salts, the maximum recommended levels are based upon limiting carbon steel coupon corrosion weight loss to less than 10 mils per year. A compilation of these amine manufacturer standards is provided in table format in Appendix 1.

Each amine system has its own unique sensitivity to specific contaminants and their concentrations. Some systems can tolerate higher levels of normally corrosive contaminants without any adverse affects, while other systems will foam, foul and corrode at the drop of a hat. Therefore these quality standards should be used as a guideline only.

SUMMARY

When it comes to amine contaminants, the areas of confusion that still exist mainly have to do with terminology and measurement.

Remember that *Heat Stable Salts are only one type of contaminant* that may exist in your amine system, and may not even be the most troublesome one. Amine degradation products can be very problematic also.

When comparing your amine analysis to amine quality guidelines, whether provided by your supplier or found in technical literature, *be sure that you are comparing on the same measurement basis.*

The best way to get the most out of your amine system is to practice good overall amine hygiene. Anything that is not amine or water is a contaminant, and at some point could cause foaming, fouling, corrosion or loss of amine strength. When requesting an amine analysis, at least periodically insist that all components be measured and reported, including degradation products and direct measurement of the water.

Appendix 1

Amine Quality Guidelines

Specific (HSS) Anion Guidelines

Organic HSS Anions	Limit, ppm	Inorganic HSS Anions	Limit, ppm
Acetate	1000	Chloride	500
Formate	500	Sulfate	500
Oxalate	250	Sulfite	500
Glycolate	500	Thiosulfate	10,000*
Malonate	500	Thiocyanate	10,000
Succinate	1000		

MEA

Free Amine (Alkalinity)	20 wt% Max
Water	70 wt% Min.
HSS	<2.5 Expressed as wt% as MEA <8.0 Percent Amine Capacity
Formamides (MEAF)	<3.0 wt%
HEED	<0.5 wt%
HEEU	<1.0 wt%

DGA®

Free Amine (Alkalinity)	50 wt% Max
Water	40 wt% Min.
HSS	<2.5 Expressed as wt% as DGA® <8.0 Percent Amine Capacity
Formamides (DGAF)	<3.0 wt%
BHEEU	<6.0 wt%

DEA

Free Amine (Alkalinity)	30 wt% Max
Water	60 wt% Min.
HSS	<2.5 Expressed as wt% as DEA <8.0 Percent Amine Capacity
Formamides (DEAF)	<3.0 wt%
THEED	<1.5 wt%

MDEA

Free Amine (Alkalinity)	50 wt% Max
Water	40 wt% Min.
HSS	<2.5 Expressed as wt% as MDEA <8.0 Percent Amine Capacity
MDEA Fragments	<2.5 wt%
Bicine	<0.4 wt%

Appendix 2

Amine Contamination and Reclaiming Options

MEA Contamination/Degradation

HSS	Potentially Corrosive	Contaminant
Formamide (MEAF)	Non-Corrosive	Contaminant/Degradation
HEED	Potentially Corrosive	Degradation
HEEU	Non-Corrosive	Degradation
Polymeric Material	Non-Corrosive	Degradation

MEA Solvent Quality Management With Merchant Reclaiming Options

Vacuum Distillation, Ion Exchange, Electrodialysis

Control of HSS	All
Control of MEAF (Slip-Stream Processing)	All
Control of MEAF (Batch Processing)	Vacuum Distillation Only
Control of HEED	Vacuum Distillation Only
Control of HEEU	Vacuum Distillation Only
Control of Polymeric Material	Vacuum Distillation Only

Best Efficiency = Batch Processing

DGA® Contamination/Degradation

HSS	Potentially Corrosive	Contaminant
Formamide (DGAF)	Non-Corrosive	Contaminant/Degradation
BHEEU	Non-Corrosive	Degradation (Reversible)
Polymeric Material	Non-Corrosive	Degradation

DGA® Solvent Quality Management With Merchant Reclaiming Options

Vacuum Distillation, Ion Exchange, Electrodialysis

Control of HSS	All
Control of DGAF (Slip-Stream Processing)	All
Control of DGAF (Batch Processing)	Vacuum Distillation Only
Control of BHEEU	Vacuum Distillation Only
Control of Polymeric Material	Vacuum Distillation Only

Best Efficiency = Batch Processing

DEA Contamination/Degradation

HSS	Potentially Corrosive	Contaminant
Formamide (DEAF)	Non-Corrosive	Contaminant/Degradation
THEED	Potentially Corrosive	Degradation
Bis-HEP	Non-Corrosive	Degradation
MEA	ASCC Concerns	Degradation
Bicine	Potentially Corrosive	Degradation
Polymeric Material	Non-Corrosive	Degradation

**DEA Solvent Quality Management With Merchant Reclaiming Options
Vacuum Distillation, Ion Exchange, Electrodialysis**

Control of HSS	All
Control of DEAF (Slip-Stream Processing)	All
Control of DEAF (Batch Processing)	Vacuum Distillation Only
Control of THEED	Vacuum Distillation Only
Control of bis-HEP	Vacuum Distillation Only
Control of MEA	Vacuum Distillation Only
Control of Bicine	Ion Exchange - Partial Vacuum Distillation
Control of Polymeric Material	Vacuum Distillation Only

Best Efficiency = Batch Processing

MDEA Contamination/Degradation In TGTU Service

HSS	Potentially Corrosive	Contaminant
MMEA	Non-Corrosive	Degradation
DEA	Non-Corrosive	Degradation
Bicine	Corrosive	Degradation
HE-Sarcosine	Corrosive	Degradation
Polymeric Material	Non-Corrosive	Degradation

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OUTLINE

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 - C. Simplified Acid Gas Chemistry
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Amine gas treating, also known as amine scrubbing, gas sweetening and acid gas removal, refers to a group of processes that use aqueous solutions of various alkylamines (commonly referred to simply as amines) to remove hydrogen sulfide (H₂S) and carbon dioxide (CO₂) from gases.[1][2][3] It is a common unit process used in refineries, and is also used in petrochemical plants, natural gas processing plants and other industries. Processes within oil refineries or chemical processing plants that remove hydrogen sulfide are referred to as "sweetening" processes because the odor of the process. Sources of heat stable salt (HSS) contaminants in amine treating solutions are discussed and their effect on reaction equilibria in acid gas-amine systems is analysed. Ralph H Weiland and Nathan A Hatcher Optimized Gas Treating, Inc. The requirement of solution electro-neutrality is used to validate solution analyses. Case studies demonstrate the important role of HSSs in determining amine plant performance, that simulations must incorporate ionic contaminants into their calculations, and the need to simulate the whole plant rather than isolated units. Introduction A common and proven way to remove the acidic components CO₂ and H₂S from gas streams is by absorption into aqueous solutions containing one or more amines. Amine gas treating, also known as amine scrubbing, gas sweetening and acid gas removal, refers to a group of processes that use aqueous solutions of various alkylamines (commonly referred to simply as amines) to remove hydrogen sulfide (H₂S) and carbon dioxide (CO₂) from gases.[1][2][3] It is a common unit process used in refineries. A typical amine gas treating process (the Girbotol process, as shown in the flow diagram below) includes an absorber unit and a regenerator unit as well as accessory equipment. In the absorber, the downflowing amine solution absorbs H₂S and CO₂ from the upflowing sour gas to produce a sweetened gas stream (i.e., a gas free of hydrogen sulfide and carbon dioxide) as a product and an amine solution rich in the absorbed acid gases.