Contaminant Reporting in Amine Gas Treating Service

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ABSTRACT

For a number of years the gas treating and refining industries have been focusing on Heat Stable Salts (HSS) contamination in amine service. As knowledge continues to improve in this area, amine system efficiencies are improved and turnaround cycles are minimized. However, two unfortunate states still exist in the industry: (1) analytical reporting for HSS is not consistent and is often times confusing to operators, and (2) HSS is only one of the major contaminants in a gas treating solution. A better understanding of the full range of contaminants and degradation products is essential to achieving total solvent quality. This paper will review current reporting and terminology so that confusion in analyzing contaminants and sample results may be minimized.

INTRODUCTION

There is a wealth of literature available in the industry on the corrosive nature and proper control targets for Heat Stable Salts (HSS).[1-4] Unfortunately it is easy to be confused about measured levels and reporting terminology of these HSS anions. This confusion is compounded by the fact that comparing these measured values to proper control points may be difficult if they are not compared on a consistent basis. HSS are also generally only a part of the contaminants present in the gas treating solution so, it is important to understand the total level of contaminants and degradation products present in the processing solution. This is important for the operator to know because, as the level of contaminants and degradation products increase, the physical properties of the solution may change. As the physical properties of the solution change there may be the potential for increased operational issues, increased corrosion concerns, and an increase in degradation rates.

Here we will talk about what a *complete amine analysis* should look like so that we may fully understand the total level of contaminants in the gas treating solution. We will list general items to be measured in any gas treating solution, as well as review specific degradation products for specific amine types. We will also show how a full material balance, a nitrogen balance, and an amine balance may dictate when a more detailed analysis is warranted. We do this since not all solvent analysis is the same and also because the cost associated with a more detailed analysis often needs justification.

As an addendum, we will also give some industry recognized control points for the contaminants and degradation products that we discuss in the body of the paper.

CONTAMINANTS AND DEGRADATION PRODUCTS - DEFINED

There are many compounds present in gas treating solutions circulating in process plants. Throughout the industry there has been a lot of focus on HSS while often the rest of the contaminants and degradation products are ignored. However often times these HSS anions may be only a portion of the total contaminants present in the solution and it is prudent to look at the total level of contaminants and degradation products. We like to refer to the total level of contaminants and degradation products in the solution as the ***residue*** of the solution. The residue of the solution is the amount of material that is generally not considered part of a healthy gas treating solution, meaning anything that is not free (active) amine or water. This residue, as equation 1 shows, is easy to calculate and encompasses all of the contaminants and degradation products present in the sample.

$$\text{Wt\% Residue} = 100 - \text{Wt\% Free Amine (FA)} - \text{Wt\% Water} \qquad (1)$$

The residue is the total level of the contaminants and degradation products present in the sample. Contaminants and Degradation Products may be defined as follows:

Contaminants

Contaminants are items that enter the process and "pollute" the amine. These items would generally include solids/particulates, hydrocarbon, process chemicals, strong cations (sodium), HSS (from their precursors entering with the gas), and degradation products.[5]

Degradation Products

Degradation Products are contaminants in solution that are derived from reactions with the base amine molecule itself, where the molecule is broken down or changes chemical form. Many of these compounds are the result of irreversible degradation of the base amine molecule; ethylenediamine derivatives (THEED in the case of DEA and HEEU in the case of MEA) would be examples of this. Some of these compounds are the results of a reversible reaction or chemical equilibrium with the base amine molecule; formamides in the case of primary and secondary amines and BHEEU in the case of DGA® would be examples of this.

For optimized unit operations, it is important to know and understand the total level of residue including all contaminants and degradation products. It is also important to understand the characteristics of the residue for evaluating concerns for unit operation, concerns for corrosion, and for evaluating merchant reclaiming options when necessary.

BASIC AMINE ANALYSIS FOR BULK COMPOSITION MATERIAL BALANCE

There are basic items that should be measured in every sample regardless of the amine type. These items are generally used as good control points for optimized unit operation, and may also be used to decide whether or not a more detailed analysis of the solution may be warranted. These items include:

1. Alkalinity

Alkalinity may be measured directly using a simple titration, and is the amount of "Free Amine" in the solution. The Amine content of the solution may be represented by equation 2.

$$FA + BA = TA \quad (2)$$

FA = Free Amine
BA = Bound Amine
TA = Total Amine

The FA is the amine that is available for acid gas pickup. The BA is the amine that is no longer available for acid gas pickup. TA is the total amine in the sample.

Alkalinity is also very often referred to as the “Amine Strength”. Alkalinity is a good control point for proper solvent performance, since it is the measurement of the material available for acid gas pickup. A low alkalinity indicates that circulation may be higher than design in order to compensate for the reduced acid gas pickup of the solvent. A high alkalinity may exacerbate corrosion, and lead to operational problems due to changes in the physical properties of the solvent.

2. Water

Water is a very important item, should be measured directly, and should have a minimum control target. This measurement is necessary for the bulk composition material balance of the sample to show sample recovery, and to calculate the residue of the sample. Water also plays a critical role in determining the actual physical properties of the solvent.[6] When water content becomes too low, solvent quality and unit operation become concerns.

3. Loading

Loadings are measured to ensure that the solvent is operating within recognized industry guidelines. A high lean loading indicates that the solvent is not being stripped properly. This may be due to improper process conditions or equipment damage or fouling. A high lean loading will also reduce your net acid gas pickup provided the rich loading stays within guidelines. A low lean loading indicates that the unit is not configured for optimal energy consumption, and over stripping may exacerbate corrosion.

We recommend that H_2S and CO_2 be measured separately since changes in H_2S/CO_2 ratio may warrant process changes and increased concern for corrosion. A change in this ratio may also indicate an accumulation of degradation products affecting solvent performance such, as the accumulation of MDEA fragments in Tail-Gas-Treater (TGTU) service.[7]

4. Strong Acid Anions

Strong Acid Anions is another name for Heat Stable Salt (HSS) anions in the gas treating solvent. These HSS anions may be speciated (see Appendix 4) to give a total, or a titration may be completed to give the total. It is important to measure all of the anions *directly* since targets are set on these HSS anions to help minimize the corrosion potential of the solvent.

It is important to understand that HSS anions may be reported at least three different ways, and it is important to understand the methodology employed to avoid confusion.

<u>HSS Anions – Weight Percent of Solution</u>

HSS Anions (Strong Acid Anions) measured as weight percent of the total solution.

HSS Anions – Expressed As Weight Percent Amine
HSS Anions listed as weight percent of the amine. Meaning, if the anion is bound to an amine molecule, what is the amount of amine expressed as weight percent of the total solution.

HSS Anions – Expressed As Percent of Amine Capacity (As Percent Total Amine)
HSS expressed as weight percent amine divided by the amine strength (Free Amine or Alkalinity).

An example of these different reporting methods for MDEA:

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

MDEA MW = 119
HSS Anion MW = 48.2

5. Strong Cations
This is the amount of strong cations (Sodium and Potassium) in the gas treating solvent. It is important to measure these items to facilitate calculating the sample recovery and the amount of Bound Amine

6. Bound Amine
This is the amount of amine that is "bound" by the HSS anions in solution, and may also be referred to as a Heat Stable Amine Salt (HSAS). This value may be measured directly or may be calculated using the amount of Strong Acid Anions and Strong Cations in solution. Bound Amine (HSAS) ***does not equal*** HSS anions since Bound Amine (HSAS) is just the amount of amine unavailable for acid gas removal. HSS anions may form a salt with a strong cation or a protonated amine molecule. Therefore it is important to understand the difference between HSS anions and Bound Amine (HSAS).

The amine solution in the system has to be electronically balanced based on equation 3.

$$\Sigma \text{ Cations} = \Sigma \text{ Anions} \quad (3)$$

Related to the chemical constituents in the amine system, equation 3 may be expressed as follows:

$$\Sigma \text{ (Bound Amine)} + \text{(Strong Cations)} = \Sigma \text{ (HSS Anions)} + \text{(Lean Loading)} \quad (4)$$

Bound Amine = Protonated Amine Molecule
Strong Cations = Na^+, K^+
HSS Anions = Heat Stable Salt anions (acetates, formates, thiosulfates, etc.)
Lean Loading = HS^-, HCO_3^-

Often companies will report the Heat Stable Salt (HSS) level as equal to the amount of bound amine in solution. This practice simplifies the analysis, but as demonstrated in equation 4, is not technically correct. Strong cation levels will affect the HSS level in relationship with the bound amine; that is why we urge caution here.

7. Recovery

The above six items are the minimum requirements for any gas treating solution to investigate the condition of the solvent. These items may be added together on a consistent basis (wt% of solution) to see how close to 100% the results have come. Poor recovery, or poor closure of the material balance may indicate that further analysis is necessary. Obviously there are other items that should be added to the list for sample recovery that are amine specific, and we will cover those under each amine type. A recovery greater than 95 percent should be adequate for monitoring purposes. A sample recovery less than 95 percent should be cause for some concern and further analysis may be warranted, particularly if operating problems or corrosion concerns are issues at the plant.

AMINE SPECIFC DEGRADATION PRODUCT ANALYSIS

There are additional items that should be measured to further understand the solvent quality and increase the percent of the sample recovery for each of the amine types. A few of these for the various amines would be:

MEA

1. Formamides

N-formyl amines (formamides) are degradation products generally found in gas treating solutions that are based on primary and secondary amines.[8] Under certain conditions primary and secondary amines react with the formic acid in solution (via dehydration) to form n-formyl amines.

The data from process solutions containing formate as a Heat Stable Salt (HSS) anion shows that there is an equilibrium relationship that exists between the amount of formate HSS in solution and the amount of MEA-F in solution.[9] See the equation 5 below.

$$\text{Formic Acid} + \text{MEA} \Leftrightarrow \text{MEA-F} + \text{Water} \quad (5)$$

Since the above equation represents equilibrium, it is then possible to also hydrolyze MEA-F back into MEA and formic acid. The heat and water present in the stripper of the amine unit will generate a new equilibrium if the balance of the equation is disturbed by removing one of the above components.

2. HEED

Hydroxyethylethylenediamine (HEED) is a well-known degradation product of MEA from reactions with CO_2. There is a wealth of literature on the reaction mechanisms and the corrosive nature of HEED.[5] While much of the literature has focused on MEA in CO_2 service only, HEED has been found in combined refinery systems treating H_2S and CO_2. While it may not be the main degradation product in refinery amine systems, it must be monitored and removed from the system due to its corrosive nature.

3. HEEU

Hydroxyethylethyleneurea (HEEU) is a degradation product of MEA that is not that well known since most of the literature has focused on degradation in CO_2 service. HEEU is formed via the same reaction pathway as HEED when COS is present in the gas.[10] COS is generally present in combined refinery treating systems where FCC, Coker and other cracking/conversion units are employed in the plant configuration. HEEU has been found to be one of the main degradation products in refinery amine systems.

DGA®

1. Formamides

Same as MEA above.

2. BHEEU

N,N bis(hydroxyethoxy-ethyl)urea (BHEEU) is an inert degradation product formed in the presence of COS and CO_2.[10] BHEEU is a degradation product that is reversible with thermal reclaiming.

3. Morpholine

This is an inert degradation product, which however rare, can occur when the solution is subjected to high temperatures.

DEA

1. Formamides

Same as MEA above.

2. THEED

Tris-hydroxyethyl ethylenediamine (THEED) is a well-known degradation product of DEA from reactions with CO_2. There is a wealth of literature on the reaction mechanisms and the corrosive nature of THEED.[5,10] While much of the literature has focused on DEA in CO_2 service only, THEED has been found in combined refinery systems treating H_2S and CO_2. While it may not be the main degradation product in refinery amine systems, it must be monitored and removed from the system due to its corrosive nature.

3. Bis-HEP

Bis-hydroxyethyl piperazine (bis-HEP) is a well-known degradation product of DEA from reactions with CO_2. There is a wealth of literature on the reaction mechanisms of bis-HEP.[5,10] While much of the literature has focused on DEA in CO_2 service only, bis-HEP has been found in combined refinery systems treating H_2S and CO_2. While bis-HEP is not considered corrosive and it does have some base strength, it needs to be removed from the circulating system to optimize water content and active amine levels.

4. MEA

In the presence certain chemical compounds or intermeadiates, it is possible to degrade or break down the DEA molecule to simpler amines. Monoethanolamine (MEA) is one of the simpler amines that may be formed from DEA degradation. It is important to monitor the level of MEA in the circulating DEA system due to Amine Stress Corrosion Cracking (ASSC) concerns associated with MEA.

5. Bicine

Bis-(hydroxyethyl) glycine (Bicine) is degradation product formed in the presence of DEA and unstable chemical intermediates, and is considered corrosive.

MDEA

1. MDEA Fragments

MDEA in TGTU and in some primary amine system service should be monitored for MDEA fragments. These include MMEA, DEA, Bicine and C2+ HSS anions.[7]

2. Special Considerations For Formulated MDEA
Depending upon the formulating agent, MDEA may need to be monitored for degradation products listed for MEA and DEA listed above. We recommend discussing this with your amine supplier if your sample recovery is low.

AMINE AND NITROGEN BALANCES

It is very difficult to get 100% recovery of a sample and it is often necessary to understand what the unknowns are in solution without spending thousands of dollars for subsequent analysis. These balance calculations are very useful when you are trying to understand your total contaminant level and further evaluate the nature of the degradation in your sample

Excess Amine
An amine balance takes the measured amine strength (alkalinity) and subtracts the actual amounts of the amine that you are utilizing in the plant (amine specifically identified). In DEA systems, for example, you will take the measured amine strength and subtract out the identified DEA in the sample. The excess amine is material that has base strength, but is not a DEA molecule. Certain degradation products of DEA (THEED and Bis-HEP) have base strength but do not perform as well in removing acid gas as DEA.[11] THEED is also considered corrosive, so there are additional concerns with it.

Excess Nitrogen
A nitrogen balance measures the total amount of nitrogen in your sample then subtracts the amount of nitrogen that was identified from the components measured in the sample. Any excess nitrogen in the sample is generally from high molecular weight, high boiling point degradation products (polymeric material).[5]

Compounds that Will Analyze as Excess Amine - DEA

THEED	Base	Corrosive
Bis-HEP	Base	Non-Corrosive
Polymeric Material (Low molecular weight analogs of THEED)	Base	Non-Corrosive
Polymeric Material (Higher molecular weight analogs of THEED)	Base	Non-Corrosive

Compounds that Will Analyze as Excess Nitrogen - DEA

Polymeric Material (Higher molecular weight analogs of THEED)	Inert	Non-Corrosive
Formamide (DEAF or NFDEA)	Inert	Non-Corrosive
HEOXD (HE Oxazolidone)	Inert	Non-Corrosive
Bicine (bis-(hydroxyethyl) glycine)	Inert	Corrosive

Appendix 1 contains similar tables for the other common amines.

EXAMPLES OF COMPLETE AMINE ANALYSIS

There have been many times when an incomplete sample analysis or confusion over the terminology of the sample results have led to problems for plant operators. There have been cases of extreme unit fouling, severe operational problems, and solvent reclamation cost escalation. We would like to show examples of how a *complete sample analysis* or clearer understanding of the results would have indicated a potential problem or would have given a better understanding of issues surrounding the analysis of available reclaiming technology and price structure.

1. MEA – Refinery Service

MEA Customer

Analytical Results

Amine Type	MEA	**Alternate Units/Notes**
Amine Strength wt%	10.74	
Water wt%	42.10	
H2S wt%	0.00	
CO2 wt%	0.01	
Strong Acid Anions wt%	6.28	
Strong Cations wt%	0.01	Percent Neutralization → 0
Bound Amine wt%	7.36	Calculated
Formamides wt%	4.95	
HEED wt%	na	
HEEU wt%	8.19	
Other wt%	na	
Percent Recovery	79.63	
Organic Acids		
Formate ppm	23300	
Acetate ppm	2764	
Oxalate ppm	796	
Lactate ppm	503	
Glycolate ppm	nd	
Propionate ppm	393	
Butyrate ppm	na	
Total ppm	27756	
Inorganic Acids		
Chloride ppm	16	
Sulfate ppm	308	
Sulfite ppm	nd	
Thiosulfate ppm	22753	
Thiocyanate ppm	11921	
Phosphate ppm	na	
Total ppm	34998	
Total HSS Anions ppm	62754	
Total HSS Anions wt%	6.28	
HSS as wt% Amine	7.38	
HSS as Percent Amine Capacity	68.68	

Three different ways to express the value of the HSS Anions.

Example - MEA

This plant operator utilizes MEA in a refinery primary amine treating system for specific reasons. The gas being treated in this unit had high levels of Carbonyl Sulfide (COS), so MEA was selected due to its reaction rate kinetics with COS. The gas being treated also had variable levels of Oxygen, so MEA was selected since it is a simple amine with slower degradation rates in the presence of oxygen. Because of MEA degradation due to oxygen and to the level of HSS precursors in the gas, a slipstream thermal reclaimer was necessary for optimal unit operation.

When the unit was started up it did perform well and fuel gas specifications could be met. Unfortunately over time it became apparent that the reclaimer was undersized since it had a hard time controlling the level of HSS anions in solution. Also over time gas rates dropped since there were some fouling issues surrounding the process equipment. Some equipment changes were made and fouling issues were somewhat minimized, but were still a concern.

Since the plant was using HSS anions as a control point for their reclaimer operations, they did not measure much else in the solution on a frequent basis. They elected to try using ion exchange to remove the HSS anions thinking that this would greatly improve unit operations. Ion exchange was effective at removing the HSS anions, but over time the unit fouling became worse and unit operation began to suffer. A decision was made to look at a *complete sample analysis*, which ended up surprising the plant operator.

MEA Customer

Residue Calculation

Amine Strength wt%	10.74
Water wt%	42.10
H2S wt%	0.00
CO2 wt%	0.01

Water, Active Amine, and Residual Lean Loading are the expected items in a healthy gas treating solvent.

Strong Acid Anions wt%	6.28
Strong Cations wt%	0.01
Bound Amine wt%	7.36
Formamides wt%	4.95
HEED wt%	na
HEEU wt%	8.19
Other wt%	na
Un-Recovered	20.37
Total Residue	**47.15**
Excess Nitrogen	**13.6**
Excess Amine	**1.9**

These remaining items in the solution are what we refer to as residue or the total contaminants in the system. These are the items that need to be controlled in the solution for optimal unit operation.

Example - MEA

As can be seen from the complete sample analysis, the sample recovery is very low at around 80 percent, meaning that with even a fairly complete sample analysis we still could not account for 20 percent of the contaminants and degradation products in the sample. As we mentioned before, the plant operator was very surprised since they thought that they had between 6 to 8 percent HSS and nothing else in the sample. The amount of residue in this sample was about 47 percent, so that while the plant had accounted for 7 percent HSS there was a significant number of other contaminants and degradation products accounting for about 40 percent of the circulating solution. We immediately began to understand that this amount of residue could account for many of the operating problems experienced at this facility.

The analytical results, and residue calculation and amine and nitrogen balances all showed that HSS were only a small portion of the concern surrounding the solvent quality. HEEU was high due to the fact that there was a high level of COS in the gas. Even though HEEU is a high boiler and may be controlled in a conventional thermal reclaimer, the undersized reclaimer was not able to remove it adequately. As the level of contaminants and degradation products increased in this sample the water content of the solution dropped. As the water level decreased, the solution properties began to change (i.e. viscosity, mass transfer rates, boiling point) and the reaction rates of the degradation products increased since they are dehydration reactions catalyzed by heat. This exacerbated unit operations problems and the degradation of the solvent over time. Since the nitrogen imbalance was very high, we can see from referencing Appendix 1 that there were also increased concerns over the fouling potential of the solvent due to polymeric material.

This case shows that it is very important to understand the total level of contaminants and degradation products in the circulating solution. Also it is important to understand how conventional thermal slipstream reclaiming or merchant reclaiming technologies may or may not improve the *total quality* of the solvent. The residue of this sample may have been controlled using adequately sized conventional thermal reclaiming. The residue of this sample may not have been substantially improved using ion exchange technology since the HSS anions were a very small part of the circulation solution. This plant operator had to decide whether or not to dump and replace the solution or choose a reclaiming technology with the capability to improve total solvent quality.

2. DEA – Refinery Service

DEA Customer

Analytical Results

Amine Type	DEA	**Alternate Units/Notes**	
Amine Strength wt%	23.65		
Water wt%	67.20		
H2S wt%	0.00		
CO2 wt%	0.00		
Strong Acid Anions wt%	2.14		
Strong Cations wt%	0.49	Percent Neutralization Calculated →	49
Bound Amine wt%	2.29		
Formamides wt%	2.64		
THEED wt%	na		
bis-HEP wt%	na		
Bicine wt%	0.17		
Other wt%	na		
Percent Recovery	98.58		
Organic Acids			
Formate ppm	11862		
Acetate ppm	510		
Oxalate ppm	nd		
Lactate ppm	360		
Glycolate ppm	nd		
Propionate ppm	89		
Butyrate ppm	na		
Total ppm	12821		
Inorganic Acids			
Chloride ppm	700		
Sulfate ppm	382		
Sulfite ppm	nd		
Thiosulfate ppm	nd		
Thiocyanate ppm	7469		
Phosphate ppm	na		
Total ppm	8551		
Total HSS Anions ppm	21372		
Total HSS Anions wt%	2.14	Three different ways to express the value of the HSS Anions.	
HSS as wt% Amine	4.52		
HSS as Percent Amine Capacity	19.10		

Example - DEA

This plant operator utilizes DEA in a refinery primary amine treating system and generally experiences excellent operational reliability. This plant does a very good job of controlling their HSS levels to ensure reliability due to problems that they have had in the past. Since the customer asked us to help them evaluate the total cost associated with reclaiming their solution, we looked at a *complete sample analysis*. The customer had utilized ion exchange and vacuum distillation in the past and wanted to understand two things, 1) would the level of sodium in the sample affect the processing cost and 2) does the formamide (DEAF) affect the processing cost.

The solution analysis showed that about 50 percent of the HSS anions were neutralized with a strong cation, which in this case was sodium. Therefore based on equation 4 showing that the solution must be electronically balanced, we had to look to see if sodium had to be removed to attain the desired HSS endpoint. Based on a HSS anion endpoint of 0.5 wt%, the strong cation level would have to be reduced to at least 0.23 wt% so that the solution was not "over neutralized". This indicated that the chosen reclaiming technology would have to be able to remove the strong cations as well as the HSS anions, and the cost associated with this had to be accounted for in understanding how each technology charged for removal.

The level of formamides did indicate that it would also have to be included in any processing cost evaluation for the reclaiming job. Based on equation 5, we see that by removing the formate HSS anion, the DEAF would reconvert to DEA and formic acid. This formic acid generated would then also have to be removed once a new equilibrium was established. Therefore the plant had to understand how each technology charged for removal, based on slipstream processing while the unit was on line. If batch processing was employed, then we also advised the customer that it would then be important to understand the removal efficiency of each technology on a once through the chosen reclaiming unit basis.

DEA Customer

Residue Calculation

Amine Strength wt%	23.65
Water wt%	67.20
H2S wt%	0.00
CO2 wt%	0.00

Water, Active Amine, and Residual Lean Loading are the expected items in a healthy gas treating solvent.

Strong Acid Anions wt%	2.14
Strong Cations wt%	0.49
Bound Amine wt%	2.29
Formamides wt%	2.64
THEED wt%	na
bis-HEP wt%	na
Bicine wt%	0.17
Other wt%	na
Un-Recovered	1.42
Total Residue	**9.15**

These remaining items in the solution are what we refer to as residue or the total contaminants in the system. These are the items that need to be controlled in the solution for optimal unit operation.

DEA Fragments	
MEA wt%	0.07
C2+ Acids wt%	0.10
Bicine wt%	0.17
Total	**0.34**
Excess Nitrogen	**1.7**
Excess Amine	**1.4**

Example - DEA

The amine and nitrogen balances from this sample show that there were some additional degradation products present in the sample (refer to Appendix 1). We also recommended that the customer consider the nature of these degradation products and how each reclaiming technology will affect their removal from the solution.

This is another example of why understanding more than the HSS levels in solution is very important. While this customer does take great efforts to keep their solvent relatively clean, it was very important for them to look at and understand the effects of the sodium, DEAF and the excess amine and nitrogen measured in the sample analysis.

3. MDEA – Refinery Service

This plant operator utilizes MDEA in a refinery primary amine treating system and generally experiences excellent operational reliability. This plant started to experience some fouling and corrosion concerns and were puzzled since they thought that their HSS levels were fairly low. We decided to look at a *complete sample analysis* to see if this would show us anything.

MDEA Customer

Analytical Results

Amine Type	MDEA	**Alternate Units/Notes**
Amine Strength wt%	30.50	
Water wt%	60.30	
H2S wt%	0.03	
CO2 wt%	0.00	
Strong Acid Anions wt%	5.33	
Strong Cations wt%	2.46	97 Percent Neutralization
Bound Amine wt%	0.41	Calculated
Formamides wt%	na	
THEED wt%	na	
bis-HEP wt%	na	
Bicine wt%	0.03	
Other wt%	na	
Percent Recovery	99.06	
Organic Acids		
Formate ppm	37411	
Acetate ppm	2026	
Oxalate ppm	50	
Lactate ppm	246	
Glycolate ppm	nd	
Propionate ppm	nd	
Butyrate ppm	na	
Total ppm	39733	
Inorganic Acids		
Chloride ppm	214	
Sulfate ppm	285	
Sulfite ppm	nd	
Thiosulfate ppm	485	
Thiocyanate ppm	12533	
Phosphate ppm	na	
Total ppm	13517	
Total HSS Anions ppm	53250	
Total HSS Anions wt%	5.33	Three different ways to express the value of the HSS Anions.
HSS as wt% Amine	13.13	
HSS as Percent Amine Capacity	43.05	

Example - MDEA

This customer thought that they had a HSS level of anywhere between 0.5 and 1 percent as MDEA. The sample analysis showed that the bound amine (or HSAS) was rather low at 0.41 percent. However the HSS anion analysis showed that the level of HSS anions expressed as MDEA were at a level of 13.13 percent. The analysis showed that there was a high level of strong cations, which effectively neutralized 97 percent of the HSS anions as a sodium salt, (refer to equation number 4). It was speculated that the high level of sodium salts associated with the HSS anions was contributing to the fouling problem. This high HSS anion level could also be accelerating corrosion rates in the system, with the resulting corrosion by-products contributing to the fouling of the unit.

MDEA Customer

Residue Calculation

Amine Strength wt%	30.50
Water wt%	60.30
H2S wt%	0.03
CO2 wt%	0.00

Water, Active Amine, and Residual Lean Loading are the expected items in a healthy gas treating solvent.

Strong Acid Anions wt%	5.33
Strong Cations wt%	2.46
Bound Amine wt%	0.41
Formamides wt%	na
THEED wt%	na
bis-HEP wt%	na
Bicine wt%	0.03
Other wt%	na
Un-Recovered	0.94
Total Residue	**9.17**

These remaining items in the solution are what we refer to as residue or the total contaminants in the system. These are the items that need to be controlled in the solution for optimal unit operation.

MDEA Fragments	
DEA wt%	0.37
MMEA wt%	0.20
C2+ Acids wt%	0.23
Bicine wt%	0.03
Total	**0.83**
Excess Nitrogen	**3.1**
Excess Amine	**1.2**

Example - MDEA

The sample analysis showed that there was also some excess nitrogen in the sample, which could also potentially be causing some of the fouling problems. A recommendation was made to improve the solvent quality by lowering the level of strong cations, HSS anions and the degradation products showing up as excess nitrogen.

SUMMARY

Please refer to Appendix 2 for industry recognized guidelines for proper solvent quality. When trying to troubleshoot operational issues at a plant, a *complete sample analysis* is a very valuable tool. Trending of analytical data is also very helpful for noting changes in operation and measured corrosion rates. The material presented here is intended as an aid in understanding the analysis and the meaning of the results. It is important when evaluating your results versus industry standards to use"voting" type logic. If one parameter is high immediate action may not be necessary, rather it is helpful to look at all of the solution parameters to see how they all compare to industry guidelines. While industry guidelines for solvent quality control are very helpful, it is important to understand that measurements within acceptable ranges do not guarantee reliable operation, nor do measurements outside of acceptable ranges guarantee imminent problems. Rather, these guidelines are simply that: guidelines for monitoring and evaluation of your system. Remember that if you are considering reclaiming you need to understand the characteristic of the residue and how each reclaiming technology removes these compounds. This will ensure that you are not disappointed with the final solvent quality and are not surprised by the final cost of the job. Please see Appendix 3 for summary of common contaminants for each amine type and merchant reclaiming effectiveness at removing these compounds.

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Appendix 1

Examples of MEA Degradation Products Containing Nitrogen

Compounds that Will Analyze as Excess Amine

HEED	Base	Corrosive
Polymeric Material **(Low molecular weight analogs of HEED)**	Base	Non-Corrosive
Polymeric Material **(Higher molecular weight analogs of HEED)**	Base	Non-Corrosive

Compounds that Will Analyze as Excess Nitrogen

Polymeric Material **(Higher molecular weight analogs of HEED)**	Inert	Non-Corrosive
HEEU	Inert	Non-Corrosive
Formamide (MEAF or NFMEA)	Inert	Non-Corrosive
OX (Oxazolidone)	Inert	Non-Corrosive

Examples of DGA® Degradation Products Containing Nitrogen

Compounds that Will Analyze as Excess Amine

Morpholine	Base	Inert

Compounds that Will Analyze as Excess Nitrogen

BHEEU	Inert	Non-Corrosive
Formamide (DGAF or NFDGA)	Inert	Non-Corrosive

Examples of DEA Degradation Products Containing Nitrogen

Compounds that Will Analyze as Excess Amine

THEED	Base	Corrosive
Bis-HEP	Base	Non-Corrosive
Polymeric Material (Low molecular weight analogs of THEED)	Base	Non-Corrosive
Polymeric Material (Higher molecular weight analogs of THEED)	Base	Non-Corrosive

Compounds that Will Analyze as Excess Nitrogen

Polymeric Material (Higher molecular weight analogs of THEED)	Inert	Non-Corrosive
Formamide (DEAF or NFDEA)	Inert	Non-Corrosive
HEOXD (HE Oxazolidone)	Inert	Non-Corrosive
Bicine (bis-(hydroxyethyl) glycine)	Inert	Corrosive

Examples of MDEA Degradation Products Containing Nitrogen

Compounds that Will Analyze as Excess Amine

DEA	Base	Non-Corrosive
MMEA	Base	Non-Corrosive
Polymeric Material (Low molecular weight analogs of THEED)	Base	Non-Corrosive
Polymeric Material (Higher molecular weight analogs of THEED)	Base	Non-Corrosive

Compounds that Will Analyze as Excess Nitrogen

Polymeric Material (Higher molecular weight analogs of THEED)	Inert	Non-Corrosive
Formamide (DEAF or NFDEA)	Inert	Non-Corrosive
Bicine (bis-(hydroxyethyl) glycine)	Inert	Corrosive
HE Sarcosine (hydroxyethyl methylglycine)	Inert	Corrosive

Appendix 2
Solvent Quality Guidelines

MEA – Refining Service

Free Amine (Alkalinity)	20 wt% Max
Water	70 wt% Min.
HSS Anions	<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%
Excess Amine	Within Allowable Ranges
Excess Nitrogen	Within Allowable Ranges

DGA® – Refining Service

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

DEA – Refining Service

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

MDEA – Refining Service

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

Appendix 3

MEA Contamination/Degradation In Refinery Service

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 In Refinery Service

HSS	Potentially Corrosive	Contaminant
Formamide (DGAF)	Non-Corrosive	Contaminant/Degradation
BHEEU	Non-Corrosive	Degradation (Reversable)
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 In Refinery Service

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
*Developmental Efforts Underway

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

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

Control of HSS	All
Control of MMEA	Vacuum Distillation Only*
Control of DEA	Vacuum Distillation Only*
Control of Bicine	Ion Exchange - Partial Vacuum Distillation
Control of HE-Sarcosine	Ion Exchange - Partial Vacuum Distillation
Control of Polymeric Material	Vacuum Distillation Only

Best Efficiency = Batch Processing
*Developmental Efforts Underway

MDEA Contamination/Degradation In Refinery Service
Special considerations based on whether generic or formulated. The compounds measured in the residue should be listed under the various amine listed here

Appendix 4
Glossary

Ash	Ash is the portion of the sample that will not burn, therefore being the inorganic portion of the sample. This would include the strong cations, inorganic HSS anions, metals, etc.
Bound Amine	This is the amine that is bound by a HSS anion.
Calculated Value	A value that may easily be calculated using the analytical results of the sample. Bound amine is an example of a value that may be measured directly or by calculation using the total HSS anions and the total strong cations in solution.
Contaminants	Contaminants are items that enter the process that "pollute" the amine. These items would generally include solids/particulates, hydrocarbon, process chemicals, strong cations (sodium) and HSS (from their precursors entering with the gas).
Control Target/Guideline	These are industry-recognized guidelines for proper solvent quality. Ranges for certain compounds are set to ensure a reasonable level of reliability.
DEA Fragments	These are compounds that are the result of DEA degradation when the DEA molecule is broken down into simpler compounds. These items would include MEA, Bicine, and C2+ HSS anions.
Degradation Products	Degradation Products are items in solution that are derived from reactions with the base amine molecule.
Direct Measurement	Measuring a certain compound in the circulating solution with an analytical technique that directly measures the value of the compound.
Free Amine	This is the amount of amine available to participate in acid gas removal. May also be referred to as amine strength or alkalinity
HSAS	Heat Stable Amine Salt (HSAS) may also be referred to as Bound Amine, meaning this amine is bound by a HSS anion forming a Stable Amine Salt.
HSS Anion	A strong acid anion having higher acid strength than the acid gases being removed.
MDEA Fragments	These are the compounds that are the results of MDEA degradation when the MDEA molecule is broken down into simpler compounds. These items would include MMEA, DEA, HE-Sarcosine, Bicine, and C2+ HSS anions.
Protonated Amine Molecule	Acid gas removal is achieved by an acid base reaction with the amine molecule. When the amine is in a water solution, it becomes protonated (base) to react with the acid gas.
Residue	The total level of contaminants and degradation products in the solution.
Sample Recovery	A total material balance based on the bulk composition of the sample will show the sample recovery, meaning how much of the compounds in the sample may be accounted for. This number is then compared to 100% to see how complete of an analysis was done.
Speciated HSS	A breakdown of the total HSS anion level into its individual components or "species (formate, acetate, etc.) The total level of HSS anions may be measured in bulk or may be speciated to see the profile of the acid anions. These speciated anions are then also then grouped into organic and inorganic HSS anions. This is done to see if there are further concerns for solvent degradation, and certain anions may also have specifc control points.
Strong Cation	Typically Sodium or Potassium in the gas treating solution.
Total Amine	This is the amount total amine in the sample, which is the sum of the free

	amine, and the bound amine.