

# **“AMINE HYGIENE AND SUSTAINABILITY”**

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## **ABSTRACT**

Amine purification technologies are compared for various applications and amine types. The proper selection and/or combination of reclamation technologies result in the most favorable amine hygiene strategy that also achieves sustainability targets for amine system operators.

The Paper will discuss an environmentally responsible approach to Amine Renewal and Hygiene in separate case studies for Tail Gas Units (TGU) and Main Acid Gas Removal Units (ARU) where the amine type, contamination variety, and incursion rates determine the appropriate reclamation technology. By comparing the advantages and disadvantages of amine renewal technologies (distillation, ion exchange and electrodialysis) in combination with evaluating the fluid compositions and application type, the best remediation option can be demonstrated and determined. The amine user can then evaluate the most economical option as well as long term sustainability impacts given their application and amine needs. The need for amine renewal to remove unwanted contaminants often depends on the gas treating application. Two different application case studies are presented, with differences in both contaminants and incursion mechanisms. In one case, amine refurbishment was needed after a sudden incident of SO<sub>2</sub> breakthrough in the Tail Gas Unit (TGU) using MDEA within a sulfur plant. In comparison a refinery ARU application is presented using DGA, where there was a gradual buildup of contaminants, both thermal and chemical degradation products, Heat Stable Salts (HSS), non-volatiles and residues. The incursion of contaminants in this ARU application is significant and ongoing such that continuous amine renewal is needed, here a combination of reclamation technologies is discussed as the best strategy for sustainable amine hygiene.

# “AMINE HYGIENE AND SUSTAINABILITY”

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## Introduction

### Background

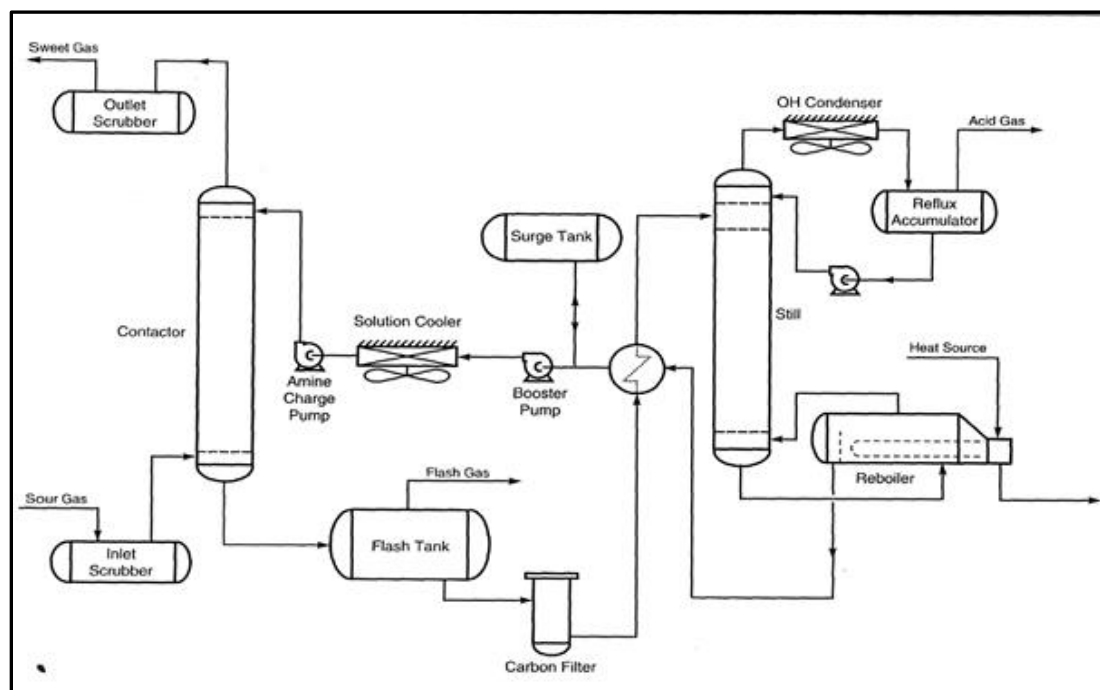
The petroleum refining industry refines crude oil into fuels (e.g., gasoline, diesel), finished non-fuel products (e.g., solvents, greases, asphalt), and raw materials for the chemical industry (e.g., naphtha, butane, propylene). Crude oils all contain some sulfur, mainly in the form of sulfides and hydrogen sulfide.

In the secondary refining process, alkanolamine processes are used for the removal of objectionable gases such as hydrogen sulfide, mercaptans, carbonyl sulfide, and carbon dioxide is necessary.

Amines, such as MEA (monoethanolamine), DEA (diethanolamine), Diglycolamine® (DGA®), MDEA (methyl DEA), and other commonly used gas treating chemicals are used to scrub objectionable acid gases from refinery C1 to C4 vapor streams.

The general process flow for an amine sweetening plant is shown in Figure 1 below. The flow scheme varies little, regardless of the aqueous amine solution used as the sweetening agent. The primary pieces of equipment of concern are the contactor and stripper column together with the associated piping, heat exchange, and separation equipment.

**Fig. 1:** Typical Flow Diagram for an Amine Sweetening Plant



All amines are subject to contamination and degradation due to the impurities either in the acid gas rich feed or those introduced to the amine system from other sources.<sup>5</sup> These impurities contaminate the amine and range from Heat Stable Salts (HSS), Amine Degradation Products, Non-Volatiles, Solids, to Hydrocarbons. Amine contamination is the primary cause of operating problems in amine systems. Such contamination causes issues that include Foaming, Fouling, Corrosion and Degradation which can severely impair the amine's ability to absorb acid gases or cause mechanical failures. Contaminants can have a significant effect on the reliability and operating cost of the amine unit operation, which is measured by: acid gas excursions; upsets to other processing units; amine losses, equipment maintenance, increased viscosity, filter changeouts and regenerator heat input all of which add to the operating costs of the amine system. Contaminants gradually reduce the effectiveness of the operating system, driving up processing costs and restricting production throughputs. Maintaining proper amine hygiene and management of these contaminants is important to reduce operating costs and protect equipment assets.

During the amine unit operation, the amine solution will become hindered by contamination and become degraded or fouled. This contamination can also be expressed as "performance barriers". As the level of contaminants increases, the performance of the amine solution decreases, causing operational problems.

Contaminants in amine solutions can arise from various sources and usually exist in several different forms. Although a single contaminant may necessitate a specific plan of action, gas-treating solutions rarely contain only one or two impurities. Instead, many different impurities exist in varying concentrations, many of which adversely affect the process.

However, most contaminants can be categorized into three primary groups.

### **1. Amine Degradation Products**

Amine degradation products are compounds that are formed either by the direct reaction of the amine and constituents of the feed gas (such as carbon dioxide, carbonyl sulfide, carbon monoxide, oxygen, and carbon disulfide) or by thermal decomposition of the amine<sup>13</sup>. Conversion of the amine represents a loss of active and valuable amine. Furthermore, some of these degradation products may cause foaming, corrosion, and reduced gas-treating capacity. See Appendix - Amine Degradation Products

### **2. Heat Stable Salts**

During the normal absorption/regeneration process, the basic amine solution reacts with acid gases entering with the raw feed gas. In the case of  $H_2S$  and  $CO_2$ , the amine salts are thermally regenerable thus providing the basis for the continuous process. If other anionic species and/or stronger acidic components are present in the raw feed gas, they too form amine salts. However, these compounds are not thermally regenerable and are hence designated as "heat stable salts". Both inorganic and organic Heat Stable Salts (HSS) occur. The former may contain chloride, sulfate and phosphate anions typically found in produced and cooling waters. Formate, acetate, oxalate, sulfate, thiosulfate, and thiocyanate can be formed by a reaction between oxygen and  $H_2S$  or cyanic acid and  $H_2S$ , the latter being more prevalent in refineries.

By allowing amine solutions contaminated with heat stable salts to circulate, the total efficiency of the absorption process cannot be realized. As a result, plant throughput is reduced, and the corrosive tendencies of the solution may increase. Heat Stable Salts are the cause of many problems in the amine system<sup>5</sup>. The recommended level in amine solution is less than 10% of the amine concentration<sup>5,7</sup>, but levels should be controlled between 0.5-1.5wt% of total HSS for the most trouble-free operations<sup>5,2</sup>.

**Table 1 - Recommended Upper Limits for Anions**

Anions	Upper Limit (ppmw)
Bicine	500
Acetate	500
Formate	1,000
Chloride	250
Sulfate	500
Oxalate	250
Thiosulfate	10,000
Thiocyanate	10,000

### 3. Non-Volatile Contaminants

Non-volatile contaminants arise from diverse sources such as oil/gas wells, make-up water, anti-foaming agents, sealants, lubricants, and anti-corrosion agents. Another common type of non-volatile contaminant is particulates, which may be carried into the amine solution by raw feed gas. Iron sulfide is very common and undesirable, usually because of its potential to stabilize foams or enhance foaming tendencies. Solid contaminants of any type can decrease the efficiency of the absorber and stripper by plugging contactor trays, contactor packings and process piping.

#### Implications of contamination

Contamination can severely affect an amine unit's capacity, operational stability, corrosion, and operating expenditures (OPEX). These implications are further explored below:

##### 1. Plant Capacity

As amine solutions become contaminated with non-regenerable impurities, such as HSS, they lose their treating effectiveness because the amine concentration is reduced. Lower free amine strength and availability decrease the treating capacity of the amine plant<sup>8</sup>. To compensate for this effect, the absorbent circulation rate can be increased. However, the increased circulation rate affects other parts of the process such as the sensible heat duty in the reboiler. It may also change the product gas composition because more liquid flows to the absorber thereby altering the gas/liquid ratio, which, in turn, can affect the total H<sub>2</sub>S and CO<sub>2</sub> removal. The temperature profile in the absorber also tends to change with circulation rate. Quite often, operators must reduce the raw gas flow to the plant to ensure satisfactory operation.

If operators do not compensate for the presence of contaminants, there is a danger of overloading the amines with H<sub>2</sub>S and CO<sub>2</sub>. Excessive amine loading can lead to unexpectedly high corrosion rates in some parts of the amine unit, mainly where there are rapid changes in pressure, temperature and/or velocity. Two-phase flow may arise resulting in water/pipe hammer and slug-type flow into downstream equipment. These problems not only affect the plant's operation but may also cause mechanical damage.

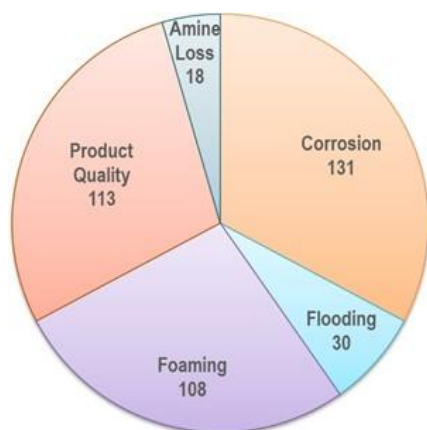
##### 2. Stability of Plant Operation

Higher contaminant levels usually increase the amine solution's viscosity, reducing the mass transfer rates in the absorber and stripper. The viscosity increases ultimately lead to the product gas no longer meeting specifications. This is particularly detrimental in tail gas treaters, where lack of performance can result in

reportable environmental excursions. Fouling is a particular concern in those parts of the unit where amine flow velocities are low and the solvent loading of  $\text{H}_2\text{S}$  or  $\text{CO}_2$  is high i.e., contactor trays, bottom, and the lean/rich heat exchanger. Fouling of the heat exchanger leads to a reduction in heat transfer and an increased steam use for regeneration. Ultimately, plugging of the exchanger may occur, restricting solvent circulation and treating capacity<sup>8,20</sup>.

Foaming is one of the primary causes of production failures<sup>19</sup> as illustrated in the figure below.

**Fig. 2:** Cases of critical failure by type for all amine systems (sweet and sour)<sup>19</sup>



The more viscous a solution, the higher its tendency to foam. Furthermore, some hydrocarbon contaminants cause interfacial tension changes, stabilizing amine foams. In extreme cases, this can cause significant pressure drops across the absorbers and amine regenerators. Activated carbon filtration is often used to contain the hydrocarbon problems. Still, heavier hydrocarbons are difficult to remove (especially if the pore size of the carbon is too small to capture the molecules).

Another cause of unstable gas plant operations is particulate matter, which also promotes foaming tendencies. Fines may be introduced with the raw gas or generated in the amine unit itself. Iron sulfide fines are "washed" off vessel walls by sudden changes in operating conditions or by foaming incidents. Increased foaming tendencies of the amine by the presence of higher amounts of suspended solids require a high rate of filter changeouts<sup>8</sup>. Mechanical filtration can be used to deal with most of the fines. However, some fines are so small that conventional filtration media cannot capture them. Leaving such fine particulates in solution can lead to fouling of heat transfer surfaces, lowering the heat transfer efficiencies.

### 3. Corrosion

Increased corrosion rates can be explained in terms of a high acid content of the solvent decreasing the pH and high molecular weight degradation products, HSS and amino acids (such as bicine) that increase the ability of the solvent to keep iron in solution (high complexing power). The overall result is a high activity of the "iron pump" mechanism leading to high corrosion rates and associated fouling problem<sup>8</sup>.

Several types of corrosion can result from contaminated amine solutions. In the case of increased circulation rates, erosion corrosion may occur which is the physical wearing away of metals by the abrasive action of either suspended solids or extremely high velocities in restricted areas. This is of greatest concern where restrictions or changes in flow direction are encountered. The rate of corrosion increases with velocity and even mildly corrosive solutions can produce extremely high corrosion rates if erosive

conditions are present. Any friable protective coating, such as iron carbonate, can be eroded and fresh metal exposed for further loss.

Fouling which causes solids deposition or scaling can result in crevice type corrosion. Concentration cells can be set up beneath the deposit or scale leading to high, localized corrosion rates. Some amines undergo reactions with CO<sub>2</sub>, are thermally degraded or attacked by oxygen entering the system resulting in undesirable degradation products. The tendency for fouling, scaling and corrosion may increase with these materials in solution.

Chlorides entering the amine plant via poor inlet filtration or cooling water exchanger leaks can accelerate pitting corrosion in stagnant areas of the amine unit. Furthermore, chlorides in the amine solutions can induce stress corrosion cracking in stainless steel components. High levels of inorganic and organic acid salts can contribute significantly to the corrosion rates found in amine units. Corrosion rates are a function of the type and quantity of amine salt(s) present.

### **Operating Expense Considerations**

All types of corrosion reduce the life expectancy of amine processing units and result in major financial losses.

It should also be noted that most recyclable amines typically contain over 80% of the original, active chemical. Consequently, the current disposal practices of deep well injection and incineration are not only environmentally unattractive, but they also constitute a loss of valuable amine.

In the early 1990's the Amine Best Practices Group (ABPG) surveyed about 74 separate amine units and benchmarked their performance based on 4 primary cost categories<sup>21</sup>:

1. Energy
2. Amine Chemical Expenditures
3. Filtration
4. Corrosion & Maintenance

**The ABPG found that there was an annual cost penalty of about \$2.68M per year (\$1.33M in 1994) between poorly operated amine units (4th quartile) versus those that were well maintained (1<sup>st</sup> quartile).**<sup>21</sup>

Careful monitoring of the amine unit operation along with frequent analysis of solvent compositions are key to practicing good amine management. Contamination mitigation is achieved by applying the appropriate amine reclamation technology. By tethering informed amine management with contamination mitigation with amine renewal technology, long term reliable and trouble-free operations can be realized. Good amine hygiene will significantly reduce operating costs and expenditures for the amine unit operation.

## Amine Renewal Technologies

Technologies like Thermal Distillation, Ion Exchange and Electrodialysis are well established technologies used to remediate the amine solution of impurities. By renewing the amine and removing problematic contaminants beneficial amine hygiene is achieved. Improved amine hygiene allows for said amine system to perform more reliably, better protected, and at a lower operating cost.

### 1. Thermal Reclamation

Thermal reclamation uses heat energy to purify an amine solvent by the evaporation of amine from the high-boiling degradation products, HSS, and non-volatiles such as suspended solids. Thermal distillation of the amine solution can be employed to remove a wide variety of problematic contaminants. To prevent thermal degradation of the amine molecule, distillation is typically performed under vacuum to vaporize the fluid at lower temperatures thereby avoiding thermal stress during the renewal of the amine solution<sup>12</sup>. This is of particular importance with DEA, MDEA and DIPA solutions that are known to thermal stressed if attempts are made to distill without reduced pressure or vacuum. Vacuum distillation can be employed either on-site with a portable unit or off-site at a merchant distillation facility. Reclaimers employing this technology can also be installed and connected to the amine unit to continuously renew a slip stream of the amine solution and remove contamination. Distillation technology's biggest advantage is that it can remove the widest range of impurities that can be found in the amine solution. Distillation removes Heat Stable Salts and ionic contaminants but is the only technology that can effectively remove high-boiling contaminants like thermal or chemical degradation products that other renewal technologies cannot. For example, N,N-bis (hydroxyethoxyethyl)urea or commonly known as BHEEU in Diglycolamine® (DGA®) solutions that forms from the reaction of CO<sub>2</sub> can only be reversed to regain the DGA by thermally reversing the reaction within a very strict and narrow temperature range.<sup>9,22</sup>

Although distillation can remove virtually all amine related contaminants, it is energy intensive and may inherently provide the lowest yield of amine back to the system. Distillation produces the highest quality distillate or renewed amine solution back to the user, generates a small but highly concentrated waste stream of the removed impurities requiring disposal and sacrifices a small portion of recoverable amine to flush the contaminants into the unwanted waste residue.

### 2. Ion Exchange

Ion exchange is a reversible exchange of ions between a solid and a liquid in which no substantial change in the structure of the solid occurs<sup>5</sup>. The solid is the ion exchange resin. See Fig. 3. Ion exchange resins have been used to remove acidic contaminants from spent alkanolamines for decades.

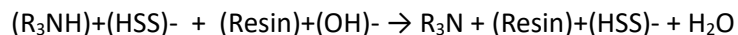
**Fig. 3:** Photo of Ion Exchange Resin



Ion exchange is a chemically clean and environmentally friendly way to remove Heat Stable Salts (HSS) and amino acids, such as bicine, from alkanol amine solutions, and maintain the necessary low levels in amine systems. The ion exchange process frees the amine from HSS and amino acids, sends the freed amine back to the amine system and sends the contaminants (as innocuous sodium salts) to waste.

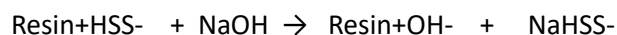
Ion exchange literally exchanges a friendly ion for the HSS ion or amino acid zwitterion. For example, anion exchange removes the HSS anion, replacing it with hydroxide ion, which frees the amine and returns free amine and water to the amine system.

#### Anion exchange reaction:



[Amine salt plus Resin-base    free amine plus Resin-salt]

The HSS anions are later removed from the resin by regeneration with caustic, which produces biodegradable sodium salts, which are friendly to the wastewater treatment system.



Cations, such as sodium, potassium, calcium, etc. are similarly removed from amine systems by cation exchange. However, ion exchange resins are not capable of removing uncharged contaminants like those produced from amine thermal degradation.

The ion exchange process operates in a specific sequence of cycles: loading (amine), washing (water), regeneration, and washing (water). The ion exchange process is favored by low temperature and is therefore typically located downstream of the lean amine cooler in an amine scrubbing process. An ion exchange unit uses a compatible specialty resin, to suit the lean amine solvent, contaminants, and temperature. The ion exchange unit consists of one or more resin vessels, valves, piping, meters etc. and a control system. The cycle is repeated to bring down or maintain a certain level of contamination in the lean amine solution. By using multiple beds this batch process can be turned into a continuous process.

Ion exchange seems chemically simple, and it has been claimed that ion exchange processes provide the optimum removal of HSS with less chemical, energy consumption and less foaming<sup>2</sup>.

Advances in ion-exchange based amine reclaiming have led to strongly reduced chemical and water consumption as compared to the early 1990's. When these ion exchange units are implemented at the plant site, there is now minimal impact on the operations of the Amine Unit. In most cases, the only operational adjustment needed is to limit the makeup water while the ion exchange unit is in use. Mobile and permanent units have become available throughout the world.

### **3. Electrodialysis (ED)**

Electrodialysis is a separation process in which ion permeable membranes are placed in an electric field to facilitate the removal of substances that ionize in solution<sup>9</sup>. These semi-permeable membranes contain electrically charged functional sites chosen such that they are selective to passage of either cations or anions. Anions and/or cations can be extracted with the correct sequencing from one solution into another. The process removes only ionic impurities and not degradation from amines, such as THEED, BHEEU and HEP.



Salts, anions, and cations are removed from the amine solution and end up in a concentrated aqueous waste stream or "brine" for disposal. The permeable membranes, whether anion and cation, have specially designed spacers between them and are configured in alternating fashion between anode and cathode end plates and thus operated in a "sheet flow" arrangement as shown in Fig 4. below.<sup>10, 11</sup>

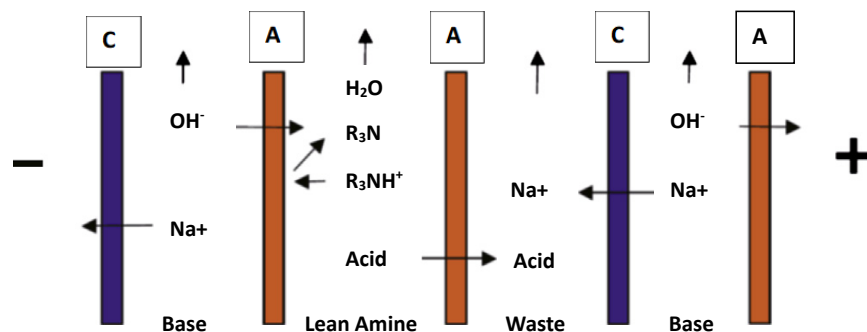


Fig. 4 ElectroSep™ ED process (Parisi and Bosen, 2006a)

The membranes are intentionally sequenced such that when the amine solution enters the channel between an anion and cation permeable membrane the anions move towards the anode through the anion permeable membrane (A) and the cations move towards the cathode through the cation permeable membrane (C). On the other side of both membranes an aqueous brine (waste) solution flows and the ions are collected and swept out of the system.

Due to temperature sensitivity and limitation of the ion-exchange membranes, electrodialysis requires cool, lean solvent. Neutralization and microfiltration are usually used upstream of the unit. The presence of hydrocarbons or suspended solids can result in fouling on the membrane surface and may impact efficiency and overall amine recoveries<sup>10,11</sup>.

### Comparison of renewal / reclamation technologies

The amine unit operators have a variety of amine hygiene and renewal options available to them. A well analytically monitored managed system will, on most occasions, be economically and environmentally favorable over band-aids like neutralization and solvent dump and replace. Vacuum distillation, ion exchange, and electrodialysis technology have matured and improved over the last two decades and are available as mobile services or permanent installations. Some advantages and disadvantages of these processes are summarized in Table 2. Comparison of commercially available amine reclamation technologies

**Table 2 – Comparison of Commercially Available Amine Reclamation Technologies.<sup>5</sup>**

	<b>Distillation</b>	<b>Ion exchange</b>	<b>Electrodialysis</b>
Applicability	Removal of ionic contaminants, solids and non-volatile species	Removal of ionic contaminants and zwitterions	Removal of ionic contaminants
Operation principle	Vaporization of volatile species (water, amine, etc.) from salt and degradation products	Ions captured by ion exchange resin	Ions removed by electrodialysis
Operation mode	Semi-continuous, on-line or batch, on and off-Site options. Mobile unit commercially available	Batch or on-line. Mobile and on-site Fixed units commercially available	Continuous on-line or batch. Mobile unit commercially available
Waste type	Non-Hazardous and Hazardous by TCLP	Aqueous Non-Hazardous	Aqueous Non-Hazardous
Volume of wastes	Low, Concentrated	High	Moderate
Waste Disposal	Off-site: downhole or incineration disposal	In plant WWT, if available	In plant WWT if available
Chemical usage	Stoichiometric NaOH	NaOH for resin regeneration	Stoichiometric NaOH
Feed requirements	Heat stable amine salts neutralized	Lean cool amine	Lean cool amine, hydrocarbon and particulate free; heat stable amine salts neutralized
Energy demand	High	Low	Moderate
Overall amine recovery	85%–95%	~99%	~98%
Special requirements	Fuel gas or high temp. heat source	Regeneration chemicals and storage	DC power
Total cost	High	Moderate	Moderate
Advantages	Full contaminant removal Of salts and degradation; Highly concentrated waste	Efficient for ionic removal only; low energy consumption	Efficient for ionic removal only; lower water and chemical consumption
Limitations	High cost, low amine recovery; energy intensive	Cannot remove non-ionic contaminants; Water intensive	Cannot remove non-ionic contaminants; membrane selection and durability

## Case Study A – Refinery Sulfur Plant SO<sub>2</sub> breakthrough in the Tail Gas Unit (TGU) Applications

### Background

A Tail Gas Unit (TGU) treating Claus sulfur plant gases experienced an SO<sub>2</sub> breakthrough event which dramatically neutralized and impaired the amine solvent.<sup>20</sup> SO<sub>2</sub> breakthrough will quickly pollute the amine with a wide range of detrimental anions and HSS. In severe cases, regulatory permit exceedances and high corrosion rates are experienced. In this case the TGU MDEA solution had a high incursion and dramatic rise in the levels of Bicine, Formate, Acetate, Thiosulfate, and other HSS in the MDEA amine system following the SO<sub>2</sub> breakthrough event. The unit was experiencing significant FeS particulate in the amine system and was running through filters at an accelerated rate.

**Table 3** – Comparison of Amine Composition before and after SO<sub>2</sub> Breakthrough

	01/2022	08/2021
Amine Concentration	SO <sub>2</sub> Event	Prior
Alkalinity, wt % amine	62.4133	42.1455
GC, wt% amine	68.7205	43.0275
<b>Anions - ppmw</b>		
Bicine	4,034.0	1,650.0
Acetate	2,310.0	925.0
Formate	1,440.0	510.0
Chloride	90.0	< 25
Sulfate	265.0	< 25
Oxalate	160.0	< 25
Thiosulfate	14,025.0	< 25
Thiocyanate	< 25	< 25
Gas Chromatography		
DEA	1.09299	1.14770
Heat Stable Salts		
HSAS Neutralized, %	0.2450	10.4940
HSAS, wt%	4.2497	0.3982
IHSS, wt%	0.0104	0.0467
Total HSS	4.2601	0.4449
Miscellaneous Analysis		
pH	9.86	10.01

### Comparison of Reclamation Options

#### 1. Thermal Distillation

Two options are available: on-site mobile or off-site.

The level of HSS and anions within this contaminated MDEA are high and without significant other high boiling or degradation product contaminants. As such it poses challenges for thermal distillation. When the salt level of an amine solution is at 10% of the amine solution, it poses the potential for plugging difficulties for thermal reclamation and low recovery and yield of the desirable MDEA content. Off-site distillation does offer an opportunity if the amine operator decides to de-inventory

and replace the amine with new product. The removed solvent could be sent off for distillation, despite the lower than optimum yield and in return have quality make-up fluid for the amine system or a spare inventory needed for similar episodes in the future.

**Advantages:** Opportunity to recover removed amine and distill for use as make up or inventory. Off-site processing will only return clean recovered MDEA and dispose of any waste or by-products as part of the project.

**Disadvantages:** Low amine recovery compared to other technologies and complex tie-ins if mobile unit is available. Can be more costly than the options provided by alternative technologies. If on-site the customer is left with a highly concentrated waste stream to dispose of.

## 2. Ion Exchange

An incidence of SO<sub>2</sub> breakthrough is where Ion exchange can be the best available technology. Amine recoveries are very high 99+% and since there are mobile units, remediation of the contaminated amine could occur in a relatively short timeframe.

**Advantages:** High amine recovery 99+%. Emergency Mobile service available to react quickly to the occurrence. Technology can effectively manage the salt level and reduce the contaminants in a short period of time. Tie-ins are relatively simple. Low level of HSS and anions achievable. High value and low cost. Low energy. Waste stream is typically easy to manage and discharge to the in-house wastewater system. Some providers of this technology also can provide filtration systems for removal of the high level of FeS particulate to remediate this issue at the same time.

**Disadvantages:** Water intensive technology and either steam condensate or DI water is required. Chemicals are required for regenerating the ion exchange beds (NaOH) and possibly acid for neutralizing the wastewater brine prior to discharge to the water system. Availability of a mobile unit.

## 3. Electrodialysis

Electrodialysis also works very well considering speed of implementation, overall MDEA recovery, and contaminant removal since there are no noticeable degradation products. However, without additional filtration this technology may be impaired by the high level of FeS particulate that typically accompanies an SO<sub>2</sub> breakthrough event. An incidence of SO<sub>2</sub> is where Ion exchange can be the best available technology. Amine recoveries are high and since there are mobile units may be immediately available the unit could mobilize and begin remediating the amine in relatively short notice. Electrodialysis has no proven record of bicine removal / amino acids removal. Bicine is a big concern after an SO<sub>2</sub> breakthrough event.

**Advantages:** High amine recovery but slightly lower than ion exchange. Mobile service available to react quickly to the occurrence. Technology can effectively manage the salt level and reduce the contaminants in a short period of time. Tie-ins are relatively simple and quick. Not as water intensive as ion exchange. Waste stream is typically easy to manage and discharge to the in-house wastewater system. Moderate value and low cost.

**Disadvantages:** May have difficulty with plugging due to the level of FeS particulate. Moderate to high energy cost. Chemicals (NaOH) may be required for neutralizing the amine to effect the process. Availability of a mobile unit that can mobilize quickly. Availability of a mobile unit that can mobilize quickly.

**Summary:** Efficient reduction of contaminants is critical to proper operation of the tail gas cleanup unit, including protecting process equipment and reducing maintenance costs. Ion Exchange with a regenerable FeS filtration system is the most advantageous and cost-effective option for the amine operator in this case.

## **Case Study B – Gulf Coast Refinery (ARU) Application**

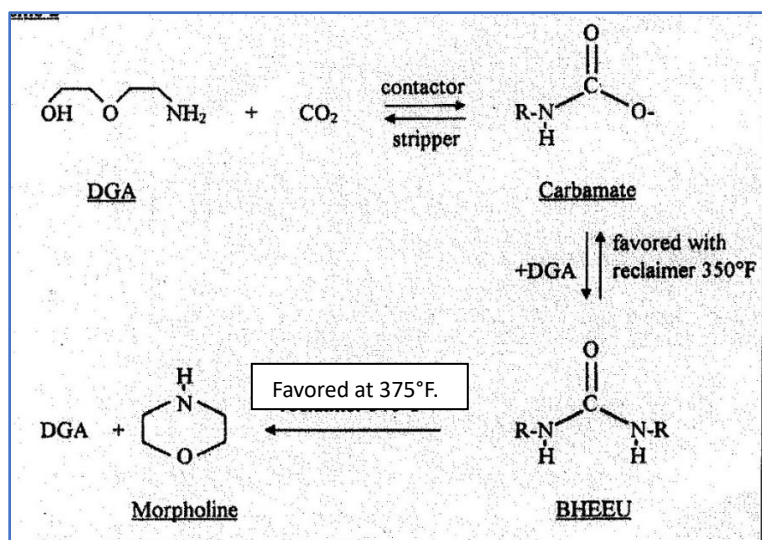
### **Background**

A Gulf Coast Refinery performed a solvent changeover from DEA to DGA<sup>®</sup>. The ARU had Heat Stable Salt mitigation already in place with an on-site ion exchange unit maintaining the HSS to ~1wt% but did not have equipment for mitigation of the potential for BHEEU formation for the newly charged 260,000 USG DGA<sup>®</sup> system. The solvent changeover was performed without a full unit shutdown so residual DEA and high boilers remained after the DGA<sup>®</sup> conversion. DGA is known to react with its carbamate to produce a thermally reversibly N, N-bis(hydroxyethoxyethyl) urea (BHEEU). The BHEEU incursion rate was estimated to be 1.5wt% per month and utilization of a mobile distillation unit was cost prohibitive due to the constant incursion rate. Due to the short schedule, the amine operator did not have time to install a DGA<sup>®</sup> reclaimer and therefore selected a hybrid approach of adopting an off-site distillation Urea mitigation strategy to manage the BHEEU formation and maintain it at 6wt% or less.

A chemical maintenance program was designed to counter the BHEEU incursion so that it could be managed and maintained at a targeted level, which was set by the customer and amine supplier.

The Project was implemented by using off-site distillation as the technology choice that could not only reduce and maintain the now primary system contaminant which was BHEEU at the desired target but could also thermally convert the BHEEU back to DGA<sup>®</sup> as illustrated in the reaction in Fig 5.<sup>22</sup>: Vacuum Distillation was employed with a very tight temperature range within which the reaction occurs and was used to effectively reverse the BHEEU and recover DGA<sup>®</sup>. The distillation requires careful attention because if the temperature approaches 375 °F, the reaction favors the degradation of the BHEEU to form of morpholine, becomes irreversible and lost. Distillation temperatures (bulk fluid or equipment skin) in this range always need to be avoided.

**Fig. 5** Thermal Reaction between DGA® and CO<sub>2</sub> to Form BHEEU



The chemical maintenance program was designed with the following criteria.

- **Needs:** BHEEU Mitigation. Reduction of chemical spend within DGA® Amine Unit, while ensuring effective amine hygiene to remove CO<sub>2</sub> and H<sub>2</sub>S.
- **Outcomes:** Thermal Distillation of DGA® to convert and remove BHEEU to counter the incursion rate and maintain less than 6wt%. An on-site Ion exchange unit on site to remove the other primary contaminant; heat stable salts.
- **Solution:** Bleed off sufficient BHEEU laden solution per month to counter the incursion rate. Truck the fluid to the off-site distillation facility to perform the BHEEU conversion/removal, generating a clean recovered DGA® distillate which was returned to the amine system's fresh make-up tank for reintroduction back into the amine system. The frequency and amount of contaminated DGA® solution reclaimed was determined by the total system volume and incursion rate of the BHEEU formation. The off-site distillation reclaimer disposed of the by-products and distillation waste as part of the chemical maintenance program.
- **Long-term Solution:** A custom-built skid mounted unit installed at the amine operator's refinery. The thermal unit would eliminate trucking off-site and provide then BHEEU conversion at the source. This option would achieve the BHEEU mitigation and drive reclamation costs down by efficiently addressing the BHEEU in situ thereby managing the DGA® hygiene in combination with the HSS mitigation provided by ion exchange skid.

This case study illustrates how the use of two separate technologies was required to effectively address the needs of the amine operator and the variety of contamination issues that may occur in the industry. By means of integrating two technologies to address the removal of the primary contaminants (HSS and degradation), effective amine hygiene can be maintained and managed to eliminate excursions and the potential operational issues associated with amine contamination.

## Conclusions and Summary

The best approach to avoid amine solvent degradation is to address the conditions and circumstances which led to the degradation in the first place<sup>5</sup>. However, it is not practical to eliminate all possible sources. Amine operators need a conscientious strategy for handling the issue of solvent contaminants, corrosion, and degradation products to manage energy, chemical, operational costs, as well as limit waste handling/disposal.

It is imperative that an effective solvent reclaiming/renewal process must be able to regenerate the solvent by removing the major contaminants which may include HSS, degradation, carbamate reactions, non-volatiles, solids, and residues. Hence a tailored solvent management strategy will be needed for each specific solvent to maintain optimal plant operation and cost reduction.

Distillation, ion exchange, and electrodialysis are technologies that can be used singularly or in combination to effectively remedy contamination issues and improve long term healthy amine hygiene and solvent sustainability.

Ion exchange and electrodialysis can be best be utilized to reduce HSS and some degradation products but are not suitable for removal of the non-ionic degradation products. Distillation (thermal reclaiming) is the only technology that can remove all degradation products, including HSS. Combinations of technologies is an important consideration to use each for its technological advantage and achieve the optimum level of amine hygiene, life, and sustainability. Any of the currently available reclaiming technologies discussed above can be used for amine solvent regeneration, but each has advantages as well as significant limitations. Integration of two or more reclaiming techniques is an approach to optimize the overall efficiency in removal of HSS and degradation products.

The future for amine reclamation is to focus on process integration of renewal technologies to assure optimal amine hygiene, prevent costly problems, and return financial vitality to amine operations.

## Acknowledgements

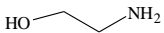
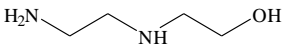
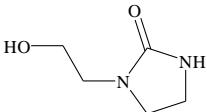
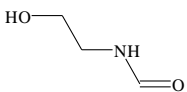
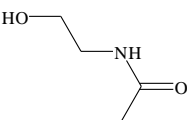
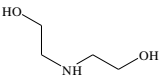
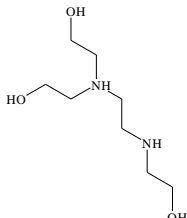
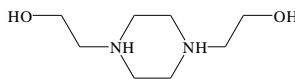
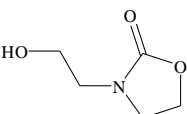
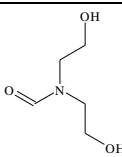
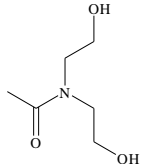
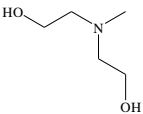
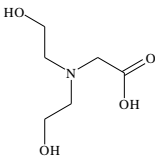
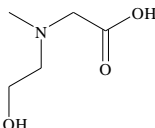
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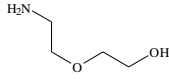
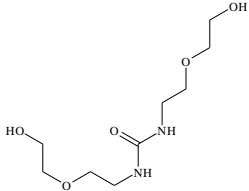
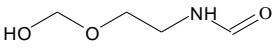

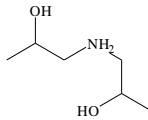
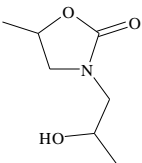
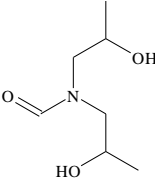
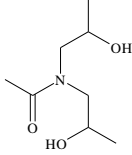
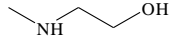
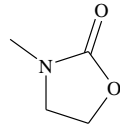
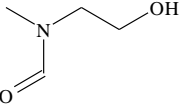
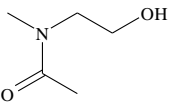
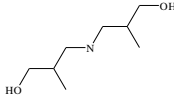
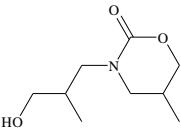
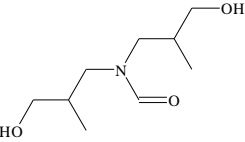
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## APPENDIX - Amine Degradation Products

Amine	Structure	Degradation Products	Degradation Product Structure	Analysis Method
MEA		<b>HEED</b> hydroxyethylethylenediamine		IC with Conductivity GC
		<b>HEEU</b> 1-(2-hydroxyethyl)imidazolidin-2-one hydroxyethylethylenediamine urea		HPLC with UV
		<b>n-Formyl MEA</b> n-formylmonoethanolamine		HPLC with UV
		<b>n-Acetyl MEA</b> n-acetylmonoethanolamine		HPLC with UV
DEA		<b>THEED</b> tris-hydroxyethylethylenediamine		IC with Conductivity
		<b>bis-HEP</b> bis-hydroxyethylpiperazine		IC with Conductivity
		<b>HEOD</b> 3-(2-hydroxyethyl)-1,3-oxazolidin-2-one		HPLC with UV
		<b>n-Formyl DEA</b> n-formyldiethanolamine		HPLC with UV
		<b>n-Acetyl DEA</b> n-acetyldiethanolamine		HPLC with UV
MDEA		<b>Bicine</b> bicine		IC with Electrochemical
		<b>HES</b> hydroxyethylsarcosine <i>no standard</i>		IC with Electrochemical

<b>DGA</b>		<b>BHEEU</b> N,N-bis(hydroxyethoxyethyl)urea		HPLC with UV detection
		<b>n-Formyl DGA</b> n-formyldigcolamine		HPLC with UV detection
		<b>Morpholine</b> morpholine		HPLC with UV or RI detection
<b>DIPA</b>		<b>HPOD</b> 3-(2-hydroxypropyl)-5-methyl-		HPLC with UV detection
		<b>n-Formyl DIPA</b> n-formyldiisopropanolamine		HPLC with UV detection
		<b>n-Acetyl DIPA</b> n-acetyldiisopropanolamine		HPLC with UV detection
<b>MMEA</b>		<b>MMEA Oxazolidone</b> 3-methyl-1,3-oxazolidin-2-one		HPLC with UV detection
		<b>n-Formyl MMEA</b> n-formylmethylmonoethanolamine		HPLC with UV detection
		<b>n-Formyl MMEA</b> n-formylacetylmonoethanolamine		HPLC with UV detection
<b>Flexsorb</b>		<b>Flexsorb Oxazolidone</b> 3-(3-hydroxy-2-methylpropyl)-5-methyl-1,3-oxazolidin-2-one		HPLC with UV or RI detection
		<b>n-Formyl Flexsorb</b> n-formyldibutanamine		HPLC with UV or RI detection