

ADVANCES IN AMINE RECLAIMING – WHY THERE’S NO EXCUSE TO OPERATE A DIRTY AMINE SYSTEM

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ABSTRACT

The benefits of reclaiming amine systems are trumpeted by many and doubted by others. Removing the contaminants generally results in smoother operations. Various methods of removing contaminants from amine solutions have been developed and improved over the years, primarily because of the enthusiasm of the users of reclaiming services. Suspended solids and hydrocarbons have been routinely dealt with by filtration and absorption technologies for longer than anyone can remember, but other contaminants have only relatively recently been targeted. Heat Stable Salts were rarely spoken of 15 years ago, but are now universally known as an operational concern. Of the several potential chemical degradation products of amines, only HEEU and BHEEU (ureas formed by MEA and DGA, respectively) have had a long-standing routine way of dealing with them. As analytical capabilities improved, more and more contaminants can be identified and have become of interest. Amino acids (bicine, HES, and others) have received particular interest because of their strong contribution to corrosion. In recent years, amides, diamines, ureas, oxazolidones have become common targets of reclaiming efforts. Amides and oxazolidones have been converted back to useable amine. Over the last 15 years, reclaiming services have become available employing a variety of technologies to remove contaminants. These are reviewed and compared.

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Introduction

Operators of acid gas scrubbing units are continually challenged to maintain and increase throughput as feedstocks change and product specs tighten. Amine systems (scrubbing units employing alkanolamine solvents) have been scrutinized more and more closely over the last 15 to 20 years, because of capacity, throughput, and costs concerns. Twenty years ago amine reclaiming consisted of built-in particle filtration and activated carbon units, and, for MEA and DGA systems, a built-in thermal reclaimer. Now operating companies can purchase mobile reclaiming services and permanent add-on reclaiming units for an ever increasing array of dissolved, entrained and suspended contaminants anywhere in the world. What has changed? Why the rise in the perceived need for reclaiming and what is now available to meet that need?

Product specifications and environmental concerns have also changed. Lower sulfur specs in finished products coupled with sourer feed stocks press ever-increasingly on the capacity of amine systems.^{1,2} Amine system downtime and upsets have a more visible connection to throughput and profits. Disposal of contaminated amine is hindered by fewer available options and higher costs. For many refineries, reclaiming is becoming the only option.

Reclaiming – removing the contaminants from amine solvents – generally results in smoother operations, which, more and more visibly, translates to improved bottom line. Table 1 shows the bottom-line benefits of reclaiming to low impurity levels that four refiners documented. The positive effects of reclaiming seen by these refiners included reduced amine losses/consumption/replacement, reduced anti-foam usage, reduced foaming, reduced filtration costs, reduced heat exchanger fouling, reduced amine unit operating costs, fewer production curtailments, fewer upsets of waste water treatment plant, record crude, coker, cracker runs, increased overall production, ability to run sourer crude, increased sulfur production.

Table 1. Annual Benefit to Bottom Line of Maintaining Low Impurity Level in Amine Systems

Refinery bbl/day	Annual Benefit
230,000	\$30 million
170,000	\$6 million
58,000	\$1 million
50,000	\$2 million

About 15 years ago, as mobile reclaiming services began to be available, only a few brave operators could be induced to try reclaiming their amine. However, the reclaiming resulted in such dramatically improved operations, that they realized that amine reclaiming had to be a necessary part of their future. The previously rarely-mentioned Heat Stable Salts (HSS) became a term that amine system engineers had to know. Replacing traditional “bleed and feed” (disposal of contaminated amine and replacing it

with new amine) are services of ion exchange, distillation and electro dialysis for dissolved salts and degradation products along with filtration and absorption for suspended solids and hydrocarbons.^{3,4,5} All these technologies have been improved and are more available than ever before as permanent on-site installations, temporary on-site mobile services, and as off-site services.

A review of the current state of reclaiming options is overdue. This paper is a review of advances and limitations of reclaiming options organized by contaminant type.

Reclaiming Methods

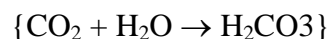
There are fundamentally two approaches to reclaiming contaminated amines: (1) remove the contaminant from the solvent, and (2) remove the solvent with or from the contaminant. A third approach, sometimes used in place of reclaiming, employs additive to negate or cover a particular symptom of a contaminant. Examples of approach (1) include Ion Exchange, Electro dialysis, filtration, and adsorption. Approach (2) includes 'bleed and feed' and distillation. The third (reclaiming avoidance) approach includes addition of caustic, corrosion inhibitors, or antifoaming agents.⁶

Heat Stable Salts

Heat stable salts (HSS) have become identified as a leading cause for reduced capacity in amine systems. They also contribute to corrosion, increased viscosity, and foaming. HSS are salts which do not decompose and release acids in the amine regenerator (stripper).

The amine system is designed to form salts from the reaction of amine with acid gases H₂S and CO₂ in the absorber (contactor), and to reverse the process in the stripper, releasing the acid gases to the stripper overhead.

Absorber reactions:



Regenerator reactions:



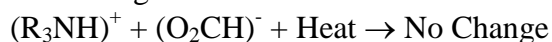
In other words, the amine system is designed to create, and later break, amine salts. Because the salt breaking is accomplished by heating the amine in the regenerator, these salts can be termed heat *labile* salts.

Other acids similarly form salts with amines. If such salts are not broken with heat and the acid is not released into the overhead of the amine regenerator, these salts are termed heat *stable* salts (HSS). This will occur if the acid is a stronger acid, less volatile, and/or less soluble than H₂S and CO₂. For example, Formic acid (HO₂CH):

Absorber reaction:



Regenerator non-reaction:



Notice that the cation of all these salts is the protonated amine (an amine bound to a hydrogen ion). The complete name of a salt includes the name of the cation and the name of the anion. However, HSS are typically called by the name of the anion. For example, the salt of formed by methyldiethanolamine (MDEA) and formic acid, is correctly named methyldiethanolammonium formate. MDEA and hydrochloric acid form methyldiethanolammonium chloride. Rather than repeat the awkward cation name (“...ammonium”), people call out only the name of the anion. Commonly recognized alkanolamine heat stable salts include formate, acetate, propionate, glycolate, oxalate, chloride, thiocyanate, thiosulfate, and sulfate salts.

Heat stable salts accumulate in the amine, resulting in a loss of acid gas absorbing capacity, because the amine can hold but one hydrogen ion. If additional amine is added to compensate for the capacity loss, water content is sacrificed; viscosity increases, and absorption and stripping efficiencies can suffer. Additionally, HSS contribute to corrosion, which reduces material life and produces solids (corrosion products such as iron sulfide), which can result in fouling, plugging, erosion, and foam stabilization.⁷ Recommendations for acceptable levels of HSS anions in amine systems range from 500 to several thousand ppm, depending on ion identity and the disposition of the author. Our experience servicing hundreds of amine systems world wide leads us to recommend, as a general rule, total HSS anion of 5000 ppm or less for the most trouble-free operations.

Here are the common approaches to remove HSS from amine solutions.

Bleed and Feed

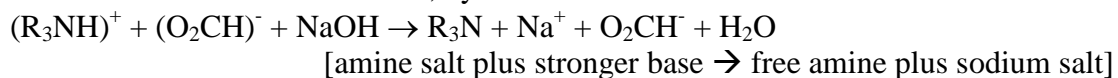
Bleed and feed (purging contaminated amine and replacing it with fresh amine) is the most widely practiced method of “cleaning” the amine systems. Bleed and feed does have the advantage of being easiest way of dealing with HSS. This method might not be opposed by your amine supplier. It is more economical if used to maintain very high levels of HSS – the higher the salt concentration the less solvent must be discarded to remove a given amount of salt. Higher salt concentrations lead to more operational problems and shorter mechanical life. Other disadvantages of bleed and feed are well known. There are amine replacement costs and disposal costs, which have risen through the years. Another difficulty with bleed and feed is large quantities of amine can cause difficulties to the site waste water facilities and can cause waste water plant upsets. This “pump and dump” also suffers from poor environmental image.

Neutralization

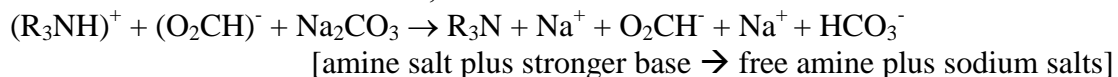
The addition of NaOH or KOH, or analogous carbonates, quickly and easily recovers the capacity of the amine. The stronger base (OH⁻) takes the hydrogen ion away from the alkanolammonium ion,

converting it to free amine available again to react with acid, but the formed sodium or potassium SALT REMAINS in the amine solution.

“Neutralization” reaction, hydroxide:



“Neutralization” reaction, carbonate:



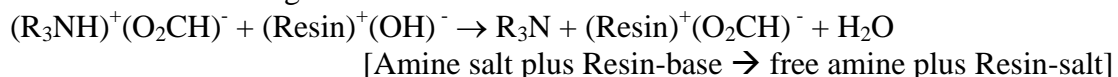
One disadvantage to neutralization is the false sense of security that it lends to the operator. While amine capacity is maintained, the amine solution becomes more and more polluted with salts which are not “seen” by the more common plant analytical methods. These salts likewise contribute to higher solution density and viscosity, reduced surface tension, and possible “soap” formation. Eventually the solution either self purges through an upset, or it must be discarded. Neutralization’s affect on corrosion has received mixed reviews – some saying it reduced corrosion; others saying it actually increased corrosion rates. Finally, it is easy to add too much caustic, which then creates heat stable salts with the acid gases, causing higher lean loadings and less efficient acid gas scrubbing.

Neutralization is easily misunderstood or wrongfully reputed to be a HSS eliminator or HSS preventative. As the neutralization reaction shows, it simply converts amine HSS to sodium or potassium HSS. There no reduction in salt content of the solution and certainly no prevention of salt formation.

Ion Exchange

Ion Exchange is a chemically clean and environmentally friendly way to remove HSS and maintain the necessary low levels of HSS in amine systems. Ion Exchange literally exchanges a friendly ion for the HSS ion. 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.^{8,9,10}

Anion exchange reaction:



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

Cations, such as sodium, potassium, calcium, etc are similarly removed from amine systems by cation exchange.

While ion exchange seems chemically simple, the practice of removing HSS from amine systems by ion exchange has presented many technical and operational challenges. Several have reported the belief that it will not work effectively for amine reclamation, based on actual attempts. MPR Services, on the other hand has been providing successful amine ion exchange reclaiming services world-wide since 1991.

The advances in ion exchange have lead to reduced chemical and water consumption. Caustic utilization: 15 years ago typically 9 to 40 moles NaOH per mole HSS, now more like 3 to 5 moles

NaOH per mole HSS, and recent advances have reduced that to just over 1 mole NaOH per mole HSS anion. Water requirements, depending on the application, now can be about 2/3 to 1/5 of the water demand 15 years ago. Mobile and permanent ion exchange units have become available throughout the world. In addition to efficiently removing HSS, another primary advantage of ion exchange is that its waste is biodegradable.

Ion Exchange has the advantage of being the most economical method by which to maintain low levels of contaminants. Particularly in gas plants, where salt incursion rates are low, Ion Exchange should be the most economical way to treat low level contaminants like chlorides and amino acids. Ion Exchange has lower energy needs than distillation and electrolysis cleaning services, generates the larger more dilute volumes of waste, and requires more water. Poorly designed and/or operated ion exchange systems have caused significant amine losses and sodium slippage into the amine. Better designed ion exchange systems, such as MPR's HSSX® process, lose no significant amounts of amine and slip no sodium.

Distillation

The virtue of distillation has long been recognized for MEA and DGA. Many MEA and almost all DGA amine systems have permanent thermal reclaimers as an integral part of the amine system. Other amines require vacuum to prevent thermal degradation upon distillation. Canadian Chemical Reclaimers has provided mobile vacuum distillation services for many years. Other companies (ChemGroup, Coastal) have offered distillation reclaiming of amines shipped to their central reclaiming operations. Improvements in distillation have reduced amine in waste and allowed for permanent units.

One important advantage of distillation is that distillation has an economic advantage when dealing with very high concentrations of HSS. Secondly there are low quantities of waste generated and it has low water and chemical consumption (close to 1 mole caustic per mole HSS). Distillation works better with the amines with low boiling points. The major disadvantage of distillation is the energy consumption needed to vaporize and distill over the amine solution. Distillation sends the most amine to waste of the discussed reclaimer methods. Other disadvantages include that it generates a concentrated waste which is considered potentially hazardous in many jurisdictions. The waste contains amines and amine degradation products, as well as salts and other contaminants. Distillation has poor economics for maintaining low concentrations of HSS, because such a large volume of solvent must be distilled to remove a small amount of salts.

DGA reclaimers are actually designed to convert a degradation product (BHEEU) back to useful DGA. A properly operated, clean (free of other contaminants), DGA reclaimer should ideally operate indefinitely. However, HSS and non-volatile impurities accumulate in the DGA reclaimer, which can upset the BHEEU conversion. The accumulation of HSS in the DGA reclaimer can lead to increased operating temperatures and the formation of another degradation product, morpholine.¹¹ To bring the reclaimer back to correct operation, the HSS and other contaminants must be purged from the reclaimer by dumping its contents, which wastes good DGA and the DGA trapped in BHEEU. Increased HSS incursion will increase reclaimer dumping frequency, which wastes more amine. It would be better to keep the amine free of HSS by means of ion exchange, thus avoiding reclaimer problems.

The DGA and MEA thermal reclaimers are periodically emptied of the accumulated salts, which are sent to waste. Very commonly the reclaimer bottoms have high amine content, causing the reclaimer to be more of a bleed and feed device. Table 2 shows the results of a survey of the amine/HSS ratio in several amine systems and their reclaimer bottoms. Ideally, the amine/HSS ratio was much, much lower in the

reclaimer bottoms than in the system, so less amine would be wasted via reclaimer bottoms than via direct bleed and feed. In only about 1/3 of the cases is the amine loss in the reclaimer less than half the loss that bleed & feed would have caused. MEA reclaimers also collect, and even cause formation of, amides and ureas, each of which entraps an MEA molecule. Thus the total amine lost in thermal reclaimers is much worse than is shown in Table 2. Table 3 shows total amine lost per mole of HSS, which is the sum of free amine, amides, and ureas. Based on amine alone, Reclaimer D seems to be least wasteful operation, but it is actually the most wasteful because of the high amount of amides and ureas.

Table 2. Thermal Reclaimers Waste Good Amine

<u>Amine</u>	System Free Amine/HSS mol/mol	Reclaimer Bottoms Free Amine/HSS mol/mol
MEA		50
MEA		10
MEA	17	3
MEA		1
MEA	82	2
MEA		26
MEA	3	4
MEA	3	2
MEA	5	6
MEA	4	4
MEA	5	5
MEA	6	3
MEA	3	4
MEA	11	2
MEA	23	1
DGA	62	77
DGA	29	44

Table 3. Thermal Reclaimers Waste Amine as Amine, Amides and Urea

Amine system	A	B	C	D
Amine/HSS, mol/mol	3.3	3.6	2.1	1.2
(Amide + Urea)/HSS, mol/mol	0.2	.7	1.4	4.4
(Total amine loss)/HSS = (Amine+Amide+Urea)/HSS mol/mol	3.4	4.3	4.5	5.6

Electrodialysis Units (EDU)

The electrodialysis units have become more available and they have improved with new membrane technologies. Electrodialysis providers have claimed a greatly reduced need to neutralize HSS before removal of anions.¹² Also electrodialysis providers are able to remove HSS salts to lower levels with less amine waste than in previous years and EDU units can remove thiosulfate impurities better than ever before. Membrane selection and maintenance is critical to the success of EDU. The various membranes have different selectivities for different ions, so one may see some ions removed and others not.

Electrodialysis has lower energy demands than vacuum distillation. EDU have an advantage of lower chemical and water usage than ion exchange. One primary difficulty with Electrodialysis technology through the years has been dealing with solids. It is recommended that EDU needs a 1 micron pre-filter. Another difficulty with electrodialysis is amine levels in the waste increase when going to low HSS endpoints. Often a trade-off has been observed between anion removal efficiency and amine losses i.e. reduce amine losses by reducing the efficiency of removal of anions from the amine. One performance example allowed 70% of the anions to slip past the membranes (stay in the amine solution).

Fouling of membranes has historically been a major cause of downtime and membrane expense. Recent advances have made this less of a problem. EDU also have much higher power consumption than ion exchange and EDU generates more waste than vacuum distillation. Salt concentration in the waste runs from 3 to 20 times the salt concentration in the amine.

Amino Acids

Amino Acids have received considerable attention recently due to their corrosive nature at relatively low concentrations.^{13,14,15,16} Bicine $\{(HOCH_2CH_2)_2NCH_2CO_2H\}$ in MDEA and DEA systems and Hydroxyethylsarcosine (HES) $\{(HOCH_2CH_2)N(CH_3)(CH_2CO_2H)\}$ from MMEA are currently reportable by many amine analysis laboratories. Bicine is a strong complexer of iron, capable of holding iron in solution in the presence of some H_2S in lean amine solutions, so it is expected to contribute to corrosion. Based on laboratory corrosion studies, bicine has been recommended to be kept as low as 250 ppm in amine systems¹⁷ especially where H_2S levels are low. Corrosion in gas plant amine has been clearly traced to bicine in the 1000 to 4000 ppm range.¹⁴ In a collection of 1739 amine samples from 273 different gas treating plants, 825 had more than 100 ppm bicine.¹⁸ Because “there have not been an extraordinary number of reports from accounts of active corrosion” these authors doubt the importance of bicine corrosivity. As bicine and other amino acids are found in more amine systems we will certainly hear more about amino acid corrosivity.

The chemical pathways for forming bicine in amine systems has not been determined. Proposed pathways include:

- a. Reaction of cyanide with formaldehyde
- b. DEA with Glyoxal
- c. Direct degradation of DEA with oxygen
- d. Disproportion reaction of MDEA to TEA and further oxidation of TEA to Bicine
- e. Reaction of cyanide with imide of MDEA (from DEA or MDEA)
- f. Thiosulfate (S_2O_3) assisted reaction with MDEA or DEA (observed in tail gas units).

Bleed and Feed

Pump and dump is not normally used to lower a bicine contamination because of the poor economics of addressing a low concentration impurity by throwing away amine.

Neutralization

Although claims have been made, and rationale published that neutralization help reduce corrosion by amino acids operator testimony and further theoretical scrutiny show neutralization to be of no value for “masking” bicine corrosion. Fully de-protonated amino acid is stronger in chelating of iron than partially de-protonated, so caustic “neutralization” of bicine serves only to assure more of the bicine is in its strongest form.

Because bicine can complex other cations, it has been suggested that sodium or potassium from caustic addition (neutralization of amine HSS and amino acids) might divert bicine from iron complexation. This theory was supported by calculations of Bosen and Bedell.¹⁸ Our literature search led us to complexation constants which, when applied to the Bosen and Bedell theoretical calculations, yielded clear evidence that bicine strongly enhances iron solubility in H₂S systems, and that this enhanced solubility is insignificantly affected by the presence of very high concentrations of sodium or potassium. Bicine’s effect on the solubility of iron in CO₂ systems is orders of magnitude higher.¹⁹ Sodium and potassium cannot be relied upon to significantly reduce bicine complexation of iron.

Field experience in gas plants and refineries attests to amino acid corrosivity and ineffectiveness of caustic addition. A Texas gas plant identified bicine as the root cause of amine system corrosion, correlated dissolved iron increases and decreases with bicine increases and decreases, found no reduction in corrosion attack upon ‘neutralization’ by caustic addition. A Gulf Coast Refinery added caustic to the amine solution to control escalating bicine levels. No impact on measured corrosion rates was observed, but unit performance continued to deteriorate. A Gulf Coast gas plant encountered escalated corrosion rates and high bicine levels. Sodium was added in an effort to control the corrosion. Minimal impact was observed.

Ion Exchange

MPR’s HSSX® ion exchange process has had considerable success for bicine removal. Ion exchange can work well for bicine removal especially when addressing low level bicine impurities.^{14, 20, 21} Other ion exchange providers have had difficulty in removing bicine due to their process conditions that result either in poor bicine removal or adding sodium to amine system.

Distillation

It has been suggested that distillation can remove amino acids but there has been no identifiable instance in the literature where distillation was used to specifically remove amino acids.²² This may be due to the fact the distillation is at its best with high concentration impurities and most bicine applications begin at relatively low concentrations (1 wt% or less) and are seeking to reduce bicine to 250 ppm or lower.

EDU

Electrolysis has shown some positive results, but amino acids removal is still being developed.

Amides

Primary and secondary amine for amides with carboxylic acids. For example, MEA and formic acid form an MEA-formamide called Formyl-MEA (also FMEA or MEAF). Similarly for DEA, DIPA, DGA, etc. Other amides, such as acetamides (e.g., Acetyl-DEA from DEA and acetate) may also form. For simplicity, the following discussion mentions only formamides, but it applies to other amides.

Formation of formamides results in a loss of one mole of useful amine per mole of formamide. The equilibrium formation of these formamides may be depicted as follows:



Temperature, time, pH and concentration affect the formation of amides. Since the first two factors are usually fixed in the system, attention must be given to concentration. There is an equilibrium relationship between formate and amine formamides in primary or secondary amines. The molar ratio of formamide to formate varies with amine type and degree of contamination, with higher ratios typically seen at higher contaminant concentrations. Formamides have been seen in operating amine systems from less than 1 wt% to 15 wt% and higher.

Of the common alkanolamines, the formamide to formate ratio is highest in DIPA, typically around 2:1. The ratio in DEA is typically about 1:1.

In an operating amine system, formamides may be converted back to useful free amine by removing the formate from the amine solution. As formate concentration is reduced, the equilibrium causes the formamide to convert back to protonated amine and formate. Further removal of formate results in further reduction in formamide concentration.

Bleed and Feed

Purging contaminated amine and replacing it with fresh amine works to remove amides but has the same advantages and disadvantages that were discussed for HSS.

Neutralization

Neutralization removes protonated amine from the equilibrium reaction by raising the pH and drives the amide to amine and formate. Thus, while caustic addition might increase the available amine concentration a little, neutralization replaces the relatively non-corrosive formamide with corrosion enhancing formate.

Ion exchange

Ion exchange removes the formate ion from the equilibrium reaction and drives the equilibrium to amine and formate. Ion exchange is extremely selective, removing only the formate, none of the formamide. Formamide can all be converted to useful amine. For example, one refiner identified 90,000 lb of new DEA from formamide conversion after removing formate and other HSS from the amine system by Ion exchange.

Distillation

Because of the dehydrating aspect of distillation, amides can actually increase during the reclaiming process. Additional good amine thus becomes trapped in the reclaimer bottoms [see Table 3 and attendant discussion of thermal reclaiming] and is wasted. This can cause difficulties for waste water

treatment facilities. Permitted the requisite time and operating skill, however, vacuum distillation and thermal reclaiming processes should be able to recover amine from amides. Commonly, however, amides remain in the bottom of the still and are thrown away, representing lost amine which is costly to discard and to replace.

EDU

Electrodialysis removes the formate ion from the system and the equilibrium consumes formamides to form amine and formate. Electrodialysis has similar advantages and disadvantages when dealing with amides as it does with heat stable salts.

Oxazolidones

Example: 3-(2-hydroxypropyl)-5-methyl-1,3-oxazolidin-2-one (HPOZD)

Oxazolidones are particularly problematic in DIPA and Sulfinol-D systems where they can build up in concentration and reduce capacity. Oxazolidones could also form in DEA and MEA, but are not commonly present at significant concentrations. Pump and dump can be used, but it is a very expensive way of dealing with oxazolidones, especially in Sulfinol-D systems. Neutralization, ion exchange, and EDU are not considered effective ways of dealing with oxazolidones.

Distillation

Oxazolidones can be separated from the amine by distillation. However, in Sulfinol-D solutions, there may be some difficulty separating the sulfolane from the oxazolidone. Because oxazolidones contain the amine molecule, there is the additional cost of having to replace the amine that was tied up as the oxazolidone. The waste is a problem, because the wasted oxazolidone contains the ammonia nitrogen functionality.

OXEX™ Process

The advantage of the OXEX™ process (patent pending) is that it converts the oxazolidones back into useful amine.²¹ The waste is easily discarded to the waste water treatment facilities because the waste contains only water and carbonate and sulfate salts. Recent advances in the OXEX™ process have led to reduced costs and improved throughput. The conversion efficiency has been greater than 95% for the batch process. The improved OXEX process has been proven in the lab and in two commercial efforts as shown in the below table. It is more economical than distillation or pump and dump.

Table 4. Oxazolidone Conversion to Amine by OXEX™ Process

Description	Commercial Job 1	Commercial Job 2
Oxazolidone Starting point, wt%	36.08	22.84
Oxazolidone Ending point, wt%	4.34	6.20
% Conversion of Oxazolidone on a per batch basis	>95%	>95%
DIPA in system at start of job, wt%	37.57	29.57
DIPA in system at end of job, wt%	53.58	42.86
Net absolute increase in DIPA Concentration, wt%	16.01	13.29

Diamines and Ureas

Examples of diamines and ureas are:

HEEU (Hydroxyethylethylenediamine urea) found in MEA

HEED (Hydroxyethylethylenediamine) found in MEA

BHEEU (N,N-bis(hydroxyethoxyethyl)urea) found in DGA

THEED (Tris-Hydroxyethylethylenediamine) found in DEA

Bis-HEP (Bis-hydroxyethylpiperzine) found in DEA

DIPA/MIPA and DIPA/DIPA dimers found in DIPA²

Diamines and ureas reduce capacity of amine solutions and can be responsible for corrosion, increased viscosity, and reduced water content.

Bleed and Feed

Pump and Dump have been used successfully when treating diamines and ureas. Pump and dump have the advantages and disadvantages discussed in the HSS section.

Neutralization

There are no known examples of neutralization being effective in treating diamines and ureas.

Ion Exchange

Ion exchange is not an effective way of removing diamines and ureas. However, field results indicate that continual operation of ion exchange to control HSS in refinery DEA systems prevents further formation of THEED. It is suspected that this is a side-effect of the improved regenerator conditions resulting from operating with cleaner amine.

Distillation

The value of thermal reclaimers for MEA and DGA is well known. Distillation of other amines has been successful in removing high concentrations of diamines and ureas. The advantages and disadvantages of distillation for treating diamines and ureas are similar to the advantages and disadvantages of distillation for HSS removal discussed above.

EDU

EDU is not an effective way of removing diamines and ureas.

Solids

Solids normally provide different types of problems for amine operators. Solids are a heterogeneous phase. Solids can settle out or combine with hydrocarbons or antifoam and coat the internal components of the amine system. The “shoe polish” that coats the internal amine system leads to filter plugging, tray plugging, and reduced thermal transfer.²³ Another difficulty with solids is they can contribute to corrosion by mechanical wear that erodes the internal surfaces. In certain circumstances it has been shown that solids can stabilize foaming. If the solids contain considerable iron sulfide, the iron sulfide can represent a fire hazard when servicing the amine system. Under normal conditions, pump and dump, neutralization, ion exchange, distillation, and EDU are not used to deal with solids.

Size Exclusion Filters

Almost always solid removal is done with permanent units using size exclusion filtering. There have been advances of the filters include an increased variety in filtering technology available, and easier to use. The vast majority of filtering media is disposable (back washable media is available but this media does require water). The advantages of the disposable size exclusion filters are they are “easy” to use and they are readily available world wide from many suppliers. The disadvantages of disposable size exclusion filters are they can require frequent replacements in dirty systems. The filters do not remove particles below rated particle size. The consumable nature of filters can make for expensive purchase and disposal costs. Another difficulty is the potential for a fire hazard from iron sulfide. There are labor costs and personnel issues involving H₂S during filter change outs. All too often filters are bypassed during operations in to avoid dealing with a plugged filter.

SSX™ Process

The SSX™ technology is a method where the solids are attracted to its media.²⁴ This leads to the advantage that the SSX™ media normally does not plug, there is a low pressure drop, and SSX™ can remove particles to less than 1 micron. The media is regenerated with water and SSX™ works well on rich or lean side treating. This technology works well for refineries, where the oily waste water is easily handled. The SSX™ process rarely plugs. The disadvantage of this technology is that may not remove 100 % of particles per pass.

Hydrocarbons

Hydrocarbons are associated with plant upsets and they are frequently blamed as a source of foaming. Hydrocarbons and antifoam combine with solids that may result in plugging. Hydrocarbons are a poison to Claus catalysts. Hydrocarbons are not normally addressed with pump and dump, neutralization, ion exchange, distillation, or EDU. Most amine systems have a permanently installed phase separator (knock-out drum) to deal with hydrocarbons that are not miscible with the amine solution. Hydrocarbons which make it past the phase separator require a reclaiming method.

Activated Carbon

The amine systems use a tank filled with activated carbon to address dissolved and entrained hydrocarbons. In practice activated carbon bed performance suffers from the problems of being undersized and neglected. The activated carbon also needs to be regularly replaced leading to purchase and disposal costs as well as the labor required. Monitoring the condition of an activated carbon filter is also difficult.

HCX™ Process

The HCX technology uses a surface attraction of hydrocarbon that removes immiscible, entrained, and dissolved hydrocarbons from the amine systems.²⁵ The advantage is the HCX media normally is back washed about every 2 to 5 days to regenerate its surface. This technology works well for refineries, where the oily waste water is easily handled.

Table 5. Hydrocarbon Content of Amine – Before and After HCX Process Installation

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

Foam Abatement

Foaming in amines systems cause system upsets that lead to loss production and amine losses. Foaming is caused by an impurity or impurities that act as surfactants in the amine system that allows the stabilization of the gas in liquid dispersion. Foaming has been attributed to number contaminants such as hydrocarbons (polar and non-polar), HSS, and solids.^{26,27,28}

De-foamers

There is a wide variety of anti-foaming or de-foaming agents available. These additives are believed to break the foam by being a heterogeneous droplet or solid enter entering the foam bubble and weakening the wall until the bubble ruptures.²⁹

There have been advances in choices, effectiveness, and stability of these de-foaming additives. The advantages of de-foaming agents are their ease of use and low initial capital expense. The primary disadvantage of antifoam agents is that they do not remove impurities that cause the foaming in the amine system. The de-foaming agents can give operations a false sense of security and hide the underlying problem/impurity that could lead to a cycle of repeated foaming. Also de-foaming additives can become inactive at high concentrations and fail break the foam.

SigmaPure™

D-Foam with the SigmaPure™ cleaning system has a unique method of effectively removing the foaming agents and any impurities which travel with the foam.^{28,30} The SigmaPure system intentionally causes controlled foaming of a slip-stream of amine outside of the amine unit. Amine is drained from the foam and the foam it is carried over into a waste container. The amine is returned to customer with the foam causing contaminates removed.

Permanent Units vs. Mobile Units vs. Offsite Treatment

Permanent Units

Permanent units are ideal for keeping contaminant at low levels continuously and are more cost effective for high incursion rates. Hydrocarbon and solid removal units are considered important enough to be permanent units in almost all amine systems. The disadvantages of permanent units are their capital costs.

Mobile Units

Mobile units are probably more economical for low incursion rates where annual or longer cleaning events are acceptable. Mobile reclaiming can be called upon to deal with emergencies and upset conditions, such as is typical of heat stable salts formation in tail gas units, sudden hydrocarbon transfers into circulating amine, and thermal or mechanical events shaking loose large amounts of solids. Mobile units can be used to demonstrate the effectiveness of a new technology.

Offsite Treatment

Transporting contaminated amine to an offsite reclaiming center can be less intrusive than mobile reclamation, but is much more hassle than permanent onsite reclamation units. Offsite reclaiming is a variation of Bleed and Feed – regardless of the method of reclaiming at the offsite center. The “bleed” is the same; the “feed” is your own amine after reclaiming. Thus, offsite reclamation is best for maintaining high concentrations of impurities. The high contamination conditions are harmful to the amine system and to operations. Another disadvantage of offsite treatment is that offsite treatment involves shipping costs and risks.

Summary and Conclusion

A variety of reclaiming options are now available to the amine system operator, whereby troublesome contaminants can be removed. These options have matured and improved over the last 15 years and are available as mobile services or permanent installations throughout the world. A comparative summary of these options is presented in Appendix A. Benefits of reclaiming have been widely demonstrated, so that it is now commonly accepted that amine system operational problems can be reduced and efficiencies increased by keeping the amine solution clean and free of contaminants.

Appendix A

Comparison of Reclaiming Methods

Table A1: Comparison of Methods for Removal of HSS and Degradation Products

	Ion Exchange	Distillation	Electrodialysis
Applicability	Removal of Ionized impurities	Removal of solids and non-volatile species	Removal of ionized impurities
Operation Principle	Ions captured by ion exchange resin	Vaporization of volatile species (water, amine, etc) from salts and degradation products	Ions removed by electrodialysis
Limitations	Can not remove non-ionic species	Energy intensive; most amines need vacuum;	Can not remove non-ionic species; membranes selection and durability
Forté	best option for low conc. salts	high conc. salts and degradation products	Amine conc remains the same
Waste Products	Dilute aqueous stream containing removed ions and excess regeneration chemicals	Reclaimer bottoms, containing salts, non-volatile organics, and some amine. Normally hazardous waste	Aqueous brine containing removed ions
Volume of Wastes	High to moderate	Low	Moderate
Amine Recovery	>99% (Some do 95 to 98%)	95-85%	98%
Amine Feed Requirements	Lean cool amine	HSAS neutralized	Lean, cool, hydrocarbon free, particle free amine HSAS neutralized
Special Requirements	Regeneration chemicals as low as 1 mol/mol (often more)	Fuel gas or high temp. heat source; chemicals 1 mol/mol	DC power; chemicals 1 mol/mol
Operating Mode	Batch or on-line	Batch or on-line	Batch or on-line
Unit Availability	Permanent and mobile units available	Mobile units available (many DGA and MEA units have permanent thermal reclaimers)	Permanent and mobile units available

Table A2: Comparison of Methods for Removal of Solids, Hydrocarbons, and Foaming Agents

	Mechanical Filtration	SSX™	Activated Carbon	HCX™	D-Foam SigmaPure™
Applicability	Removal of particles and sludge; many choices available;	Removal of particles and sludge, can remove particles smaller than 1 micron	Removal of high molecular weight, polar organics, and anti-foam, many choices available	Will remove broad range of organics and anti-foam	Removes foaming agents
Operation Principle	Size exclusion filtration; some regenerable	Attraction to media; regenerated with water	Adsorption (usually with filtration)	Attraction to media; regenerated with hot water	Expulsion of Foam
Limitations	Removes only particulate matter; often requires media change out, Particle size removal depends on filter rating	Removes only particles; may not remove 100% particles per pass	Require particle filtration before and after		
Waste Products	Filter sludge, filter bag, cartridges, normally hazardous solid waste	Aqueous waste with solids and hydrocarbons normally handled in plant waste water facilities	Spent carbon, normally hazardous solid waste	Oily Water, normally handled in plant waste water facilities	Foaming agents and small amounts of amine; potentially hazardous liquid waste
Volume of Wastes	Low to high	High	Low	High	Very Low
Amine Recovery	High	High	High	High	High
Amine Feed Requirements	None, but caution has to be used for H ₂ S exposure during rich side filter change outs	None, SSX can be safely used on lean or rich amine solutions	Pre-filtered Lean Amine	Can be used on lean or rich amine (does <u>not</u> need to be pre-filtered)	Can be used on lean or rich amine (does <u>not</u> need to be pre-filtered)
Special Requirements	Periodic clean out required; if regenerable require air, nitrogen, water, etc.	Water for regeneration	Periodic clean out required	Hot Water for regeneration	Nitrogen or fuel gas for purge gas
Operating Mode	Continuous	Continuous	Continuous	Continuous	Continuous
Unit Availability	Normally in permanent units	Permanent or mobile units	Normally in permanent units	Permanent or mobile units	Mobile units

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