

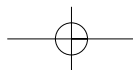


**Reprinted from PTQ Winter 2001-2 issue**

# Understanding gas treating fundamentals

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James L Jenkins and Randy Haws  
*CCR Technologies Inc*



## REFINING

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At a recent symposium regarding the challenges of the new clean fuels regulations, refiners were particularly interested in ways to improve capacity, efficiency and reliability of amine systems and sulphur units. Much of the focus on improving the operation of the amine unit, and the associated affects on the downstream sulphur plant, has been in the area of amine solvent conversion. Some of these solvent conversions have improved plant operation dramatically, while others have not been so successful.

When comparing successful cases to those less so, it may be found that focus on the basic fundamentals of gas treating has a significant role to play in the outcome of any new plant amine selection or existing plant amine conversion. Understanding the fundamentals of gas treating and applying them to any evaluation may seem commonplace, while in actuality marketing efforts of suppliers and lack of funds for detailed engineering evaluations has led to deviation from fundamental best practice.

A review of the fundamentals of gas treating with an evaluation of an actual case study of amine selection and further optimisation gives an excellent basis of understanding for refiners to use in evaluating their own systems.

Considerations for evaluating an amine type in refinery main system service are numerous. It is important to consider all aspects of the amine chemistry

Solvent	MEA	DGA	DEA	MDEA
Wt%	20	45	30	45
MW	61	105	105	119
Molarity	3.3	4.3	2.9	3.8

DEA < MEA < MDEA < DGA  
Increasing capacity →

Table 1

and type since the omission of a single issue may lead to operational issues. While studying each issue, it is important to understand each amine type based solely on fundamentals and measured data instead of making decisions based solely on marketing information from suppliers or service companies.

## Common amines

Amines used in refinery main system service may be categorised into three groups, primary, secondary, and tertiary. Primary amines react directly with hydrogen sulphide (H<sub>2</sub>S), carbon dioxide (CO<sub>2</sub>) and carbonyl sulphide (COS). Examples of primary amines used in refineries includes monoethanolamine (MEA) and the proprietary Diglycolamine agent (DGA).

Secondary amines react directly with H<sub>2</sub>S and CO<sub>2</sub>, and react directly with some COS. The most common secondary amine used in refineries is diethanolamine (DEA), while diisopropanolamine (DIPA) is another example of a secondary amine which is not as common any more in refinery main treating systems.

Tertiary amines react directly with H<sub>2</sub>S, react indirectly with CO<sub>2</sub>, and react indirectly with little COS. The most common example of tertiary amine used in refineries is methyldiethanolamine (MDEA).

Focus will be placed during the review of selection fundamentals on the most common amines employed in refinery main system service. These amines are used by engineering companies for grass roots design evaluations, and are the amines used in comparison for solvent conversion studies and include MEA, DGA, DEA, and MDEA.

## Fundamentals

The fundamentals for amine selection in refinery main system service are based on the features of each amine type. These features are based on industry recognised

guidelines and actual measured data or physical properties. Evaluation of these fundamentals will lead to proper solvent selection and serious issues may arise when solvent selection is based solely on marketing information and word of mouth.

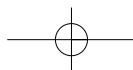
## Capacity

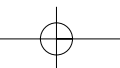
Capacity is generally the first item evaluated for a new plant design or solvent conversion. Capacity of the circulating solution is one of the most basic and critical principals in a treating plant, but is often misunderstood. Plant operators measure the strength of the circulating solution on a very frequent basis to ensure that they have enough capacity to meet treating specifications.

Solvent strength is measured on a weight per cent of solution basis due to the ease of measurement and interpretation of results. However, when comparing the relative strengths of the amines to each other the relative molecular weights of the amines need to be accounted for to fully understand what their actual capacities towards acid gas really is. For example, each mole of H<sub>2</sub>S reacts with one mole of amine, so the actual acid gas removal capacity of each amine is related to how many moles of amine are contained in one unit volume of circulating solution. Molarity (moles/litre) is the actual measure of amine strength from a reaction (or chemistry) standpoint and properly expresses how potent each circulating volume of circulating solution is.

Actual capacities of the various amine types based on typical maximum use strengths in refinery primary systems are listed in Table 1.

This concept is important to understand in light of much of the publications and claims in the industry that may lead to confusion. For example, MDEA has been stated to have many advantages over MEA due to the fact that it is operated at higher concentrations in solution.





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Solvent	MEA	DGA	DEA	MDEA
PKa, 77°F	9.5	9.5	8.8	8.6

$MDEA < DEA < MEA = DGA$   
 Increasing base strength →

Table 2

While this statement is true, one must understand what the true capacity difference is between the two amines. If one compares 20 wt% MEA to 45 wt% MDEA, on the surface it looks like MDEA may effectively more than double the capacity of the MEA if only the weight per cent of circulating solution is considered. However, the above shows that the molarity of the two solutions are the true expression of the capacity of the circulating solutions with MEA circulating at 3.3 molar and MDEA circulating at 3.8 molar in truly optimised plants. Therefore, MDEA will give an increase in capacity over MEA of approximately 15 per cent (on a molar basis), which is much lower than the perceived increase when looking at the weight percent of solution strength only.

Relative base strength

Another key component to understanding the potency of unit of circulating volume is the relative base strength of the circulating solution. A higher base strength indicates a higher affinity for the acid gas to be removed. Relative base strengths of various gas treating solutions is often referred to as the pKa of the solvent. Ka is the acidity constant and chemists often express it as its negative logarithm, pKa ( $pKa = -\log Ka$ ). The larger the value of the pKa, the weaker the acid (or stronger the base). The pKa values for the gas treating solvents under discussion are listed in Table 2.

It is vital to understand this concept and it affects the maximum loading guidelines of the solution and may prove critical when comparing solvents types treating gas at relatively low partial pressures and elevated temperatures. A stronger base will give better performance with regard to acid gas removal when process conditions limit the driving force of partial pressure and temperature.

Maximum loading

In order to achieve maximum capacity of each volume of solution circulated, refiners will often set the circulation rate to achieve the recommended maximum loading guideline. While this is an excellent practice for unit optimisation, it is important to understand what the maximum acid gas loading (or rich loading) of

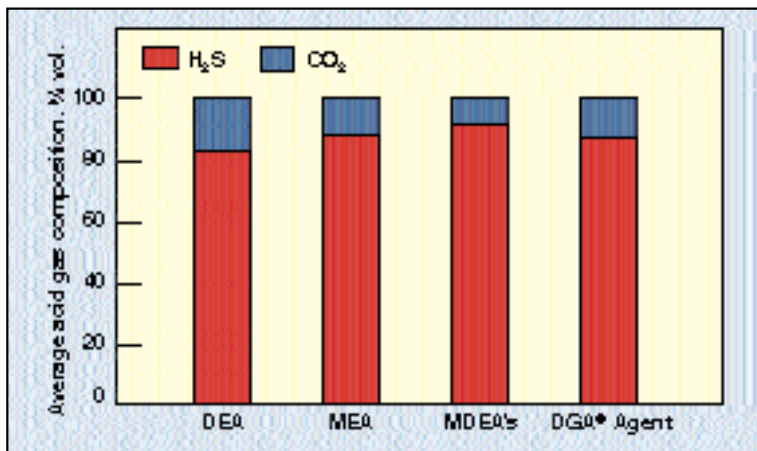


Figure 1 Comparison of produced acid gas composition

the solution really should be. The industry likes to talk about maximum rich loadings on a mole-to-mole basis. This is due to the fact that the measurement is relatively easy to accomplish in the lab and the units of measurement make sense.

However, rich loadings on a mole-to-mole basis need to account for the relative partial pressure of the acid gas and the relative base strength of the gas treating solution. A rich loading of 0.4 mole-to-mole means one thing in a system operating at 10 bar (145psi) versus a system operating at 70 bar (1015psi). It is critical to understand that constant mole-to mole loadings mean different things for different amines at different pressures. Therefore, a unit of measurement for

maximum loading must be used that accounts for process conditions and amine type.

Vapour-liquid equilibrium (VLE) data is the basis for selecting the maximum loading guidelines for the various amines and is probably the most important piece of data required to design and optimise any amine treating plant. These data account for the pressure and temperature of the treating application as well as the characteristics of the individual amine types. The data in these curves represent the concentration of acid gas in the liquid phase as moles of acid gas per mole of amine (the mole-to mole representation that we mentioned earlier).

The value of these data varies with the partial pressure of the acid gas, tempera-

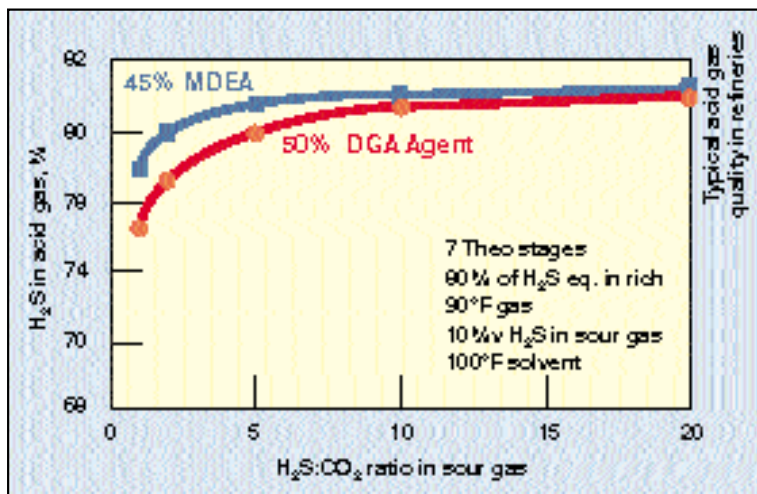
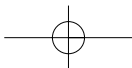
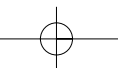


Figure 2 Acid gas quality from simulation results





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Solvent	DEA	MDEA
Equilibrium loading (mole/mole)	0.69	0.52
80% of Equilibrium (mole/mole)	0.55	0.42

Table 3

ture, type of amine, and amine concentration. When plants are designed, typically the maximum loading guidelines are set or represented as an approach to the equilibrium set by the VLE data. For example, some engineering companies and operating companies will specify that the plant will be designed with a maximum loading of 80 per cent of equilibrium. This means that they will set the design around the process conditions to load the solvent to 80 per cent of the value of the equilibrium set by the VLE data.

While this may sound confusing, these values are quite easily calculated with computer simulation models. Once again it is critical to design the plant based on these data versus a concrete mole-to-mole loading, since it will vary from application to application and will also vary by amine type. The concept of per cent of equilibrium loading is well illustrated in the following example: 2 molar MDEA and DEA will be compared at an H<sub>2</sub>S partial pressure of 20kPa at 20°C in the absence of CO<sub>2</sub> (Table 3).

This example shows that a quick check of available curves indicates that percent of equilibrium shows a dramatic difference between these two amines at similar conditions.

Amine suppliers have published that amines may be loaded to an average of 0.475 (mole/mole) in refinery service, but this example shows that under certain circumstances the mole-to-mole loading guideline, set as an absolute, gives a solvent loading above the recommended 80 per cent of equilibrium. Under these conditions the 0.475 mole/mole loading target is well within the equilibrium guideline for DEA, while the target is outside the guideline for MDEA.

Therefore, instead of setting an arbitrary rich loading on a mole-to-mole basis, the maximum rich loading needs to be set as a percent of equilibrium and then translated back to a mole-to-mole basis for monitoring purposes.

CO<sub>2</sub> slip

The literature published by some of the amine suppliers has claimed benefit to the utilisation of MDEA in refinery main system service due to its ability to slip

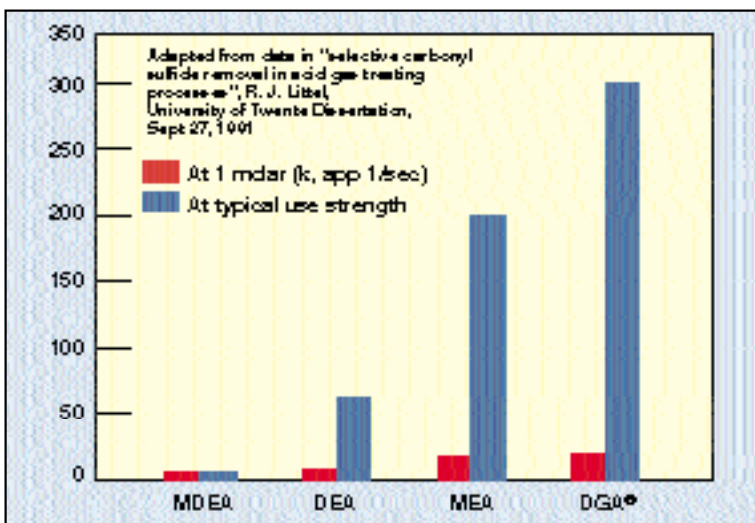


Figure 3 Pseudo-first order rate constant for COS at room temperature

CO<sub>2</sub>. This benefit is reported to increase the capacity of the main amine system and helps unload the front end of the sulphur plant. While MDEA is a tertiary amine, does not react directly with CO<sub>2</sub>, and provides excellent slip characteristics in tail-gas treater and gas plant service, the benefits of this characteristic have not proven itself in refinery main system service. Actual measured produced acid gas from various refinery main amine systems and third party computer simulations show that there is very little differentiation in acid gas quality to the sulphur plant between the various amines, as shown in Figure 1 and Figure 2 (on previous page).

These figures show that an amine conversion for CO<sub>2</sub> slip to improve the capacity of the amine system or to improve the capacity of the sulphur plant has very lit-

tle promise. The money spent on the study and conversion of the amine plant in these cases would be better spent on study and implementation of proven and emerging technologies to de-bottleneck existing sulphur plants.

Another important aspect of considering a solvent for CO<sub>2</sub> slip is the CO<sub>2</sub> specification that needs to be met in the treated gas. Some refineries sell part of their treated gas to chemical plants as a feedstock and removal of CO<sub>2</sub> to a particular level is often required in these cases. Some gas and many liquid treated products from the amine plants are also further treated with once through or regenerative caustic systems. CO<sub>2</sub> left in these product streams will increase the use of caustic or will increase the size of the regenerative caustic system employed.

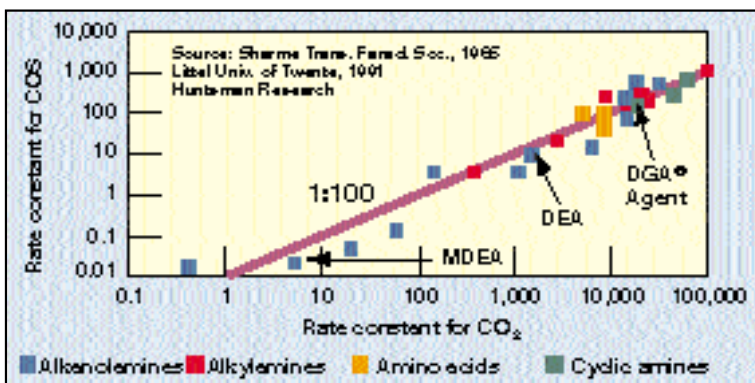
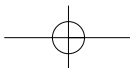


Figure 4 COS and CO<sub>2</sub>: Reaction rate constants with amines



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	Moles	Percent of total
Solvent, moles	4	11
Gas loading, moles	2	5.6
Water, moles	30	83.4
Total, moles	36	100

Table 4

Trace sulphur

The removal of COS is very important in refinery applications when the crude slate is sour and conversion units are in the refinery scheme (FCC and coking). With tougher clean air regulations being constantly implemented, trace sulphur removal is a key component in new unit design, and has also been the driver in some amine conversions.

Figure 3 shows the relative reaction rates of the various amines with COS. Reaction of COS with amines closely follows the kinetics of CO<sub>2</sub> for the various amines as is shown in Figure 4.

These data show the effectiveness of the various gas treating amines in the removal of COS.

COS is often overlooked in some refinery gas treating evaluations, and later we will look at a case study where this issue essentially drove the amine selection for the process. It is also important to remember this issue when reviewing amine supplier information that often tries to drive conversions to tertiary amines. These amines, specifically MDEA is not effective at removing COS as shown in the reaction rate kinetic data and the fact that COS removal kinetics are closely related to CO<sub>2</sub> removal.

Energy consumption

The industry has tried to use energy consumption as a selling point for MDEA based on the heats of reaction compared to the other amines. While the differences

in heats of reactions may be as much as 15 to 30 per cent, the energy required reversing heat of reaction is rather small when compared to the amount of heat required to raise the bulk solution temperature in the regenerator.

For example, if we look at a typical 4 molar gas treating solution with 0.5 mole-to-mole loading (for ease of calculation, the solution will contain 4 moles of amine, and 2 moles of acid gas loading). The balance of the solution will be water and will equate to about 30 moles. Table 4 shows the relative amount of each component when compared to the total.

This table shows that the heat of reaction associated with the acid gas pick up is 5.6 per cent of the total solution on a molar basis, so the effect of the relative heat of reactions and its effect of the regeneration energy requirements will be minimal and is largely offset by the water content. The data presented here shows that from a fundamental standpoint amine type plays a minor role in the energy requirements of an amine system and also shows that optimisation of circulation rate (maximising the potency of each unit volume circulated) is the key to energy optimisation.

This point is further stressed by actual data taken from a multitude of gas treating plants shown in Figure 5. These data show that there is very little difference in regeneration heat requirements for the various gas treating solvents, which validates the earlier discussion based on fundamentals.

In order to appropriately interpret the graph in this figure, remember to compare the steam consumption as a function of the actual amine strength on a molar basis; meaning that if a 3.5 molar solution is required as the capacity, look at the steam consumption for the various amines in that range and then verify that it is acceptable amine strength.

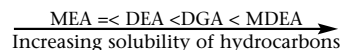
It is also important to note that while energy consumption may be an issue in offshore and remote gas plant operations, many refiners are venting low-pressure steam and energy savings typically do not factor into amine selection.

Another aspect to evaluate surrounding this issue is the fact that if the plant is fully optimised from an energy standpoint, it may not be able to handle upsets and changes in composition common in refinery primary treating systems. The Amine Best Practices group has also stated that those plants surveyed with the highest energy consumption were also the plants with the least amount of off-spec product incidents [Scott B, ABPG cost survey update; 1997 Brimstone Sulfur Recovery Symposium].

Hydrocarbon solubility

Some data have been published on hydrocarbon solubility and the various gas treating solvents. The only thing consistent with them thus far has been the fact that they did not use consistent reporting methods, and often based conclusions on word of mouth [Plaumann D, Stewart E, Kuroda R; Performance of specialty amines in gas processing; *Petroleum Technology Quarterly*, Summer 1999]. However, recently good data was published on hydrocarbon solubility in gas treating amines [Critchfield J et al, Solubility of hydrocarbons in aqueous solutions of gas treating amines; 2001 Laurance Reid Gas Conditioning Conference].

The data does summarise hydrocarbon solubility as the following:



The reason why this recent data is considered and listed here is due to the fact that this is the first time that the hydrocarbon solubility work was completed for the whole range of amines and amine strengths that encompassed typical use strengths. These data also directly measured the solubility via a well-respected third party laboratory, reported the results on a consistent basis, and did not report any data based on word of mouth.

While hydrocarbon solubility in the various amines has not always been factored, or factored well, in solvent selection or solvent conversion studies, it needs at least some review. Changes in solubility may not affect plant operations greatly, but flash gas rate changes and sulphur plant pressure drop may need to be monitored if switching amines from one end of the hydrocarbon solubility spectrum to the other (MEA to MDEA for example).

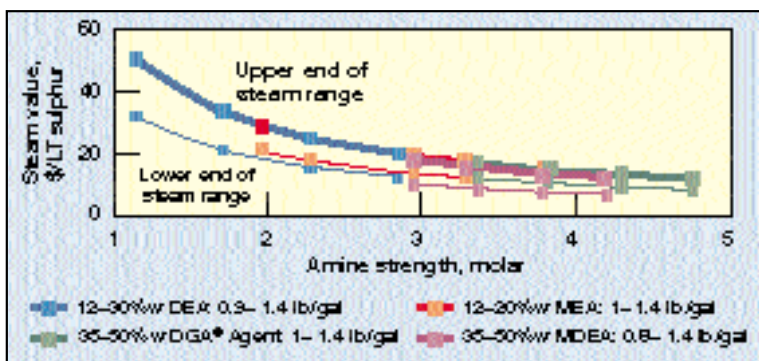
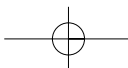


Figure 5 Steam consumption in refinery treating at maximum m/m load



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**Common contaminants and degradation products: solvent quality guidelines**

<b>MEA</b>	
Free amine (alkalinity)	20 wt% solution max
Water	70 wt% solution min
<b>HSS anions reporting basis**</b>	
(1) Expressed as wt% of solution	<1.2 wt% solution - or
(2) Expressed as wt% amine	<2.5 Expressed as wt% as MEA - or
(3) Expressed as percent amine capacity	<8.0 Percent amine capacity
Formamides (MEAF)	<3.0 wt% solution
HEED	<0.5 wt% solution
HEEU	<1.0 wt% solution
<b>DGA</b>	
Free amine (alkalinity)	50 wt% solution max
Water	40 wt% solution min
<b>HSS anions reporting basis**</b>	
(1) Expressed as wt% of solution	<1.2 wt% solution - or
(2) Expressed as wt% amine	<2.5 Expressed as wt% as DGA - or
(3) Expressed as percent amine capacity	<8.0 Percent amine capacity
Formamides (DGAF)	<3.0 wt% solution
BHEEU	<6.0 wt% solution
<b>DEA</b>	
Free amine (alkalinity)	30 wt% solution max
Water	60 wt% solution min
<b>HSS anions reporting basis**</b>	
(1) Expressed as wt% of solution	<1.2 wt% solution - or
(2) Expressed as wt% amine	<2.5 Expressed as wt% as DEA - or
(3) Expressed as percent amine capacity	<8.0 Percent amine capacity
Formamides (DEAF)	<3.0 wt% solution
THEED	<1.5 wt% solution
Bicine	<1.0 wt% solution
<b>MDEA</b>	
Free amine (alkalinity)	50 wt% solution max
Water	40 wt% solution min
<b>HSS anions reporting basis**</b>	
(1) Expressed as wt% of solution	<1.2 wt% solution - or
(2) Expressed as wt% amine	<2.5 Expressed as wt% as MDEA - or
(3) Expressed as percent amine capacity	<8.0 Percent amine capacity
MDEA fragments	<2.5 wt% solution
Bicine	<0.4 wt% solution

\*\*Since there are three bases in common use for reporting HSS anion levels, guidelines are provided for all three reporting bases.

**Hydrocarbon handling**

Hydrocarbon handling and solubility in the amine plant greatly affects the performance of the upstream sulphur plant. If hydrocarbons carryover from the amine plant to the sulphur plant, oxygen demand will increase and the potential exists to "soot up" the first converter bed.

If the upset is large enough, the increase in pressure drop or a drop in bed conversion may bring the sulphur plant down for a catalyst change out. Therefore, hydrocarbons need to be handled in the amine plant with proper flash drum size, design and operation. The flash drum needs to be designed as a three-phase sep-

arator as opposed to single baffle designs that were employed in early treating plants.

The flash drum is the best and only way to handle hydrocarbons in the amine since the vessel sees the whole flow of the stream and can effectively dispense the hydrocarbons continuously until the hydrocarbon ingress is brought under control. There have been efforts to use carbon as a way to remove hydrocarbons from the amine solution but this has proven to be inefficient. While the carbon does effectively remove the hydrocarbons from the amine solution it is quite expensive due to its limited capacity.

Carbon filtration was employed to remove small amounts of foam promoters from the amine solution and this has proven effective and is the basic fundamental reason to employ carbon filtration.

**Degradation/quality control**

Understanding the nature of degradation specific to each amine type and the effectiveness of available reclaiming technology on removing these compounds is also critical. The Amine Best Practices Group has stated that corrosion is the biggest cost element in amine plant operations, and proper solvent quality control is one way to control this cost.

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, these HSS anions may often 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 [Haws R and Jenkins J, Contaminant reporting in amine gas treating service; 2000 Brimstone Sulfur Recovery Symp].

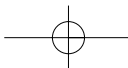
The total level of contaminants and degradation products in the solution may be referred to as the residue of the solution. The residue of the solution is the amount of material that is generally not considered part of a healthy gas treating solution, meaning anything that is not free (active) amine or water. This residue, as the equation below shows, is easy to calculate and encompasses all of the contaminants and degradation products present in the sample:

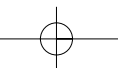
$$\text{wt\% residue} = 100 - \text{wt\% free amine (FA)} - \text{wt\% water}$$

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:** 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.

**Degradation products:** 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.





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**Common contaminants and degradation compounds: removal by reclaiming type**

<b>MEA</b>	
Control of HSS	All
Control of MEAF (slipstream 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
<b>DGA</b>	
Control of HSS	All
Control of DGAF (slipstream processing)	All
Control of DGAF (batch processing)	Vacuum distillation only
Control of BHEEU	Vacuum distillation only
Control of polymeric material	Vacuum distillation only
<b>DEA</b>	
Control of HSS	All
Control of DEAF (slipstream 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
<b>MDEA</b>	
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

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 optimised 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.

The adjoining panel carries a list of the most common contaminants and degradation products and recommended guidelines for total solvent quality control for the amines most commonly used in refinery treating systems.

Since it was stated earlier that corrosion is the biggest cost element associated with amine system operations, it is important to understand how the contaminants and degradation products listed above affect the solution from a corrosion or physical property standpoint. Care must also be taken when choosing a reclaiming technology to control these contaminants and degradation products since the available technologies do not all remove the same types of materials from the solution.

A list of the common contaminants and degradation compounds for the various amines used are listed in the panel on the next page, along with the effectiveness of the various reclaiming technologies on removing them.

*MDEA contamination/degradation:* Special considerations based on whether

generic or formulated. One aspect of MDEA that may be cause for concern is due to the fact that since it is a tertiary amine it does not form formamides in the presence of formates. The primary and secondary amines in the presence of formates under go hydrolysis where the amine formate HSS forms a formamide [Koike et al, N-formyl-diethanolamine: a new artefact in diethanolamine solutions; *Chemistry & Industry*, 1987].

This compound is not considered corrosive and effectively acts as a way to "hide" some of the corrosive formate anions in solution. This may be one of the main reasons that MDEA is just as corrosive in refinery treating systems despite early claims that its corrosion rates would be much lower than those for the primary and secondary amines.

**Case study**

While many of the papers published lately concerning amine selection or amine conversions have focused on the utilisation of MDEA over the "older generic amines", there are many recent cases where these "older generic amines" have been the best and, even perhaps, the only choice for recent new plant design.

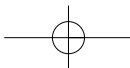
**MEA – refinery service**

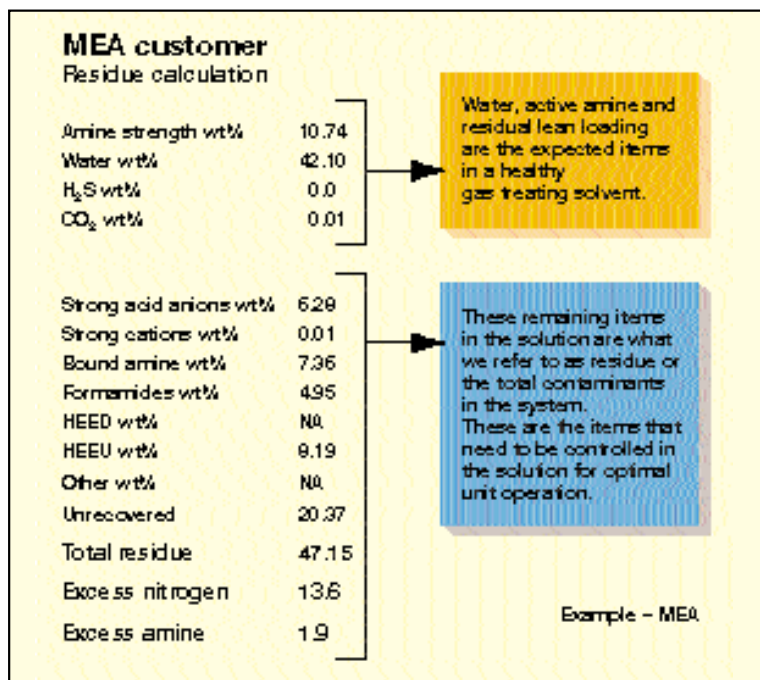
A plant operator selected MEA for a relatively new refinery primary amine treating system for specific reasons. The gas being treated in this unit had high levels of COS, so MEA was selected due to its excellent reaction rate kinetics with COS. The gas being treated also had variable levels of oxygen, so MEA was also 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. Based on this information, it may be seen that most if not all of the fundamentals were considered from performance of the solvent to understanding the need for solvent quality control to ensure reliability and efficiency.

When this unit was started up it performed 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, gas rates dropped since there were some fouling issues surrounding the process equipment. Some equipment changes were made and fouling issues were somewhat minimised, but were still a concern.

Since the plant was using HSS anions as





a control point for its reclaimer design and operations, not much else was measured in the solution on a frequent basis. It was decided 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, with 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.

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

The analytical results, and residue calculation and amine and nitrogen balances, all showed that HSS was 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 has a high boiling point and may be controlled in a conventional thermal reclaimer, the undersized reclaimer was not able to remove it adequately since this compound was not considered during the design of the unit.

While HEEU should have been considered in the design of the unit, it was not due to the fact that the amine suppliers were hesitant to supply technical service to the design of a new MEA plant, and most of the amine suppliers do not even analyse for HEEU. 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 (viscosity, mass transfer rates, boiling point) and the reaction rates of the degradation products increased since they are dehydration reactions catalysed by heat. This exacerbated unit operations problems and the degradation of the solvent over time. Since the nitrogen imbalance was very high, there were also increased concerns over the fouling potential of the solvent due to polymeric material. Through the use of vacuum distillation technology and the dumping and replacement of the solvent during plant outages, the plant has restored the solution quality to an acceptable level and has efficient and reli-

able operations.

This case shows that even when a detailed evaluation is completed for new plant design, it is possible to miss a fundamental issue that will effect the operation of the plant. While often not considered in full detail, more often than not it is very important to understand the total level of contaminants and degradation products that may form 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.

### Conclusion

When dealing with the capacity, efficiency and reliability of the amine plant and its effect on the upstream sulphur plant it is important to look at and understand the fundamentals of the amine solution. When the fundamentals are studied and understood, then the salesmanship or marketing of the amine supplier or service company cannot lead the plant owner in the wrong direction. When thinking of these fundamentals, think of the following key points:

#### Capacity

1. Capacity – study on a molar basis.
2. Maximum loading – study on a per cent of equilibrium basis.

#### Efficiency

1. CO<sub>2</sub> slip – generally unachievable in refining systems.
2. Trace sulphur removal – often overlooked but becoming very important.
3. Energy savings – function of circulation rate, not amine type.

#### Reliability

1. Hydrocarbon solubility – understand where the solvents rank.
2. Hydrocarbon handling – flash drum handles full flow effectively and continuously.
3. Solvent quality – key for reliability, is solvent specific.
4. Solvent quality control – understand features and benefits of reclaiming options.

The figures in this article are by courtesy of Jenkins J L, from his paper, Use amine features to guide selection for refinery application; Brimstone Sulfur Recovery Symposium, 1999.

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