



# CCR Technologies Inc.

## Technical Bulletin

### MDEA Reclaiming In TGTU

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#### **MDEA**

Methyl Diethanolamine (MDEA) was introduced to the industry as one of the first amines used extensively in tail gas treating (TGTU) service. MDEA is one of the solvents of choice due to its ability to slip CO<sub>2</sub> while still meeting stringent H<sub>2</sub>S specifications. While generic MDEA is often employed, many suppliers offer formulated solvents to enhance the performance of the amine. While MDEA was initially thought not to degrade, recently it has been shown that it often will degrade in TGTU service and efforts are being focused on improved reclaiming options for solvent quality control.<sup>(1)</sup> There are currently a few commercially available reclaiming alternatives in the industry, and it is important to understand fully the chemistry involved in amine systems, and how each reclaiming technology affects these chemical compounds.

#### **Heat Stable Salts**

Heat Stable Salts (HSS) are acid anions with a stronger acid strength than the acid gases that are removed from the process gas. These anions bind to the usable amine (in this case MDEA), making the MDEA unavailable for acid gas absorption. The industry has agreed that these HSS anions increase the corrosive nature of the solvent, and that they must be controlled to insure unit reliability.<sup>(2)</sup> All available amine-reclaiming options are able to remove HSS anions in batch mode or while processing a slipstream of the circulating solution.

While removal of HSS often plays a critical role in optimizing MDEA system performance, it is important to remember that HSS anions are not the only contaminant that must be removed. Products formed from the degradation of the MDEA molecule may also need to be removed from the solution for optimum unit operations and reliability.

#### **DEA**

In the presence of certain chemical compounds or intermediates, it is possible to degrade or break down the MDEA molecule to simpler amines. Diethanolamine (DEA) is one of the simpler amines that may be formed from MDEA. It is important to monitor the level of DEA in the circulating MDEA system due to the concerns associated with DEA and selectivity. Since DEA is a secondary amine, it will react directly with CO<sub>2</sub> and will begin to affect the performance of the MDEA solvent. Ion Exchange and electro dialysis are not able to remove non-ionic compounds, so amines cannot be separated from each other. Vacuum distillation is able to remove certain amine compounds from each other since it is a distillation process.

#### **MMEA**

Monomethylethanolamine (MMEA) is another of the simpler amines that may be formed from MDEA degradation. It is important to monitor the level of MMEA in the circulating MDEA system due to the concerns associated with MMEA and selectivity. Since MMEA is a secondary amine, it will react directly with CO<sub>2</sub> and will begin to affect the performance of the MDEA solvent. Ion Exchange and electro dialysis are not able to remove non-ionic compounds, so amines cannot be separated from each other. Vacuum distillation is able to remove certain amine compounds from each other since it is a distillation process.

#### **Bicine**

Bis- (hydroxyethyl) glycine (Bicine) is a degradation product formed in the presence of DEA and unstable chemical intermediates. It is considered corrosive and may be removed by vacuum distillation. It has been shown that ion exchange is not very effective in removing this compound since it is dipolar or a zwitterion (essentially meaning it may behave as an anion or a cation depending on the pH of the solution).<sup>(3)</sup>

#### **The Importance of Total Solvent Quality Control**

While HSS anions (and to some extent strong base cations such as sodium or potassium) have received much industry attention due to their adverse affects on amine solvent quality, it is important to understand there are many other possible contaminants in an amine system. The accumulation of all of these contaminants adversely

affects the physical properties of the solvent. At constant amine strength, the accumulation of contaminants essentially “backs out” the corresponding percentage of water from the circulating solution. Water content probably has the greatest effect on the physical properties of the solvent, such as viscosity. A higher viscosity will lower mass transfer rates and decrease acid gas removal efficiency. A higher viscosity may increase amine losses in liquid treating service. While these are only two examples of the effects of a change in physical properties of the circulating solution, numerous other examples exist. Whenever a plant is not running optimally, physical property changes should be considered as a possible contributor to the problem.

### Customer TGTU Example – Before and After Vacuum Distillation

This table contains data from a third party laboratory for an actual vacuum distillation-reclaiming job completed for a customer on their TGTU specialty MDEA based solvent. This customer experienced corrosion problems that they were associating with the condition of the solvent for some months prior to reclaiming the solution. However, the actual main driver in the decision to improve the solvent quality was the fact that the plant had

	Before	After	Removal
<b>Amine Strength wt%</b>	35.00	35.00	
<b>Strong Acid Anions wt%</b>	2.14	0.17	91.86%
<b>Bicine wt%</b>	0.55	0.10	81.40%
<b>MDEA Fragments</b>			
<b>DEA wt%</b>	1.76	1.02	41.87%
<b>C2+ Acids wt%</b>	0.17	0.03	84.83%
<b>Bicine wt%</b>	0.55	0.10	81.40%
<b>Total Fragments</b>	2.48	1.15	53.63%
<b>Total Residue</b>	8.01	1.12	85.99%

difficulty achieving treat gas specifications with the accumulation of the MDEA fragments during summertime operating conditions.

The data shows that the removal of the items causing a concern from a corrosion standpoint, the strong acid anions (or HSS) and the Bicine, was very efficient. The data also shows that the removal of the MDEA Fragments, which were causing the summertime operation concerns, was also rather effective. Improvements in the removal of

these MDEA Fragments have been accomplished with a newer version of mobile vacuum distillation reclaiming units that have a second distillation tower. It is important to note that this customer did not monitor MMEA (one of the MDEA Fragments) during this job due to the fact that they see it “weather” out of the system, consistent with the industry data.<sup>(1)</sup>

### Summary

When evaluating merchant reclaiming options remember that HSS anions are not the only issue, and may not even be the biggest issue. Please see the attached to help you in your evaluations.

### REFERENCES

1. Critchfield, J. E. and J. L. Jenkins, “Evidence of MDEA Degradation in Tail Gas Treating Plants”, Petroleum Technology Quarterly, Spring 1999.
2. Rooney, P. C., T. R. Bacon and M. S. Dupart, “Effect of Heat Stable Salts on MDEA Solution Corrosivity”, Hydrocarbon Processing, March 1996.
3. Howard, M. and A. Sargent, “Operating Experiences at Duke Energy Field Services Wilcox Plant with Oxygen Contamination and Amine Degradation”, Proceedings of the 2001 Laurance Reid Gas Conditioning Conference.

For more information contact CCR Technologies Inc. in Houston at 281-988-5800, or visit us at [www.reclaim.com](http://www.reclaim.com).

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## MDEA Degradation In TGTU Service

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### ❖ Main Contaminants

- HSS – Heat Stable Salts
  - Potentially Corrosive (Contaminant)
- Secondary Amines (MMEA & DEA)
  - May Adversely Affect Unit Operations
    - Potentially Corrosive – Partial Pressure Of Acid Gas In Hot Lean
- Bicine & HE-Sarcosine
  - Potentially Corrosive (Degradation)
- Polymeric Material
  - Relatively Benign (Degradation)



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## Solvent Quality Management MDEA - TGTU

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### ❖ Merchant Reclaiming Options

- Vacuum Distillation, Ion Exchange, Electrodialysis
  - Control of \_\_\_\_\_ All
  - Control of MDEA
    - Control of C2+ Acids: All
    - Control of Bicine: Vacuum Dist.  
Ion Exchange-Partial
    - Control of MMEA/DEA: Vacuum Dist. Only
  - Control of Polymeric Vacuum Dist. Only

### ❖ Best Efficiency – Batch

- Batch vs. Side Stream (PFR vs. CSTR)  
Plug Flow Reactor vs. Continuous Stirred Tank Reactor



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