CCR Technologies Inc.
Technical Bulletin
Mixed Amines In Gas Treating Service

Current Challenges

A recent trend in the gas treating industry has been to employ higher capacity solvents and solvent blends to meet the challenges of stringent environmental regulations, as well as the desire to de-bottleneck processing plants while minimizing capital expenditures. The implementation of predominantly MDEA blends has lead to the need for increased awareness of the issues surrounding solvent quality and performance. The degradation of both the MDEA *and the formulating additive*, as well as the interaction of the two groups of degradation products, require that diligent efforts take place to understand the characteristics of the circulating solution.

"Unintentional" amine blends, formed from the on-line conversion of one gas treating solution to another (while the system continues to operate), have also lead to these same issues surrounding degradation interactions. Unintentional amine blends occur because of difficulty in removing all of the old amine when the new amine is added during an on-line conversion.

Amine Blends and Additive Degradation

There are a number of amine blends predominantly based on MDEA, many of which are considered proprietary while others are not. When amine blends are employed, it is critical to understand how *degradation of the additive* will affect solvent quality and corrosion. When an amine blend is considered proprietary, it is difficult to list degradation products due to the potential disclosure of formulation. However, if requested of amine suppliers it may be possible to get these compounds listed as a *type of compound* based from component X. For example, MDEA/DEA blends have been employed in gas treating plants, and information in the published literature specifically covers some of the degradation associated with these amines. Tris-hydroxyethyl ethylenediamine (THEED) is a degradation product of DEA that has been found in these blends.[1,2] THEED may be characterized as an ethylenediamine derivative *of the additive* (DEA) in these blends. If a proprietary additive has a similar degradation product, it could simply be called the ethylaminediamine derivative of compound X. This example shows a type of reporting that allows the gas treating plant operator to understand the nature of the solution, without divulging the exact proprietary additive.

Amine Blend Reclaiming

When choosing a reclaiming option, it is critical to understand any degradation that has taken place and how effective each option will be in removing these compounds. Recently we reclaimed an MDEA blend and the customer had three major concerns. The first concern arose from the fact that they wanted to make sure that the additive (DEA) would not be removed from the blend. We determined that this could be achieved by simply adjusting the operating conditions of the vacuum distillation process. The second concern had to do with plant corrosion in spite of a low Heat Stable Salts (HSS) content. The analysis of the sample showed a high level of THEED and plant personnel suspected that this was causing some of the corrosion. The third concern was to insure that vacuum distillation could effectively remove THEED from the solution. The actual results of the side stream reclaiming job are shown in Table 1.

Table 1

	Start	**End**
Amine Strength, wt%	31.9	36.4
HSS, wt%	0.02	0.0*
THEED, wt%	10.6	0.08

*Below Detection Limits

The data in Table 1 shows that vacuum distillation was able to lower the THEED considerably by reclaiming the circulation solution while the system remained online. The data also shows that HSS were not the main concern with the solvent quality of the circulating solution. Degradation of the MDEA *additive* was the main issue in this plant and was effectively resolved while maintaining the integrity of the amine blend.

Amine Conversions

When a gas processing plant decides to do an amine conversion (switch from MEA to MDEA for example), the plant can either change the solvent out when the unit is down (dump and replace), or attempt to change solvent while the system is operating. Due to the desire to maximize the time between plant outages, we have seen that more plant operators are electing to do the conversion when the system is operating. Performing an amine conversion while the plant remains on-line may be accomplished three ways: (1) The plant operator may simply start adding new amine as make up and let the old solution "weather out" over time, (2) The plant operator may reduce circulating inventory as much as feasible and then introduce new amine into solution in bulk quantity, and (3) The most preferable but most complex on-line conversion can be done by the addition of new solvent while simultaneously drawing off the old solvent. Regardless of which method is employed, when the solution has been changed out there is still some amount of the old amine left in solution with the new amine. In some cases concerns arise over the interaction of degradation products from the two types of amines, and in other cases plants have found it imperative to remove the original amine from the new due to physical property differences.

Recently a customer had a substantial amount of MEA in their MDEA as a result of an on-line conversion from MEA to MDEA. Reducing the MEA inventory substantially and adding a bulk amount of MDEA achieved the conversion of the solvent. The customer had very serious concerns because the plant operations had been unstable since the conversion took place. The amine supplier in this case attributed the operational problems to the MEA left in the MDEA solution, which ultimately affected CO2 slip and the heat of reaction of the solution. It was recommended that the plant remove the MEA from the circulating solution. The plant operator contacted us and requested that we remove the MEA from the MDEA while simultaneously reducing the amount of HSS that accumulated in the solution. The results of the job are listed in Table 2. The data shows that the MEA was effectively removed below the target of 1.5 wt%, and the HSS in solution were reduced as well below the target of 1.5 wt%, and the HSS in solution were reduced as well below the target of 0.25 wt%.

Table 2

	Start	**End**
Amine Strength, wt%	44.2	46.1
MDEA, wt%	33.1	44.8
MEA, wt%	11.1	1.3
HSS, wt%	0.67	0.19

Word of Caution

When changing from one gas treating solution to another, it is imperative to understand the true nature of the fundamental differences between the solutions. More than once we have assisted a customer with concerns arising after an amine conversion has taken place. We have customers tell us that post conversion reviews have shown that the basic fundamentals of amine treating solution chemistry and performance were not adequately reviewed during the decision making process. As a result of this we urge caution and urge an understanding of the fundamentals so easily forgotten.

Summary

Since amine blends and amine conversions will be in integral part of the future in gas treating, it is important to understand the true solvent quality and physical property characteristics of the circulating solution in the plant. This is vital to enhancing the reliability, efficiency, and effectiveness of the treating plant.

For more information or to inquire about a *complete* sample analysis contact CCR Technologies Inc. in Houston at 281-988-5800, or visit us at www.reclaim.com.

References

1 Dupart, M. S., P. C. Rooney, and T.R. Bacon, "Comparison of Laboratory and Operating Plant Data of MDEA/DEA Blends", Proceedings of the 1999 Laurance Reid Gas Conditioning Conference.

2 Holub, P. E., J. E. Critchfield and W. Y. Su, "Amine Degradation Chemistry in CO_2 Service", Proceedings of the 1998 Laurance Reid Gas Conditioning Conference.