CCR Technologies Inc.
Technical Bulletin
DEA Reclaiming

DEA

Diethanolamine (DEA) was introduced to the industry as one of the first amines used extensively in gas treating service. DEA is very popular in refinery gas/liquid treating service and had many advantages over MEA due to the Amine Stress Corrosion Cracking (ASCC) concerns in the early units. DEA removes both H_2S and CO_2 and is somewhat reactive towards COS, all of which are of a concern in refinery combined treating systems. One disadvantage of DEA (say when compared to MEA) is the fact that due to its high boiling point, slipstream thermal reclaiming may not be employed. This has proven to be an issue in refinery service where HSS contamination and amine degradation have been issues.

Due to more stringent amine treating specifications, and due to efforts to minimize amine consumption, efforts are being focused on improved reclaiming options for solvent quality control. There are currently a few merchant-reclaiming alternatives in the industry, and it is important to understand fully the chemistry involved in amine systems, and how each merchant reclaiming technology affects these chemical compounds.

Heat Stable Salts

Heat Stable Salts (HSS) have received a lot of attention in the industry. HSS are acid anions with a stronger acid strength then the acid gases that are removed from the process gas. These anions bind to the usable amine (in this case DEA) and then therefore make the DEA unavailable for acid gas absorption. The industry has agreed that these HSS anions raise the corrosive nature of the solvent, and that they must be controlled to assure unit reliability. All available amine-reclaiming options are able to remove HSS anions in batch mode or while processing a slipstream of the circulating solution.

The industry has focused on this issue very much lately, but it is important to remember that HSS anions are not the only contaminants that must be removed.

Formamides

N-formyl amines (formamides) are generally found in gas treating solutions that are based on primary (MEA and DGA®) and secondary (DEA) amines. Under certain conditions primary and secondary amines react with the formic acid in solution (via dehydration) to form n-formyl amines. For the rest of the discussion we will focus only on n-formyl DEA (also called DEA-F).

The data from process solutions containing formate as a Heat Stable Salt (HSS) anion shows that there is an equilibrium relationship that exists between the amount of formate HSS in solution and the amount of DEA-F in solution. See the equation below.

$$\text{Formic Acid} \quad + \quad \text{DEA} \quad \Leftrightarrow \quad \text{DEA-F} \quad + \quad \text{Water}$$

Since the above equation represents equilibrium, it is then possible to also hydrolyze DEA-F back into DEA and formic acid. The heat and water content both present in the stripper of the amine unit will generate a new equilibrium if the balance of the equation is disturbed by removing one of the above components. If a slipstream of the circulating solution is processed while the amine unit is on line, it is then possible to remove a portion the DEA-F from solution *indirectly* by removing the formate anion and disturbing the above equilibrium. This removal mechanism takes place when ion exchange, electrodialysis, and vacuum distillation are used. On the other hand, the vacuum distillation process is able to remove both the formate anion, ***and*** the DEA-F *directly* from the circulating solution.

If the DEA solution is reclaimed in a batch mode (tank to tank) rather than processing an on-line slipstream, it necessary to understand what happens to the DEA-F in solution. If you use ion exchange or electrodialysis to remove the formate anion (since they both only remove ions), the DEA-F still remains in solution. The DEA-F remaining in the solution will "liberate" a formate anion to reestablish equilibrium when the solution is placed back in the circulating solution. On the other hand if you use vacuum distillation to process in a batch mode, the formate ***and*** the DEA-F will be removed since the process achieves complete removal on a per pass basis.

THEED

Tris-hydroxyethyl ethylenediamine (THEED) is a well-known degradation product of DEA from reactions with CO_2. There is a wealth of literature on the reaction mechanisms and the corrosive nature of THEED. While much of the literature has focused on DEA in CO_2 service only, THEED has been found in combined refinery systems treating H_2S and CO_2. While it may not be the main degradation product in refinery amine systems, it must be monitored and removed from the system due to its corrosive nature. Vacuum distillation is the only merchant reclaiming technology that is able to remove THEED.

Bis-HEP

Bis-hydroxyethyl piperazine (bis-HEP) is a well-known degradation product of DEA from reactions with CO_2. There is a wealth of literature on the reaction mechanisms of bis-HEP. While much of the literature has focused on DEA in CO_2 service only, bis-HEP has been found in combined refinery systems treating H_2S and CO_2. While bis-HEP is not considered corrosive and it does have some base strength, it needs to be removed from the circulating system to optimize water content and active amine levels.

MEA

In the presence certain chemical compounds or intermediates, it is possible to degrade or break down the DEA molecule to simpler amines. Monoethanolamine (MEA) is one of the simpler amines that may be formed from DEA. It is important to monitor the level of MEA in the circulating DEA system due to ASSC concerns associated with MEA. Ion Exchange and electrodialysis 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 degradation product formed in the presence of DEA and unstable chemical intermediates. It is considered corrosive and may be removed by vacuum distillation. We are not sure how effective ion exchange or electrodialysis may be 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).

Polymeric Material

Under certain high temperature conditions in the presence of HSS, it has generally been agreed upon that DEA forms high boiling point polymeric material. It is also possible that THEED may continue to degrade in the presence of CO_2 to form longer substituted ethlyenediamines, which may also then be characterized as a polymeric material. Vacuum distillation is the only merchant reclaiming technology that is able to remove THEED.

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 degradation products does adversely affect 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 affect 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 effects of a change in physical properties of the circulating solution, others must be considered when plants are not running optimally.

Summary

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

For more information contact CCR Technologies Inc. in Houston at 281-988-5800, or visit us at www.reclaim.com.

DEA Degradation In Refinery Service

- Main Contaminants
  - HSS – Heat Stable Salts
    - Potentially Corrosive (Contaminant)
  - DEA-F – nFormylDEA (Formamide)
    - Relatively Benign (Contaminant/Degradation)
  - THEED – tris-hydroxyethyl ethylenediamine
    - Potentially Corrosive (Degradation)
  - bis-HEP – bis-hydroxyethyl piperazine
    - Relatively Benign (Degradation)
  - MEA
    - ASCC Concerns (Degradation)
  - Bicine
    - Potentially Corrosive (Degradation)
  - Polymeric Material
    - Relatively Benign? (Degradation)

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Solvent Quality Management DEA

- Merchant Reclaiming Options
  - Vacuum Distillation, Ion Exchange, Electrodialysis
    - Control of HSS: All
    - Control of DEA-F (On-Line): All
    - Control of DEA-F (Batch): Vacuum Dist. Only
    - Control of THEED & bis-HEP: Vacuum Dist. Only
    - Control of MEA: Vacuum Dist. Only †
    - Control of Bicine: Vacuum Dist.
Ion Exchange - Partial
    - Control of Polymeric Material: Vacuum Dist. Only
- Best Efficiency – Batch
  - Batch vs. Side Stream (Plug Flow vs. CSTR)

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† Development Efforts Underway