CCR Technologies Inc.
Technical Bulletin
MEA Reclaiming

MEA

Monoethanolamine (MEA) was introduced to the industry as one of the first amines used extensively in gas treating service. MEA is very popular in refinery gas/liquid treating service and has many advantages that some of the newer amines introduced into the industry have not been able to match. MEA removes both H_2S and CO_2 and is very reactive towards COS, all of which are of concern in refinery combined treating systems. Another advantage of MEA is the fact that due to its low boiling point, slipstream thermal reclaiming may be employed. This has proven to be beneficial in refinery service where HSS accumulation and MEA degradation have been issues.

Due to more stringent disposal considerations for reclaimer bottoms and efforts to minimize amine consumption, there has been focus on improving reclaiming options. There are currently several alternatives to conventional thermal reclaimers used by refiners, and it is important to understand fully the chemistry involved in these 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 than the acid gases that are removed from the process gas. These anions bind to the usable amine (in this case MEA) making the MEA unavailable for acid gas absorption. The industry has agreed that these HSS anions also raise the corrosive nature of the solvent, so 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.

While the industry has focused heavily on this issue lately, it is important to remember that HSS anions are not the only contaminants that must be removed from solution.

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 MEA (also called MEA-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 MEA-F in solution. See the equation below.

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

Since the above equation represents equilibrium, it is then possible to also hydrolyze MEA-F back to MEA 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 unit is on line, it is then possible to remove a portion the MEA-F from solution *indirectly* by removing the formate anion and disturbing the above equilibrium. This removal mechanism takes place regardless of which reclaiming technology - ion exchange, electrodialysis, or vacuum distillation - is used. However, vacuum distillation is the only process able to directly remove both the formate anion ***and*** the MEA-F.

If the MEA solution is reclaimed in batch mode (tank to tank) rather than processing a slipstream of solution while on line, it necessary to understand what happens to the MEA-F in solution. If ion exchange or electrodialysis is employed to remove the formate anion (since these processes only remove ions), the MEA-F remains in solution. The remaining MEA-F will then "liberate" a formate anion to reestablish equilibrium when the treated solution is returned to the circulating solution. However, using vacuum distillation to process in a batch mode, the formate ***and*** the MEA-F will be removed since the process achieves complete removal on a per pass basis.

HEED

Hydroxyethylethylenediamine (HEED) is a well-known degradation product of MEA from reactions with CO_2. There is a wealth of literature on the reaction mechanisms and the corrosive nature of HEED. While much of the literature has focused on MEA in CO_2 service only, HEED 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 HEED.

HEEU

Hydroxyethylethyleneurea (HEEU) is a degradation product of MEA that is not that well known since most of the literature has focused on degradation in CO_2 service. HEEU is formed via the same reaction pathway as HEED when COS is present in the gas. COS is generally present in combined refinery treating systems where FCC, Coker and other cracking/conversion units are employed in the plant configuration. HEEU has been found to be one of the main degradation products in refinery amine systems. Vacuum distillation is the only merchant reclaiming technology that is able to remove HEED.

Polymeric Material

Under certain high temperature conditions in the presence of HSS, it has generally been agreed upon that MEA forms high boiling point polymeric material. It is also possible that HEED 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 these polymeric materials.

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 likely to be many other contaminants in an amine system. Degradation products reduce the activity of solution, but since they often titrate as amine, their presence may go undetected leaving a refiner to think the amine solution is stronger than it really is, creating an amine deficiency. As more amine is added to compensate for reduced solution activity, the physical properties of the solvent are affected by reducing the water content of 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 also 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 summary to help you in your evaluations.

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.

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MEA Contamination/Degradation In Refinery Service

- Main Contaminants
  - HSS – Heat Stable Salts
    - Potentially Corrosive (Contaminant)
  - MEA-F – nFormylMEA (Formamide)
    - Relatively Benign (Contaminant/Degradation)
  - HEED – hydroxyethyl ethylenediamine
    - Potentially Corrosive (Degradation)
  - HEEU – hydroxyethyl ethyleneurea
    - Relatively Benign (Degradation)
  - Polymeric Material
    - Relatively Benign? (Degradation)

Solvent Quality Management MEA

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

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