CCR Technologies Inc.
Technical Bulletin
Sample Analysis Program

CCR Provides A Detailed Analysis Program To The Industry

For a number of years the gas treating and refining industries have been focusing on Heat Stable Salts (HSS) contamination in amine service. As knowledge continues to improve in this area, amine system efficiencies are improved and turnaround cycles are minimized. However, two unfortunate states still exist in the industry: (1) analytical reporting for HSS is not consistent and is often times confusing to operators, and (2) HSS is only one of the major contaminants in a gas treating solution. A better understanding of the full range of contaminants and degradation products is essential to achieving total solvent quality. In response to the issue of maintaining total solvent quality control to minimize the corrosion potential in these systems and to increase efficiency and reliability, CCR is offering its existing analytical services to its customers and the rest of the industry.

Basis

There is a wealth of literature available in the industry on the corrosive nature and proper control targets for Heat Stable Salts (HSS). Unfortunately it is easy to be confused about measured levels and reporting terminology of these HSS anions. This confusion is compounded by the fact that comparing these measured values to proper control points may be difficult if they are not compared on a consistent basis. HSS are also generally only a part of the contaminants present in the gas treating solution so, it is important to understand the total level of contaminants and degradation products present in the processing solution. This is important for the operator to know because, as the level of contaminants and degradation products increase, the physical properties of the solution may change. As the physical properties of the solution change there may be the potential for increased operational issues, increased corrosion concerns, and an increase in degradation rates.

MDEA Customer

Analytical Results

Amine Type	MDEA	**Alternate Units/Notes**
Amine Strength wt%	30.50	
Water wt%	60.30	
H2S wt%	0.03	
CO2 wt%	0.00	
Strong Acid Anions wt%	5.33	
Strong Cations wt%	2.46	97 Percent Neutralization
Bound Amine wt%	0.41	Calculated
Formamides wt%	na	
THEED wt%	na	
bis-HEP wt%	na	
Bicine wt%	0.03	
Other wt%	na	
Percent Recovery	99.06	
Organic Acids		
Formate ppm	37411	
Acetate ppm	2026	
Oxalate ppm	50	
Lactate ppm	246	
Glycolate ppm	nd	
Propionate ppm	nd	
Butyrate ppm	na	
Total ppm	39733	
Inorganic Acids		
Chloride ppm	214	
Sulfate ppm	285	
Sulfite ppm	nd	
Thiosulfate ppm	485	
Thiocyanate ppm	12533	
Phosphate ppm	na	
Total ppm	13517	
Total HSS Anions ppm	53250	
Total HSS Anions wt%	5.33	Three different ways to express the value of the HSS Anions.
HSS as wt% Amine	13.13	
HSS as Percent Amine Capacity	43.05	

Example - MDEA

At CCR we do what we call a *complete amine analysis* so that we may fully understand the total level of contaminants in the gas treating solution. We will measure and list general items that should be accounted for in any gas treating solution, as well as measure and list specific degradation products for specific amine types. We will also show a full material balance, a nitrogen balance, and an amine balance to see how much of the sample we have accounted for, and to illustrate is an even more detailed analysis is warranted. We do this since not all solvent analysis are the same and also because the cost associated with a more detailed analysis often needs justification.

Example – MDEA In Refinery Service

This plant operator utilizes MDEA in a refinery primary amine treating system and generally experiences excellent operational

reliability. This plant started to experience some fouling and corrosion concerns and were puzzled since they thought that their HSS levels were fairly low. We decided to look at a *complete sample analysis* to see if this would show us anything. This customer thought that they had a HSS level of anywhere between 0.5 and 1 percent as MDEA. The sample analysis showed that the bound amine (or HSAS) was rather low at 0.41 percent. However the HSS anion analysis showed that the level of HSS anions expressed as MDEA were at a level of 13.13 percent. The analysis showed that there was a high level of strong cations, which effectively neutralized 97 percent of the HSS anions as a sodium salt, (refer to equation number 4). It was speculated that the high level of sodium salts associated with the HSS anions was contributing to the fouling problem. This high HSS anion level could also be accelerating corrosion rates in the system, with the resulting corrosion by-products contributing to the fouling of the unit.

MDEA Customer

Residue Calculation

Amine Strength wt%	30.50
Water wt%	60.30
H2S wt%	0.03
CO2 wt%	0.00

Water, Active Amine, and Residual Lean Loading are the expected items in a healthy gas treating solvent.

Strong Acid Anions wt%	5.33
Strong Cations wt%	2.46
Bound Amine wt%	0.41
Formamides wt%	na
THEED wt%	na
bis-HEP wt%	na
Bicine wt%	0.03
Other wt%	na
Un-Recovered	0.94
Total Residue	**9.17**

These remaining items in the solution are what we refer to as residue or the total contaminants in the system. These are the items that need to be controlled in the solution for optimal unit operation.

MDEA Fragments	
DEA wt%	0.37
MMEA wt%	0.20
C2+ Acids wt%	0.23
Bicine wt%	0.03
Total	**0.83**
Excess Nitrogen	**3.1**
Excess Amine	**1.2**

Example - MDEA

The sample analysis showed that there was also some excess nitrogen in the sample, which could also potentially be causing some of the fouling problems. A recommendation was made to improve the solvent quality by lowering the level of strong cations, HSS anions and the degradation products showing up as excess nitrogen.

Summary

We can provide a technical bulletin that covers industry recognized guidelines for proper solvent quality. When trying to troubleshoot operational issues at a plant, a *complete sample analysis* is a very valuable tool. Trending of analytical data is also very helpful for noting changes in operation and measured corrosion rates. The material presented here is intended as an aid in understanding the analysis and the meaning of the results. It is important when evaluating your results versus industry standards to use" voting" type logic. If one parameter is high immediate action may not be necessary, rather it is helpful to look at all of the solution parameters to see how they all compare to industry guidelines. While industry guidelines for solvent quality control are very helpful, it is important to understand that measurements within acceptable ranges do not guarantee reliable operation, nor do measurements outside of acceptable ranges guarantee imminent problems. Rather, these guidelines are simply that: guidelines for monitoring and evaluation of your system. Remember that if you are considering reclaiming you need to understand the characteristic of the residue and how each reclaiming technology removes these compounds. This will ensure that you are not disappointed with the final solvent quality and are not surprised by the final cost of the job. We can also provide a technical bulletin that covers a summary of common contaminants for each amine type and merchant reclaiming effectiveness at removing these compounds.

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.