



# Reclamation Q & A

The following are answers to typical questions raised by prospective customers about contamination and on-site reclamation.

### **QUESTION 1**

#### **Who is ChemGroup Services and what services do they provide?**

Chem Group Services offers an economical, hassle-free alternative to on-site reclamation services. We provide professional, custom distillation services, high quality products and reclamation projects that are all-inclusive and transparent. Chemical maintenance programs can be developed to maintain improved amine hygiene long term.

### **QUESTION 2**

#### **Why reclaim our amine solution?**

Contamination is the major cause of operating problems in amine systems. Foaming, corrosion and degradation can severely impair the amine's ability to absorb acid gases or cause mechanical failures. Contaminants can have a significant affect on the reliability and cost of the amine unit operation, which are measured by: H<sub>2</sub>S exceedences; upsets to other processing units; amine losses; equipment maintenance; filter changeouts and regenerator heat input.

In order to optimize the amine unit it is necessary to have clean, workable amine. Operators of *clean amine* solutions experience the following:

- Treated gas consistently on spec
- High quality acid gas to SRU with no upsets or trips caused to the sulfur plant
- Low amine losses
- Low corrosion
- High reliability - mechanical and processing
- No unscheduled downtime
- Operating goals met at minimum cost

### **QUESTION 3**

What indicators tell me that reclamation needs to be considered?

#### 1) Operating Problems

- Foaming
- Fouling
- Corrosion
- Loss of Absorption Capacity
- High Amine Losses
- High Energy Input
- Frequent Filter Changeouts
- Environmental Non-Compliance
- Off-Spec Gas

- Unstable Operations

## 2) Poor Amine Quality

Condition and proper hygiene of the amine solvent is as important to successful operations as equipment maintenance and performance. Amine should be near color free and void of particulate matter.

### **QUESTION 4**

What are the implications of contamination?

Contamination can severely affect an amine unit's capacity, operational stability and corrosion.

#### Plant Capacity

As solvents become contaminated with non-regenerable impurities, they lose their effectiveness because the amine concentration is reduced. To compensate for this effect, the absorbent circulation rate can be increased. However, the increased circulation rate affects other parts of the process such as the sensible heat duty in the reboiler. It may also change the product gas composition due to the fact that more liquid is flowing to the absorber thereby altering the gas/liquid ratio, which, in turn, can affect the total H<sub>2</sub>S and CO<sub>2</sub> removal. The temperature profile in the absorber also tends to change with circulation rate. Quite often, operators have to reduce the raw gas flow to the plant to ensure satisfactory operation.

If operators do not compensate for the presence of contaminants, there is a danger of overloading the amines with H<sub>2</sub>S and CO<sub>2</sub>. Excessive amine loadings can lead to unexpectedly high corrosion rates in some parts of the amine unit, particularly where there are rapid changes in pressure, temperature and/or velocity. Two-phase flow may arise resulting in pipe hammer and slug-type flow into downstream equipment. These problems not only affect the plant operation but may also cause mechanical damage.

#### Stability of Plant Operation

Higher contaminant levels usually increase the viscosity of the amine solutions, which reduces the mass transfer rates in the absorber and stripper. The viscosity increases ultimately lead to the product gas no longer meeting specifications. This is particularly detrimental in tail gas treaters where the lack of performance can result in reportable environmental excursions.

The more viscous solutions also have a higher tendency to foam. Furthermore, some hydrocarbon contaminants cause changes in interfacial tension, which stabilize amine foams. This can, in extreme cases, cause significant pressure drops across the absorbers and amine regenerators. Activated carbon filtration is often used to contain the hydrocarbon problems but heavier hydrocarbons are difficult to remove (especially if the pore size of the carbon is too small to capture the molecules).

Another cause of unstable gas plant operations is the presence of particulate matter, which promotes foaming tendencies. Fines may be introduced with the raw gas or they may be generated in the amine unit itself. Iron sulfide fines are "washed" off vessel walls by sudden

changes in operating conditions or by foaming incidents. Mechanical filtration can be used to deal with most of the fines. However, some fines are so small that conventional filtration media cannot capture them. Leaving such fine particulates in solution can lead to fouling of heat transfer surfaces, which in turn lowers the heat transfer efficiencies.

### Corrosion

Several types of corrosion can result from contaminated amine solutions. In the case of increased circulation rates, erosion corrosion may occur which is the physical wearing away of metals by the abrasive action of either suspended solids or extremely high velocities in restricted areas. This is of greatest concern where restrictions or changes in direction of flow are encountered. The rate of corrosion increases with velocity and even mildly corrosive solutions can produce extremely high corrosion rates if erosive conditions are present. Any friable protective coating, such as iron carbonate, can be eroded and fresh metal exposed for further loss.

Fouling which causes solids deposition or scaling can result in crevice type corrosion. Concentration cells can be set up beneath the deposit or scale leading to high, localized corrosion rates. Some amines undergo reactions with CO<sub>2</sub>, are thermally degraded or attacked by oxygen entering the system resulting in undesirable degradation products. The tendency for fouling, scaling and corrosion may increase with these materials in solution.

Chlorides entering the amine plant via poor inlet filtration or cooling water exchanger leaks can accelerate pitting corrosion in stagnant areas of the amine unit. Furthermore, chlorides in the amine solutions can induce stress corrosion cracking in stainless steel components. High levels of inorganic and organic acid salts can contribute significantly to the corrosion rates found in amine units. Corrosion rates are a function of the type and quantity of amine salt(s) present.

All types of corrosion reduce the life expectancy of amine processing units and result in major financial losses.

### QUESTION 5

What contaminants should I be concerned about?

- The primary contaminants of concern are:
  - Amine Strength
  - Heat Stable Salts/Ash
  - Degradation Products
  - Chlorides
  - Metals
  - Particulates

### Categories of Contaminants

Contaminants in amine solutions can arise from various sources and usually exist in several different forms. Although a single contaminant may necessitate a certain plan of action, gas-

treating solutions rarely contain only one or two impurities. Instead, many different impurities exist in varying concentrations, many of which have some adverse effect on the process.

However, most contaminants can be categorized into three basic groups.

### Amine Degradation Products

Amine degradation products are compounds which are formed either by the direct reaction of the amine and constituents of the feed gas (such as carbon dioxide, carbonyl sulfide, carbon monoxide, oxygen, carbon disulfide) or by thermal decomposition of the amine. Conversion of the amine, irrespective of the mechanism, represents a loss of active and valuable amine. Furthermore, some of these degradation products may cause foaming, corrosion and reduced gas-treating capacity.

### Heat Stable Salts

During the normal absorption / regeneration process the amine solution, which is basic, reacts with acid gases entering with the raw feed gas. In the case of  $H_2S$  and  $CO_2$ , the amine salts are thermally regenerable thus providing the basis for the continuous process. If other anionic species and/or stronger acidic components are present in the raw feed gas, they too form amine salts. However, these compounds are not thermally regenerable and are hence designated as “heat stable salts”. Both inorganic and organic heat stable salts occur. The former may contain chloride, sulfate and phosphate anions typically found in produced and cooling waters. Sulfates, thiosulfates and thiocyanates can also be formed by reaction between oxygen and  $H_2S$ , cyanic acid and  $H_2S$ ; with the latter is more prevalent in refineries.

By allowing amine solutions contaminated with heat stable salts to circulate, the full efficiency of the absorption process cannot be realized. As a result, plant throughput is reduced and the corrosive tendencies of the solution may increase.

### Non-Volatile Contaminants

Non-volatile contaminants arise from diverse sources such as gas wells, make-up water, anti-foaming agents, sealants, lubricants and anti-corrosion agents. Another common type of non-volatile contaminants is particulates, which may be carried into the amine solution by the raw feed gas. Iron sulfide is very common and undesirable, usually because of its potential to stabilize foams or enhance foaming tendencies. Solid contaminants of any type can decrease the efficiency of the absorber and stripper by plugging contactor trays, contactor packings and process piping.

**See Supplement A**

### **QUESTION 6**

What clean-up options do I have?

When the concentration of contaminants in amine solutions becomes excessive, there are basically four types of remedial action: (i) partially purging the contaminated solution and replacing it with reclaimed amine; (ii) replacing the entire inventory of contaminated amine solution; (iii) injecting caustic to free the amine bound up as heat stable salts.

## Bleed and Recycle

With this scenario, appropriately sized volume batches of Amine solution will be bled from the circulating system, custom distilled to remove the various contaminants and returned back to the system. Bleed and Recycle. The frequency of the batches is dependant on the initial HSAS and other contamination levels and then based on the incursion of HSAS within the circulating system over time.

### **Bleed and Recycle Service Benefits**

- NO Expensive And Time Consuming Equipment Set Up
- NO Expensive Utilities And Chemicals To Supply
- NO Waste Streams To Manage And Dispose by The Customer
- NO Operational Interruptions
- Reduced Solvent Costs And Contamination Problems
- Reduced Solvent Disposal, Emission And Environmental Costs
- DEA System Optimization
- Reduced Amine Make-Up Costs
- Reduced Operational Costs and Labor
- Guaranteed On-Time Delivery
- Full Logistics Management

A Maintenance Program can be developed whereby appropriately sized batches are processed and returned for reuse. This bleed and recycle procedure can be used to remove the contamination to any desired level and maintained there. Once the desired level of contaminants is achieved, the frequency of future batch processing can be determined based on the incursion (build-up) rate of the contaminants.

The Contaminant Reduction will be achieved by performing a batch, custom distillation of the spent amine solution to reduce/eliminate the primary contaminants, which include Heat Stable Salts, Degradation Products, Bicine, Solids and hydrocarbon. For example, the Heat Stable Salts (HSAS) would be equal to or less than 0.2 wt% in the Refined Amine Product at > 80 wt% Amine. The spent Amine solution will be drawn out of the amine storage system and loaded onto a railcar or truck tanker. The loaded railcar / truck tanker will then be transported to our permitted facility in Hot Springs, AR. Samples will be taken during the loading procedure, one for determining the solution composition and the other as a retention sample. The contaminated amine solution then will be custom distilled to remove the contaminants and water meeting the Refined Product Specification stated within this proposal. The refined Amine product will be sampled and tested for quality assurance. Retention product samples will be taken. The refined Amine product will then be returned to your facility via truck or railcar for storage and subsequent use.

## Inventory Replacement

Complete replacement of the contaminated amine also eliminates the contamination problem but, once again, its effect may be short-lived if the causes of the problem are not understood and remedied. Furthermore, the high cost of amine replacement and the increasingly high disposal costs of the contaminated amine make this option generally undesirable. It should also be noted that most "spent" amines typically contain over 80% of the original, active chemical. Consequently, the current disposal practices of deep well injection and incineration are not only environmentally unattractive, but they also constitute a loss of valuable amine.

## Neutralization

The addition of bases such as NaOH, KOH and  $K_2CO_3$  converts the heat stable amine salts to the corresponding sodium or potassium salt, thereby returning the amine to its active form. However, the addition introduces another impurity into the system, which heightens solution viscosity, corrosivity and scaling potential. This is especially true for sodium salts, which have low solubilities and, if they precipitate on heat transfer surfaces, not only reduce heat transfer but may also liberate acids thereby causing additional corrosion.

## Solution Reclamation

The overall objective of the ChemGroup process is to remove all major groups of impurities regardless of the specific impurities or concentration of impurities in the contaminated amine feed solution. The ChemGroup process has been successfully applied to amines such as MEA, DEA, MDEA, SULFINOL and formulated amines. In addition, ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol have been successfully purified.

The ChemGroup process incorporates a special flash-distillation unit, which removes the water fraction, the concentrate is then sent to a Wiped-film Evaporator (WFE) to purify the solvent by removing the various impurities. The WFE operates under vacuum conditions and has an innovative heating scheme. Up to 99% of contaminants can be removed while generating only a small waste stream (typically 5% of the contaminated amine feed, on a water free basis). Consequently, only small amounts of concentrated waste residuals need to be disposed.

## QUESTION 7

What are the key benefits of reclaiming the solution?

### 1. Effective Contamination Control

- Cost Effective
- Full Contaminant Removal

### 2. Removes Root Causes of Major Problems

- Heat Stable Salts
- Degradation Products
- Solids & Particulate

### 3. Production Capabilities Enhanced

- Improved Absorption Capacity
- Reduced Circulation Rates
- Reduced Foaming Upsets
- Reduced Filter Changeouts
- Improved Process Reliability

#### 4. Allows Amine Plant Optimization

##### **QUESTION 8**

Our facility has never reclaimed in the past why should we do it now?

In the course of the amine unit operation, the amine solvent will become contaminated through degradation or fouling. As the level of contaminants increase, the performance of the amine solution decreases, causing operational problems

In today's economic environment, processors are placing more and more emphasis on facility optimization and cost minimization. Particular attention is being paid to methods and procedures, which lower processing costs and allow higher throughputs. Also due to the ever-increasing environmental restrictions, product specification requirements are more stringent, requiring processors to have smooth gas treating operations. Aside from mechanical considerations, most operational difficulties can be attributed to contaminants entrained in the solvent. Contaminants gradually reduce the effectiveness of the operating system, driving up processing costs and restricting production throughputs. Thus, in today's market all operators should weigh the economics of clean versus dirty chemical solutions. ChemGroup Services provides a cost-effective solution for increasing throughputs and minimizing costs.



## **Supplement A**

### **Contaminants Identification and Quantification**

To understand what is happening in a contaminated amine unit, operators should consider special analytical tests. It is quite possible that some or all of the tests described below will fall outside the range of routine analyses provided by the solvent supplier. If so, plant personnel should expect to cover additional charges resulting from any tests performed. However, the potential savings gained by understanding the causes of contamination will be large. The following analytical methods should be considered.

#### *Active Alkalinity (AA)*

This is an acid-base titration in which a standardized acid is quantitatively added to a known amount of amine. Either a pH probe or an indicator dye is used to determine the endpoint of the titration. The value determined is supposed to be the wt% of amine. This test works very well for clean solutions and solutions without degradation products. High readings result from the presence of glycols (perhaps originating from tube leaks), free caustic (due to over addition during heat stable salt treatment), amine degradation products with basic functional groups and ammonia (possibly entering with the raw feed gas).

#### *Total Kjeldahl Nitrogen (TKN)*

This procedure determines the total amount of nitrogen present. An equivalent total amine concentration is then back calculated from the data. Any differences between the AA wt% and the TKN wt% give the operator a good indication of how efficient the used amine solution is relative to the virgin solution. A large difference between these two values indicates that considerable quantities of degradation products are present.

#### *Gas Chromatography (GC)*

A small sample of filtered amine is injected into a gas chromatographic column where the various components in the sample are separated, eluted and detected. Considerable work may have to be done to standardize the GC for quantitative work. This is especially true for degradation products. The accuracy of the GC analysis is strongly dependent on the availability of reference standards for calibration. Excellent results are obtained when all peaks on the chromatogram can be matched to known standards. The final interpretation depends greatly on the library of degradation products in possession of the analyst. The results are reported as weight percentages of each known component in solution. These data can be used to compare with and complement the TKN and AA values.

#### *Lean Amine Loadings (LAL)*

These values can be determined by wet chemical methods using iodine and thiosulfate for residual H<sub>2</sub>S levels and anhydrous KOH and thymolphthalein indicator for CO<sub>2</sub>. More elaborate equipment, which involves sample neutralization, carrier gas bubblers and remote detectors, can also be used to determine residual acid gas loadings. In either case, by monitoring the lean amine residual acid gas loading, operators can track how well the system is stripping the acid gases from the amine. Increases in these residual loadings may point to some adjustment required. If contamination is an issue, these values should be monitored closely so that all

treated gas outlet specifications are met. As solutions become more highly contaminated, it is more difficult to maintain low residual acid gas loadings.

#### Anion Analyses (IC & ICE)

Ion Chromatography (IC) is used to separate and quantify classic inorganic heat stable salt anions. For example, chloride, sulfate, carbonate, bicarbonate, thiosulfate and thiocyanate concentrations can be determined using ion chromatography. Separation and resolution are controlled by a buffer solution used to elute the sample through the IC column. Results are generally reported in ppmw.

Ion Chromatography Exclusion (ICE) uses the properties of strong acids / weak acids to selectively separate weak acids from each other. This method is very useful for quantifying the organic heat stable salt anions present. By controlling the pH of the solution used to elute the sample through the ICE column, good resolution and separation can be achieved. As with IC, results are generally reported in ppmw.

#### Metals Analysis (ICP)

Samples of the amine solution are injected into an argon plasma. The intensity of the emission spectrum from most metals in the sample are isolated and measured by the instrument. Results are generally reported as ppmw. High sodium or potassium values, without any visible counter ions like chloride or sulfate, indicate that NaOH, KOH/K<sub>2</sub>CO<sub>3</sub> addition is taking place. These data are also very informative when looking for corrosion by-products such as nickel, chromium, iron, etc.

#### Residual Amine Salts (RAS)

A small amount of amine is mixed with a strong action resin that has been pre-washed with deionized water. After an initial short mixing time, about 50 mL of deionized water are added to the amine and resin. Air is then bubbled through the resin/water slurry for 90 minutes to remove residual traces of H<sub>2</sub>S and CO<sub>2</sub>. The liquid is separated from the resin by filtering through an appropriate filter paper. A back titration is then performed on the clear liquid using 0.01 N NaOH. Caustic is added until the endpoint pH of 8.0 is reached. The total residual amine salts are then calculated and reported as wt% of the amine. This test cannot differentiate between inorganic and organic heat stable salts. An alternate method can be found in the Dow Chemical Gas Conditioning Fact Book.

#### Hydrocarbon Analysis (HCA)

Hydrocarbon contamination is one of the more difficult items to quantify. In almost all instances, atmospheric samples of warm, lean amine solution are taken. Losses of the hydrocarbon can occur during sampling. It is also possible that erroneous readings result because the contaminating hydrocarbon may accumulate at a point away from the sampling location (e.g. in the stripper overhead/reflux accumulator).

Bulk hydrocarbon analysis can be used if the presence of heavy species is suspected. Generally, a known mass of amine is extracted with a general-purpose solvent. This solvent is then evaporated, leaving a residue. The mass of the residue is determined and a ppmw Oil & Grease

value is calculated. If lighter or more volatile hydrocarbons are suspected, a headspace hydrocarbon analysis should be considered. A sealed vial of the amine solution is heated to the desired temperature and a sample of the vapor in the headspace above the liquid is extracted; it is then injected into a GC. The concentrations are then reported in ppmw.

#### Foam Test (FT)

Foam tests can be performed in the field or laboratory. Consistency is the key to running the foam test. A constant flow of air or nitrogen is sparged into the amine solution through a glass frit. Ideally, the bubbling gas is nitrogen the pressure of which has been reduced to a maximum of 5 Psig. The foam height and foam break time give indications on the foam stability.

#### Total Suspended Solids (TSS)

A known mass of sample is passed through a pre-weighed, 0.45  $\mu\text{m}$  filter medium. The filter is first rinsed with deionized water and then dried to determine how much material was collected on the filter. Results are reported in ppmw. This test provides an indication of the free solids burden in the solution.

#### Ash Content (TDS)

To determine the ash content or total dissolved solids, a sample of amine is filtered through a 0.45  $\mu\text{m}$  filter medium to remove any suspended solids. A known amount of filtrate is then placed in a pre-weighed crucible. Gentle heating is used to dry the sample. Once dry, the crucible is placed in a muffle furnace where the organic components are burnt off. The cooled crucible is then reweighed to determine the amount of inorganic residue or ash. The results are reported in ppmw or wt%.

#### Karl-Fischer Analysis (KF)

This method is used to determine the amount of water in amine samples. A known amount of the sample is injected into the apparatus. Special reagents are then used to titrate the sample. At the end of the titration, most newer instruments will automatically calculate the amount of water present in the sample. Reporting is done in wt%.

Caution should be used when evaluating KF results. The more water the sample contains, the greater the potential for error. This test is best suited for concentrated samples. It does however provide a quick check on whether the AA, TKN and GC results are of the correct magnitude.