

# **The UCARSEP® Process For On-Line Removal Of Non-Regenerable Salts From Amine Units**

David Burns  
Union Carbide Corporation  
Houston, TX

R. Alan Gregory  
Union Carbide Corporation  
Bound Brook, NJ

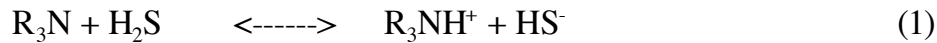
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## **ABSTRACT**

Amine unit contamination with non-regenerable salts, whether as a result of acid or inorganic salt incursion, or solvent degradation, is a common industry problem. In MEA systems this is usually redressed by the use of a "reclaimer" but this is not a practical solution for DEA, MDEA or formulated solvents. Similarly, the old approach of "purging" solvent is no longer economically or environmentally justifiable. Neutralization of amine salts with a strong base can significantly prolong the useful life of an amine solution but, eventually, some of the salt may have to be removed, especially if mechanical losses are low. Electrodialysis (ED) has recently been applied to this problem and has been found to overcome many of the disadvantages of vacuum distillation and ion exchange technologies, both of which have been used in recent years for solvent clean-up. Union Carbide adapted ED technology to the unique conditions encountered in an amine system and developed the UCARSEP® Process. A mobile UCARSEP® Unit has been built to achieve on-line salt removal rates of 40 lbmol/day (about 3,300 lb/day). This has been successfully used to clean up UCARSOL® Solvents as well as DEA. Case studies are presented and the relative merits of this and other clean-up options are discussed.

## INTRODUCTION

Aqueous alkanolamine solutions are widely used to remove acid gas contaminants, usually H<sub>2</sub>S and CO<sub>2</sub>, from a variety of gas and liquid streams through reactive absorption".<sup>1</sup> The acid gases are absorbed, along with the liberation of heat, in an acid base equilibrium reaction of the type shown in equation 1 for H<sub>2</sub>S with a tertiary amine:



The resulting "rich" liquid containing the absorbed acid gases is then heated in a stripper and the reaction reversed. The reaction proceeds to the left, the acid gases are liberated and discharged, and the amine is reactivated for further contact with the gas stream. However, if the absorbed acid is relatively strong (with a pK<sub>a</sub> at least 3-4 units lower than that of the amine) then although equation 1 will proceed to the right in the absorber, it cannot be reversed at stripper conditions, and the amine has essentially been deactivated from a gas treating perspective. An example of this is shown in equation 2 for acetic acid:



The introduction of any relatively strong and/or non-volatile acid into the amine system will thus lead to deactivation of the amine. The acids can be introduced via the process gas, makeup water, entrained liquids or, in some instances depending upon the amine in question, through the oxidative degradation of the amine or sulfur species present in solution. For obvious reasons the amine salts that result are referred to as heat stable amine salts (HSAS). A great deal of work has been undertaken over the years developing better amine products that are, for example, more selective, or which require less energy to reverse equation 1, but none are immune from the problems represented by equation 2.

HSAS problems are particularly serious in the refining industry. Substantial levels of HSAS's, especially formates and thiocyanates, are often seen in the solutions used to treat the gas and liquid streams originating from the various catalytic and thermal processes prevalent in this industry. However, in the natural gas industry the acetic and hydrochloric acids used in various well treatment activities, such as acid fracturing, can also lead to the formation of HSAS's if they are introduced into the amine unit. Similarly, entrainment of formation water can add chlorides and sulfates, although in this case they will most probably enter as an inorganic salt and will not result in amine neutralization. Another significant source of acids and salts can be make-up water that has been treated by a water softener or conditioner, particularly if not well maintained. Although anions entering as a salt rather than the acid do not lead to the formation of HSAS's and the deactivation of the amine, they can lead to many of the same problems associated with HSAS's, namely increased potential for corrosion<sup>2,3</sup>, fouling, and generally poor performance.

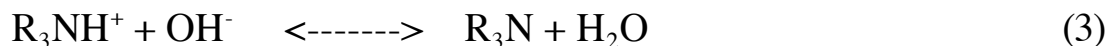
Historically HSAS and salt contamination problems were often offset by high amine losses "inadvertent" purge and makeup. As the economic impact of high losses has

become more pronounced in recent years there has been a trend towards reduced amine consumption and a corresponding increase in problems relating to accumulated salts and HSAS's. In MEA systems a reclaimer, basically a semicontinuous distillation process, can be used to eliminate salts as well as degradation products but this is not a practical solution for DEA, MDEA, or formulated MDEA based products because of the potential for degradation if exposed to very high temperatures for prolonged periods. MDEA and MDEA based solvents benefit from being less susceptible to degradation than other amines but are still affected by salt and acid incursion. Several technologies have been developed and commercialized to address the problem of "reclaiming" DEA and MDEA systems on-site and their characteristics are summarized in Table 1. The most widely used processes have utilized ion exchange<sup>4,5,8,10</sup> or vacuum distillation<sup>6</sup> technology, but they also have drawbacks. A modified electro dialysis process<sup>7</sup> developed by Union Carbide's Gas Treating Service and Technology Group overcomes many of the limitations inherent in these other commercially available processes.

## ON-SITE CONTROL AND REMOVAL STRATEGIES

### Heat Stable Amine Salt Control Via "Neutralization"

When the salts accumulating in an amine system are the amine salt, that is a HSAS, resulting from the incursion of acids into the system rather than the incursion of inorganic salts, such as KCl, it has been shown<sup>2,3</sup> that they can be effectively controlled by the addition of a stronger base such as UCARSOL® Neutralizer DHM, a proprietary neutralizer, or if the contaminants and situation allow, NaOH. The addition of the stronger base raises the pH of the system and converts the amine salt to the inorganic salt, with the benefit of deprotonating the amine and making it available for acid gas removal purposes again. The overall effect is shown in equation 3:



The result is the same as if the acid had entered the system as the inorganic salt and therefore, if the level of the "neutralized" salt builds to a sufficiently high level, it can still be detrimental, but obviously much less so than the equivalent HSAS. Depending upon the relative rates of incursion and amine loss from the system it may well turn out that the equilibrium inorganic salt level in the system is acceptable and no further remedial action is required, other than regular solution monitoring and the addition of strong base as necessary. However, if the equilibrium level is high, because either the incursion rate is high or the solvent loss rate is low, a point may still be reached below this where the inorganic salt level has to be reduced if problems are to be avoided. By adding a strong base the time taken to reach a salt level requiring action is extended and in some cases completely avoided since higher concentrations of inorganic salts than HSAS can be tolerated without adverse effects. When action is required two basic options are available: "purge and makeup", with the purged amine being either reclaimed off-site or disposed of,

**Table 1 - Comparison Of Commercially Available On-Line Amine Reclamation Technologies**

	<b>Ion Exchange</b>	<b>Vacuum Distillation</b>	<b>UCARSEP® Process</b>
<b>Applicability</b>	Removal of ionic contaminants. Very low salt levels achievable.	Removal to very low levels of ionic contaminants, degradation products, and non-volatile materials in general.	Removal of ionic contaminants. Complements HSAS neutralization program.
<b>Mode Of Operation</b>	Salts extracted out of solution by ion-exchange resin. Resins subsequently "regenerated" and salts purged from system in aqueous stream.	Water and amine stripped away from salt and degradation product residue. Reduced pressure used to limit temperature.	Modified electro dialysis process used to extract salts out of amine solution and into aqueous brine stream.
<b>Limitations</b>	Cannot remove degradation products and non-ionic contaminants. Best suited to low salt level applications. High salt levels lead to frequent bed exhaustion and regeneration.	Caution with "formulated" products - may affect performance. Energy intensive compared to other methods since everything -- water plus amine -- is stripped overhead.	Cannot remove degradation products or other non-ionic contaminants. Limited use in very low salt level applications.
<b>Waste Characteristics</b>	Salts extracted into aqueous brine stream. Volume and concentration increased by presence of regenerants and rinses. May require further treatment (pH reduction) before discharge to waste-water treatment plant.	Residue containing salts and degradation products. Need to treat as hazardous waste.	Salts extracted into aqueous brine stream. Non-hazardous and can be discharged to conventional waste water treatment plant.
<b>Volume Of Wastes</b>	High -- aqueous.	Low (5-15 % inventory) -- non-aqueous.	Moderate (~ 200 gal per lbmol) -- aqueous.
<b>Overall Amine Recovery</b>	~99 %	85-95 %	~98 %
<b>Additional Raw Materials Required</b>	NaOH and H <sub>2</sub> SO <sub>4</sub> solutions required for resin regeneration and brine conditioning. Used in large excess of salt removed (eg. 240-720 lb NaOH/lbmol salt removed <sup>11</sup> ).	If system not already neutralized need NaOH to convert HSAS to "free" amine. Used in same stoichiometric amount as salt removed (40 lb NaOH/lbmol).	If system not already neutralized need NaOH or DHM to convert HSAS to "free" amine. Used in same stoichiometric amount as salt removed (40 lb NaOH/lbmol).
<b>Amine Feed Requirements</b>	Cool, lean, hydrocarbon and particulate free. Require 60-80 gpm feed on intermittent basis.	HSAS neutralization required.	Cool, lean, hydrocarbon and particulate free. Require continuous 15 gpm feed. HSAS neutralization required.
<b>Special Items Needed</b>	Regeneration chemicals and storage.	Fuel gas supply.	440V/200A power source.
<b>Type Of Operation</b>	Semi-continuous (cyclic) on-line or batch (from storage tank). Mobile unit commercially available.	Batch (from storage tank) or on-line. Mobile unit commercially available.	Continuous on-line or batch (from storage tank). Mobile unit commercially available.

and on-site/on-line reclamation. The latter is usually preferable and the techniques described below are the commercially available alternatives.

### **Vacuum Distillation**

The atmospheric pressure boiling points of the three commonly used amines MEA, DEA and MDEA, are 171 °C, 268 °C, and 247 °C respectively. MEA can be reclaimed by distillation at atmospheric pressure but this is impractical for DEA and MDEA without causing significant degradation, given their high boiling points, and reduced pressure distillation processes are usually used instead. Several companies in the US practice offsite vacuum reclamation of amines but at least one on-site service is also available<sup>6</sup>. The reference to this latter process discusses how caustic is first added to the amine solution to "free" any HSAS amine, as detailed in equation 3, and then the amine is stripped away from the contaminants, along with the water, and condensed and collected overhead. A novel heater design and mode of operation is used to minimize the time the solution is exposed to high temperatures in the direct-fired heater, thereby reducing the potential for amine degradation. It is claimed that recovery efficiencies as high as 95% can be attained, with the generation of only a 5% waste stream (on a water free basis), although obviously these values will depend upon the level of contamination. Unfortunately the waste generated by this process has to be treated as hazardous waste. This technology not only removes salts but also any degradation products, assuming that they are of different volatility than the amine in question. Thus it is particularly suited to reclaiming DEA, since DEA can suffer extensive thermal and CO<sub>2</sub> induced degradation, but this feature is not advantageous for the significantly more stable MDEA. Care should also be exercised when reclaiming MDEA based formulated products since, given that their compositions are usually proprietary, some of the enhanced performance capabilities may be diminished by vacuum reclamation.

### **Ion Exchange**

In ion exchange processes contaminated lean solvent is passed sequentially through beds of cationic and anionic exchange resin. The former removes the cations from solution, for instance replacing Na<sup>+</sup> with H<sup>+</sup> and the latter removes the anions, for instance replacing Cl<sup>-</sup> with OH<sup>-</sup>. The reactions are reversible so that when the beds have been exhausted the resins can be regenerated. In the case of the cation exchange resin an acid solution, such as sulfuric, is passed through the bed, replacing Na<sup>+</sup> with H<sup>+</sup> on the resin. In the case of the anion exchange bed a basic solution, such as NaOH, is passed through the bed replacing the Cl<sup>-</sup> with OH<sup>-</sup>. The resulting effluent, basically an aqueous salt solution, is collected for disposal. Depending upon the system being treated and mode of disposal the effluent may need further treatment (e.g. the solution pH may be above 12 and need acid addition). Unfortunately with ion exchange resins the usage of regeneration chemicals is quite high since, for optimum performance, the amount of acid or base required to regenerate the resins are several times greater than the amount of salt removed by the resins in the

cleanup cycle<sup>11</sup>. Given the increasing cost of caustic this can have a significant impact on the overall cost of reclaiming. The brine solution resulting from ion exchange contains not only the ions removed from the amine solution but also the counter-ions from regeneration and post-treatment. This serves to increase both the volume and concentration of the material to be disposed of. The volume is also increased by the requirement to rinse the bed thoroughly after regeneration to prevent regeneration chemicals from being "washed" into the amine system once the subsequent amine cleaning cycle is repeated.

Ion exchange processes of this type are inherently cyclical in nature but they can be made to appear continuous by utilizing multiple beds in such a way that when one bed becomes exhausted, and in need of regeneration, the amine solution flow is switched to another bed that has already been regenerated. The exhausted bed is then rinsed and regenerated and the sequence continued. It is not imperative in gas treating applications that the process be continuous from a salt removal perspective but discontinuous processes do have the drawback of imposing perturbations on the amine plant itself.

A lot of work has gone into selecting ion exchange resins for this application that combine selectivity for the typical contaminants with ease of regeneration, as well as being able to survive the harsh environment. One potential pitfall when removing cations from solution is that protonated amine, the  $R_3NH^+$  cation, can be absorbed in the cation exchange process as well. During the subsequent regeneration step this would be lost from the system with the brine. Techniques have been developed for minimizing this problem by, for example, first washing the amine off the cation exchange resin with a strong base before regenerating the resin with an acid. Although this reduces the amine loss it increases the amount of effluent generated as well as the amount of chemicals required for regeneration.

It would obviously be easier from a clean-up perspective if the cation exchange process did not have to be used and only anions had to be removed. Unfortunately, as already discussed, cations such as  $Na^+$  are frequently encountered as a contaminant. If left in solution, but the associated anions removed, to maintain electrical neutrality non regenerable  $HS^-$  or  $HCO_3^-$  salts will form with dire consequences from a treating perspective. However, caustic is also frequently added as a way of controlling HSAS problems and the desire to minimize ion exchange cleanup costs has led to some recommendations to stop this practice. Unfortunately, although this does make ion exchange reclamation easier it also means that the system has to be cleaned up more frequently, as the maximum recommended anion level is only  $\sim 3,000$  ppm<sup>9,10</sup> without neutralization, and the overall amount of salt that has to be removed can be also substantially increased in the long run. Experience has shown that the benefits of caustic "neutralization" far outweigh any benefits to be gained by simply making the subsequent clean-up process easier<sup>2,3</sup>. As discussed earlier, the use of caustic can in some instances eliminate the need for reclaiming altogether. Depending upon the system in question and the rigorousness of the neutralization program, if the HSAS level is maintained at  $<1-2\%$ ,

trouble-free operation has been seen at anion levels as high as 50,000 ppm (NB. the HSAS level is defined as the wt% of amine associated as a HSAS).

A typical ion exchange system capable of removing ~25 lbmol/day of salts would need an amine feed rate of ~80 gpm. The process is favored by cooler feed temperatures and so additional cooling could be required if the lean amine temperature is too high (>110 °F). Depending upon the solvent condition, both carbon and mechanical filtration might also be needed. The solution should be as lean as practical during the cleanup since, if the lean loading is high, significant amounts of HCO<sub>3</sub><sup>-</sup> and HS<sup>-</sup> will be removed along with the anions of interest in the amine cleaning cycle, prolonging the process and increasing costs.

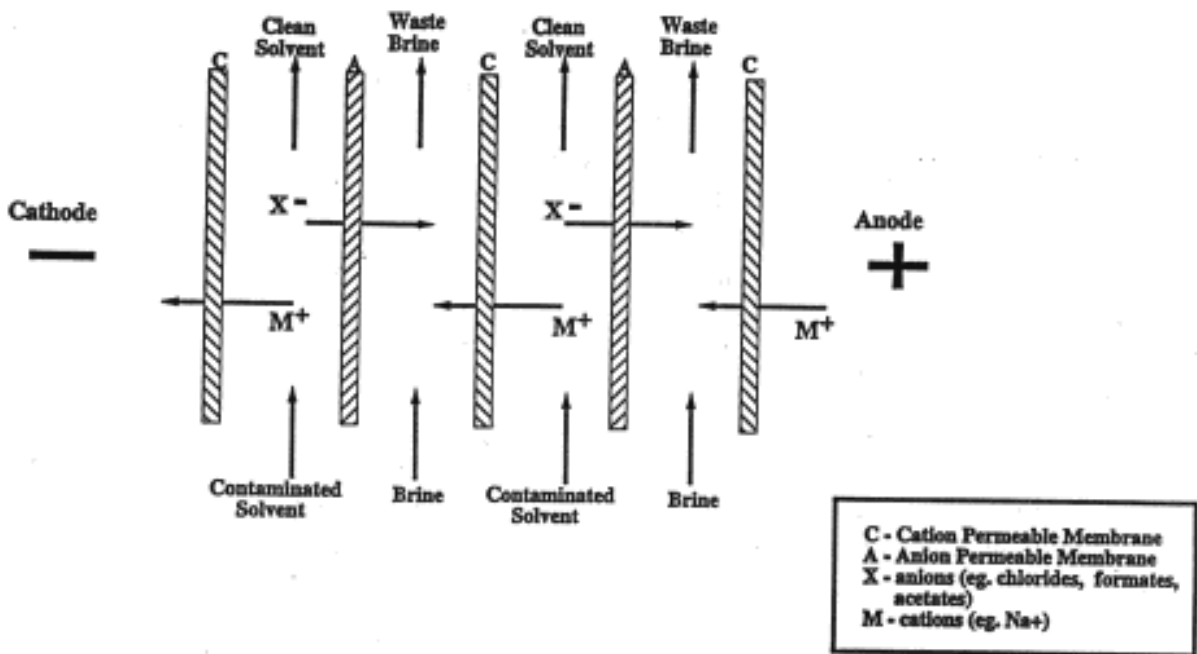
### **Modified Electrodialysis: The UCARSEP® Process**

Electrodialysis is a separation process in which ion permeable membranes (sometimes called ion selective or ion exchange membranes) are placed in an electric field to facilitate the removal of substances that ionize in solution. These semipermeable membranes contain electrically charged functional sites chosen such that they are selective and allow the passage of either anions or cations, but not both. By correct sequencing, anions and cations can be extracted from one solution into another. Although not as well known as ion exchange this technology is widely used in other fields and, recognizing that it would have beneficial characteristics for salt removal from amines, Union Carbide adapted it to the unique conditions encountered in an amine system and developed the UCARSEP® Process around it. In this process salts are separated from the amine solution and concentrated in an aqueous "brine" stream for disposal.

In the UCARSEP® Process anion and cation permeable membranes, separated by specially designed spacers, are assembled in alternating fashion between anode and cathode end plates and operated in a "sheet flow" arrangement as shown in Fig 1. The spacers serve to promote good flow distribution between the membranes and direct the amine and brine solutions to the appropriate channels. The membranes are sequenced such that when the amine solution enters the channel between an anion and cation permeable membrane the anions move towards the anode through the anion permeable membrane and the cations move towards the cathode through the cation permeable membrane. On the other side of both membranes an aqueous brine solution flows and the ions are collected and swept out of the system. The ions are prevented from further migrating out of the brine stream towards their respective electrodes by the alternating sequence of ion exchange membranes: the anion on passing through the anion permeable membrane into the brine stream is prevented from migrating further (into a solvent channel) since the next membrane encountered is a cation permeable membrane, which will not allow the passage of the anion. Similarly the cation migrating through the opposite side of the solvent channel will next encounter an anion permeable membrane.

The salt removal rate in ED is primarily a function of the number of membrane cell pairs and the applied current. However, the membrane type, surface area, and solution

conductivity's also affect the removal rate since they limit the current that



**Fig 1 - Principal Of Amine Reclamation Via Electrodesis**

can be applied. The overall removal rate ( $r$ ) can be calculated from:

$$r = \frac{EnI}{F} \quad (4)$$

where:  $r$  = removal rate (g-eq/s)  
 $I$  = current (Amps)  
 $n$  = number of membrane cell pairs  
 $F$  = Faradays constant (96,480 Coulombs/g-eq)  
 $E$  = efficiency factor

A significant amount of development work went into selecting and designing the most suitable membranes and spacers for this application. Working on actual contaminated amine solutions, in a pilot plant as well as on-site, membranes were selected which combined high salt removal rates (high  $E$  and  $I$  values attainable), low amine permeability, and high mechanical strength.

In ED as the applied current increases so does the electrical transport of ions until the boundary layer at the membrane surface is depleted—at this point the limiting current density is said to have been reached. This causes an increase in stack resistance, and with it the voltage drop, and water in the boundary layer is ionized to  $\text{OH}^-$  and  $\text{H}^+$ . This can lead to membrane fouling with pH sensitive materials and a reduction in the overall efficiency of the process. Spacers were therefore developed to maximize the limiting



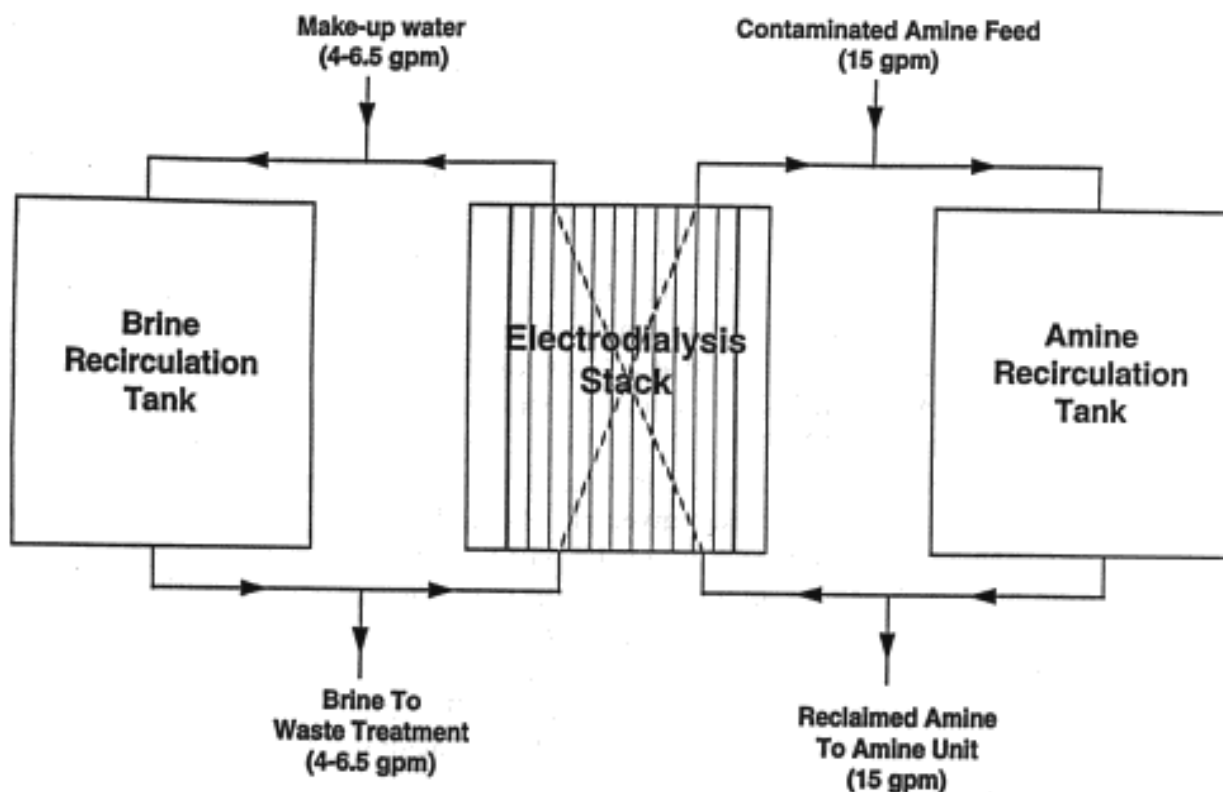
current density over a wide range of operating conditions by ensuring turbulent fluid flow within the channels while minimizing pressure differences between them.

The UCARSEP® Process technology fits in very well with the strategy of HSAS control by neutralization, and this is one of the reasons the technology was selected. For every anion transferred out of the amine solution a corresponding cation must also be transferred. Obviously it is preferable that the cation be, for instance,  $\text{Na}^+$  rather than  $\text{R}_3\text{NH}^+$ . By neutralizing the solution to a HSAS of  $<1\%$ , and deprotonating most of the amine, the amount of amine that is "lost" to the brine via cation transfer is minimized. This is further helped since the cation permeable membranes used are more selective towards transport of  $\text{Na}^+$  than  $\text{R}_3\text{NH}^+$ . If the above strategy is followed, field experience with the mobile unit described below has shown amine loss to be very low: typically only 1-2 wt% of the amine system inventory should be lost in reducing the salt level to an acceptable value. In other words, the UCARSEP® Process results in an amine recovery of  $\sim 98$  wt%. The base required for neutralization represents the only chemicals that are required by the UCARSEP® Process. However, by neutralizing to control the negative effects of HSAS's, considerable benefit is also obtained from its use and this is preferable to neutralizing just to facilitate the UCARSEP® Process. If the ionic contaminants entered the system as an inorganic salt then neutralization is not required and no chemicals are consumed at all.

The technology is modular in concept and can be easily tailored to the specific requirements of an amine unit to provide a dedicated on-site HSAS removal capability. The number and size of membranes needed is governed by the salt removal required but the overall process is very compact and the "footprint" consequently small. Although the UCARSEP® Process technology was first developed and tested on proprietary MDEA based UCARSOL® Solvents it has proven to be equally well suited to DEA systems, as is detailed in the case histories below.

For systems where a permanent unit cannot be justified, because the contamination problem is periodic or controllable through judicious neutralization, a mobile UCARSEP® Unit capable of removing up to 40 lbmol/day of salts has been developed. The unit can be brought on-site and, given the high capacity, clean up on-line in the minimum amount of time. Experience has shown that the operation of the amine unit is not affected. A  $\sim 15$  gpm slip stream of cool lean amine is required; salt depleted amine is fed back to the low pressure rich side of the amine unit at the same rate. The unit is fully automated and operates 24 hours per day when on-site. In addition to the usual process and utility hookups a source of good quality water for brine make-up and a 200A/440V power supply are also required. The actual power consumption costs are minimal since, even with the unit running at maximum rates, the total power cost should be no more than \$60 per day, assuming an energy cost of \$0.05 per kWhr. To put this in perspective, this is equivalent to 2.5 cents per lb of acetate removed (if that were the anion in solution).

Large variations in the salt concentration are experienced between the beginning and end of reclamation and the process is therefore run in a "feed-and-bleed" mode, as shown in Fig 2, to ensure stable operation. This means that depleted solution from the ED stack is



**Fig 2 - UCARSEP® Process Flow Arrangement**

returned to a 100 gal holding tank and mixed with fresh feed solution (entering at ~15 gpm). This blended solution is the actual feed to the ED stack. A portion of the material in the holding tank is bled off and returned, at the same rate as fresh feed is added, to the low pressure rich side of the amine unit. The brine side of the system operates in the same way except that the fresh feed in this case is makeup water. The rate of addition is controlled to maintain a constant brine conductivity in the holding tank. When the system is removing 40 lbmol per day the brine generation rate is ~6.5 gpm. Given that the brine conductivity is controlled at a constant level, the rate of brine generation is essentially proportional to the rate of salt removal. At the beginning of a cleanup, when salt levels are high, the unit is run under current control. In this regime the applied current is constant and therefore the salt removal rate is constant. As the salt level and conductivity of the solution being treated decreases the voltage slowly increases up to 400 V. At this point, indicative of the cleanup coming to an end, the system is switched over to voltage control and as the salt concentration is further reduced, the current gradually decreases.

## CASE HISTORIES

The following three case histories show how the problem of HSAS contamination was resolved at three refineries. They already had neutralization programs in place, to varying degrees, to control HSAS problems and were therefore natural fits with the UCARSEP® Process when it came time to reclaim. However, although involving HSAS's and

neutralization, they also illustrate the applicability of this process to salt removal in general from amine systems. Case study details are summarized in Tables 2 and 3.

### **Case 1: Mid-West Refinery**

A mid-western refinery used UCARSOL® HS Solvent 101 in their 10 Mgal main amine system and had experienced a steady build up of anions, particularly formates, over the last few years. The HSAS level was well controlled at <2 wt% by the periodic use of UCARSOL® Neutralizer DHM but the point was finally reached where reclamation was required due to the high formate level. After studying all the options it was decided that the UCARSEP® Process represented the most cost effective solution to the problem.

The unit was brought on-site and was up and running within 36 hours. An ancillary chiller had to be used to cool the lean amine temperature to 105 °F but otherwise no additional equipment was required. The formate level was steadily reduced from 2.9 wt% to 0.4 wt%, as shown in Figure 3, without any interruption to the operation of the amine plant. The improved solvent condition allowed the refiner to reduce circulation rates and achieve an immediate steam saving of 2 Mlb/hr (a \$35,000/year saving) and a reduction in lean amine temperature. Additional longer term benefits, resulting from lower corrosion costs and improved system performance, are more difficult to assess but are expected to be significant given the need for the amine system to be on-line and in compliance at all times.

Approximately 50 lbmol of salts were removed and this resulted in the production of 10.4 Mgal of brine. Loss of amine with the brine represented ~3.4 wt% of the amine inventory, which was higher than predicted, primarily because of a high HSAS level on start-up (2.4 wt%). Additional neutralizer had been added prior to the arrival of the unit to get the HSAS level down to 1% but continued incursion in the interim had raised it again. This problem was corrected before the end of the run by adding more neutralizer. The refiner disposed of the brine through their waste-water treatment plant without further treatment.

### **Case 2: Gulf Coast Refinery**

A gulf coast refiner using UCARSOL® HS Solvent 101 to treat coker off-gas and liquids experienced significant HSAS incursion problems. This was well controlled by the judicious use of caustic, which they added as necessary to maintain a HSAS level of ~2%, but by the time the formate level reached 5.3 wt%, and the "ash" level 9 wt%, it was obviously time to clean-up the system.

No further treatment of the 15 8pm of lean amine feed to the UCARSEP® Unit was required as it was well filtered, hydrocarbon free, and cool (100 °F). However, a suitable power source was not conveniently located and a skid mounted diesel generator (200 kW) had to be rented for the duration of the cleanup. The unit was brought on-site Monday morning and was up and running by the following lunch time. During that time the utility

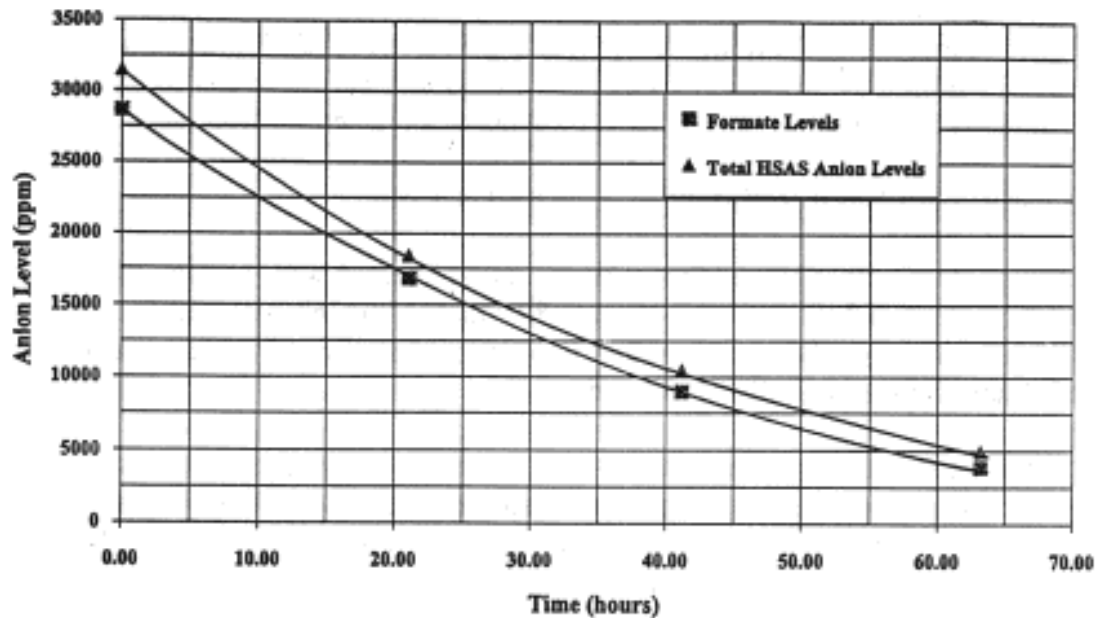
**Table 2 - Summary Of Reclamation Case Studies: Solution Conditions**

	Case 1 Mid-West Refinery		Case 2 Gulf Coast Refinery		Case 3 Gulf Coast Refinery Plant A		Case 3 Gulf Coast Refinery Plant B	
	Initial Condition	Final Condition	Initial Condition	Final Condition	Initial Condition	Final Condition	Initial Condition	Final Condition
Heat Stable Amine Salt (wt%)	2.38	1.06	1.85	1.04	3.95	1.23	1.3	0.4
Formate (ppm)	28,662	3,876	52,886	14,628	5,363	2,251	4,506	3,314
Thiocyanate (ppm)	876	<60	15,543	1,252	15,695	1,781	14,241	3,882
Acetate (ppm)	1,499	977	4,982	2,149	4,342	2,381	5,362	3,862
Total HSAS Anions (ppm)	31,490	4,969	74,526	18,662	29,386	10,605	28,774	15,450
Solvent Conc. (wt %)	38.66	38.13	37.4	39.5	29.9	29.7	28.9	28.6
Ash (wt%)	3.56	0.72	8.69	2.78	3.08	2.40	-	-

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**Table 3 - Summary Of Reclamation Case Studies: Removal And Equipment Details**

	Case 1 Mid-West Refinery	Case 2 Gulf Coast Refinery	Case 3 Gulf Coast Refinery Plant A	Case 3 Gulf Coast Refinery Plant B
Solvent Type	UCARSOL® HS Solvent 101	UCARSOL® HS Solvent 101	D E A	DEA
System Volume (gal)	10,000	30-35,000	330,000	80,000
Salt Removed (lbmol)	50	349	1,225	211
Brine Produced (gal)	10,360	82,260	300,000	53,000
Amine Recovery (% Of Inventory)	96.6	96.1	96	98.2
Additional Equipment Required	1. Amine Feed Chiller	1. Generator (200 kW)	1. Generator (200 kW) 2. Amine feed chiller 3. Makeup water chiller 4. Carbon bed	1. Generator (200 kW) 2. Amine feed chiller



**Fig 3 - Rate Of Contamination Reduction In Case Study 1**

and process hookups were completed, Union Carbide's operating personal received safety certification, and a pre-startup safety review was completed.

The formate level was steadily reduced from 5.3 wt% to 1.4 wt%, the thiocyanate level from 1.6 wt% to 0.1 wt%, and the overall ash level from 9 wt% to 2.8 wt%. In this system, given the high rate of incursion, reducing the contamination level below this would not be particularly cost effective. The classic asymptotic shape of the contaminant concentration versus time profile shows that salt levels build up very quickly initially but more slowly as the contamination level increases. In fact, it had taken the system nearly two years to reach an ash level of 9 wt% since it had been last cleaned up to ~2 wt% (using the UCARSEP® Process). If at that time the level had been reduced below 2%, the length of time before this latest cleanup would not have been increased by more than a month at most, but the time required for cleanup, and indirectly the cost, would have been. More importantly the performance and costs associated with running the amine unit in the interim would not have been improved.

The system inventory was estimated at 20 Mgal but, as is often the case, this was on the low side. By the time additional contaminated material was added to the system from holding tanks an estimated 30-35 Mgal of solution was treated altogether. A total of 349 lbmol of salts were removed resulting in the production of 83 Mgal of brine. Amine representing ~3.9 wt% of the total amine inventory was lost with the brine. The level of amine loss on an inventory basis was high, because of the high level of contamination, but on a salt removal basis it was low, primarily because the HSAS level was maintained at ~1% throughout the cleanup period. The brine was readily disposed of in the waste water treatment plant without further treatment.

One immediate benefit from the cleanup of the solvent was a reduction in solvent specific gravity from 1.11 to 1.06. This should lead to a direct reduction in energy usage, and indirectly through the opportunity it presents optimize circulation rates.

### **Case 3: Gulf Coast Refinery With Two DEA Units**

A gulf coast refiner had two main amine units, Plants A and B, using DEA. Plant A had an inventory of 330 Mgal and Plant B 80 Mgal. Although both plants had accumulated HSAS's the level of amine degradation products was very low and therefore suitable for cleanup using the UCARSEP® Process.

Plant A had a HSAS anion level of ~3 wt%, mainly thiocyanate and formate, but a HSAS level of ~4 wt%. Caustic neutralization had been tried with some success but precipitation problems had been encountered as a result of unusually high oxalate levels and they were obviously nervous about further neutralization. With an incursion rate estimated at 7 lbmol/day, even though the system was very large, the contamination level was slowly increasing and processing problems could be expected at some point in the future. Rather than wait for the inevitable they decided that the system needed to be cleaned up. After studying the available reclamation options they determined that the UCARSEP® Process represented the most cost effective solution.

Unfortunately the lean amine and condensate makeup-water temperatures available in Plant A were both too high and a rented chiller package had to be used to provide ~15 gpm of lean solvent, and ~4-6 gpm of condensate, at ~105 °F. This was powered by a skid mounted diesel generator that also provided the power for the UCARSEP® Unit. As the solvent was heavily contaminated with hydrocarbons a skid mounted carbon bed was needed to pretreat the lean solvent (after it had been cooled). Given the high HSAS level, and the reluctance to neutralize the whole system, the caustic injection system on the UCARSEP® Unit was used to provide on-line feed neutralization.

Although the extra feed pre-treatment steps increased the amount of time taken to get the unit on-line, everything was completed and commissioned within a few days of spotting the trailer at Plant A. A total of 1225 lbmol of salt were removed from Plant A, reducing the HSAS anion level to <1.0% and the HSAS level from ~4 wt% to 1.2 wt%. As the caustic injection rate was limited by precipitation of the oxalate salt in the feed line, the HSAS level could not be reduced to the optimum level in the early part of the cleanup and the amine loss rate was consequently higher than normal. However, as the salt levels were reduced the caustic injection rate was gradually increased until the HSAS level in the feed was <1% and the amine loss rates fell. The overall amine loss represented ~ wt% of the amine inventory. Brine was accumulated in a frac tank and analyzed daily by the refinery environmental lab before final discharge to the waste-water treatment plant, but no problems were encountered.

Once Plant A was in good condition the mobile unit was moved over to Plant B. Although this plant was not as badly contaminated as Plant A, and it had been possible to "neutralize" to a greater extent, it was still in need of cleanup. The solution in this system

did not need to be carbon treated and a supply of cool makeup water was available which simplified the hookups. As the HSAS level was ~1.3 wt% the on-line caustic neutralization system did not have to be used. A total of 211 lbmol of salt were removed from the system, reducing the total anion level from 2.9 wt% to 1.5 wt%, and the HSAS level from 1.3 wt% to 0.4 wt%. A total of 53 Mgal of brine was generated in total and disposed of through the waste water treatment plant without problem. The amount of DEA lost with the brine represented ~1.8 wt% of the Plant B amine inventory.

## **SUMMARY**

The best approach to solvent contamination is to address the conditions and circumstances which lead to the problem in the first place. This may range from making sure that inlet separators and makeup water conditioners are functioning properly to installing feed-gas water wash systems. However, even in the best run systems solvent contamination will still occur to some extent as it is not practical to eliminate all sources. It is therefore important to monitor the solvent condition and take appropriate steps to prolong the solution life. Regular monitoring will also allow the prediction of when, and if, the solvent will need to be reclaimed. If it is, on-line reclamation makes the most sense from an operating and economic perspective. Any of the three commercial technologies discussed above could be used for on-line reclamation but each has advantages as well as disadvantages depending upon the specifics of the problem. The technology chosen will be influenced by the type of contaminants as well as the final reclaimed solvent requirements. It has been shown that ion exchange is best suited for applications where very low salt levels are required whereas vacuum distillation is best suited for applications where solvent degradation is an issue. The UCARSEP® Process on the other hand represents the most practical solution to on-line reclamation in the absence of these two issues. It has been found to be a particularly logical choice when there is a HSAS problem, especially if it is being controlled by neutralization. Solution monitoring, neutralization and, if appropriate, UCARSEP® Process reclamation, form the basis of Union Carbides' Amine Management Program, whose goals are maximizing solvent life while minimizing operating and treating problems and costs.

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