

AMINE RECLAMATION WITH MINIMAL OPERATIONAL IMPACT THROUGH ELECTRODIALYSIS

Dr. Paul Parisi
ElectroSep Technologies Inc.
116 Dulwich,
St. Lambert, QC
Canada, J4P 2Y7
514-943-0494
paulp@electrosep.com

Dr.
The Dow Chemical Company
6046 FM 2920, #309
Spring, TX, 77379
281-320-8746
bosensf@dow.com

ABSTRACT

The UCARSEP™ process has been in commercial use for over 10 years as a method of removal non-regenerable salts from amine solutions. Electrodialysis is the only method of salt removal that does not have a direct impact on the operation of the amine unit. Amine is sent to the electrodialysis unit and is returned in exactly the same state, except that the level of salts has been reduced. There is no need to modify the operation of the amine unit in any manner when the electrodialysis unit is on line. Electrodialysis units are also now available as fixed units for location that find it impractical to use a mobile unit.

AMINE RECLAMATION WITH MINIMAL OPERATIONAL IMPACT THROUGH ELECTRODIALYSIS

*Dr. Paul J. Parisi, ElectroSep Technologies Inc., St. Lambert, QC
Dr. Sid F. Bosen, The Dow Chemical Company, Houston, TX*

INTRODUCTION

The use of reclamation methods such as electrodialysis is becoming increasingly popular as a method of controlling heat stable amine salts (HSAS) in refinery and natural gas plant amine solutions. Up until recently proper control of the level of heat stable salts was not considered a priority for many operators. Salt levels were often well above recommended levels. HSAS were essentially non-controlled. The concentration was controlled by the often-important losses of amines from various points in the amine system and by the resultant high quantity of make-up amine that was added to the units.

The situation has been evolving because of a) the availability of reclamation technologies¹ b) increase scrutiny by government regulators c) the increase in the price of amine and d) the desire to improve operation of amine units.

The importance of HSAS in the operation of amine units have been well documented^{2,3,4}. HSAS levels play important roles in optimising the energy efficiency of amine units, are critical for the control of corrosion and are a factor in the amount of amine lost due to foaming.

Electrodialysis has been utilised since 1991 when The Union Carbide Corporation (now The Dow Chemical Company) introduced the UCARSEP™ mobile electrodialysis unit. It has been in continuous use since then. Recently smaller permanent units have been installed and process enhancements are being incorporated in both the mobile and permanent units.

Aqueous alkanolamine solutions are widely used to remove acid gas contaminants, usually H₂S and CO₂, from a variety of gas and liquid streams through reactive absorption".⁵ 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 H₂S 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 pKa 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:

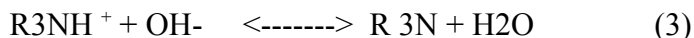


The introduction of any relatively strong and/or non-volatile acid into the amine system will thus lead to deactivation of the amine. The acids can be introduced via the process gas, makeup water, and entrained liquids or, in some instances depending upon the amine in question, through the oxidative degradation of the amine or sulfur species present in solution.

HSAS problems are particularly serious in the petroleum refining and coal gasification industries. Substantial levels of HSAS's, especially formate and thiocyanate, are often seen in the solutions used to treat the gas and liquid streams originating from the various catalytic and thermal processes prevalent in these industries. 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 chloride and sulfate, 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 fouling, and generally poor performance.

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 ⁶ that they can be effectively controlled by the addition of a stronger base such as 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, action is required to control the level salts. Two basic options are available: "purge and makeup", with the purged amine being either reclaimed off-site or disposed of, or amine reclamation such as electrodialysis.

Control of Heat Stable Amine Salt (HSAS) anions is an ongoing issue with amine plants that have low inventory losses. To avoid any confusion we define HSAS content of the amine solution as the amount of amine that is needed to neutralize the non-heat regenerable acids present in the amine solution. When stronger bases, e.g. NaOH, are added to the amine solution, the amount of amine required to neutralize the non-heat regenerable acids is reduced. This is easily measured in the laboratory by titration to pH 11.2 of a fully regenerated sample of the amine solution with a strong base. We report the HSAS content as weight percent amine.

The concept of neutralizing an amine solution with a strong base has been practiced for over 25 years. Neutralization provides several benefits. First the percentage of amine available in the solution for acid gas removal is increased since the non-heat regenerable acid content has been neutralized by another base. A second benefit is the risk of corrosion does not increase as the level of most of the usually encountered anions increases; an exception is chloride. Third, the amount of contaminant lost per unit volume of solution by natural routes, liquid loss, increases. Occasionally this equals the rate of ingress/formation and no further remedial action other than addition of strong base is required.

Many of the reported problems with neutralization, stress cracked flow lines, flow lines plugged, were most likely due to how the concept was put into practice rather than the concept itself. Proper design of the neutralizing process is essential as it is more difficult than “just adding a shovel full or two of flake sodium hydroxide to the sump”. Briefly, slow addition of suitably dilute base to a flowing stream with good mixing is all that is needed. Most plants can implement a neutralization program at minimal cost with a minimum amount of engineering provided by either plant or vendor personnel.

ELECTRODIALYSIS

PROCESS DESCRIPTION

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 semi-permeable 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/or cations can be extracted from one solution into another. This process has been adapted to remove heat stable anions from amine solutions. The process does not remove non-ionic impurities from amines, such as HEP and THEED.

Two variations of this process have been developed. The UCARSEP™⁶ originally developed by Union Carbide (now The Dow Chemical Company), both anions and cations are removed from the treated amine solution. In a modified process developed by ElectroSep Technologies Inc. only anions are removed from the amine solution. The use of one or the other would depend on the nature and type of salt incursion in the amine process.

In the UCARSEP process salts (anions and cations) are separated from the amine solution

and concentrated in an aqueous "brine" stream for disposal. 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 (A) and the cations move towards the cathode through the cation permeable membrane (B). On the other side of both membranes an aqueous brine (waste) 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. In Fig. 1 caustic is assumed to be the base utilized to neutralize the amine solution.

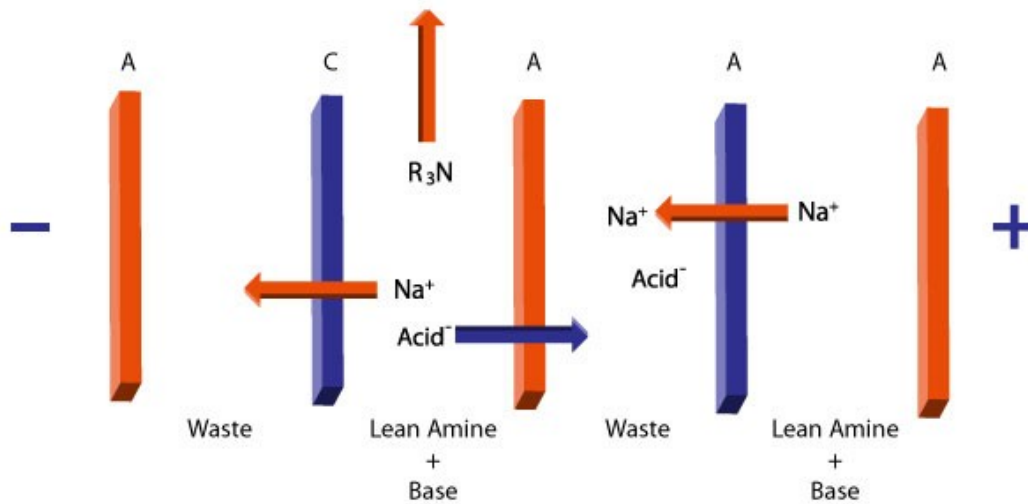


Fig. 1 - Principles of UCARSEP Electrodeialysis Process

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 all play an important role.

The ElectroSep process⁷ differs from the UCARSEP process in the manner in which the base is added to the amine. Instead of adding base directly to the amine solution, base is added into the electrodeialysis stack. Using this method only the base anion (OH⁻) for example is added to the amine. The base anion reacts directly with the protonated amine to produce a free base amine molecule (Eq. 3)

Electrical neutrality is maintained in the amine solution by removing one anion molecule for every base anion that is transferred into the amine solution.

The electro dialysis module or stack is composed of the same membranes and specially designed spacers as the UCARSEP stack. The only difference is the sequence of membranes, illustrated in Fig. 2.

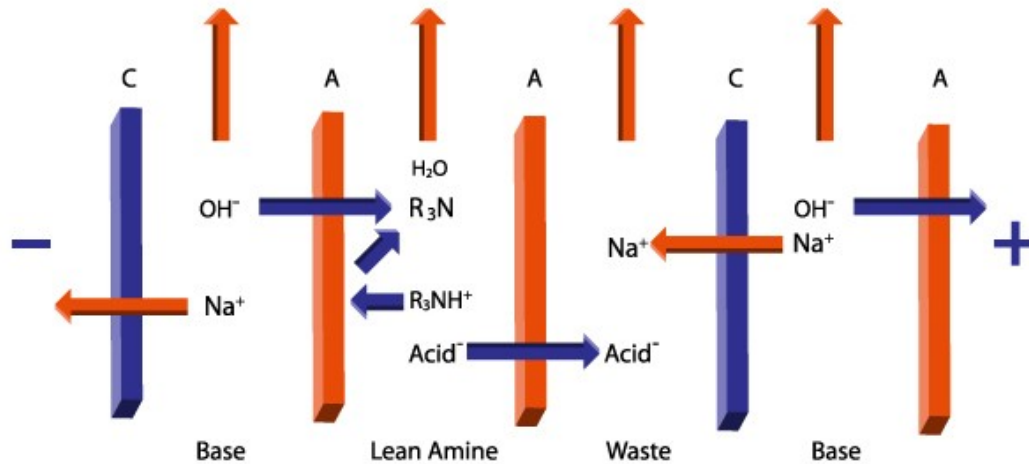


Fig. 2 – The ElectroSep Electro dialysis Process

In Fig. 2, caustic is used for illustrative purposes as the base.

For both electro dialysis processes the rate of salt removal is proportional to the operating current. The electro dialysis process is continuous. Once the unit is in operation, the process may operate for months with little to no change in operating conditions. Base consumption is almost exactly stoichiometric. As no excess base is required volume and quantity of waste generated is minimized. The amine that has been treated and is returned to the amine system is identical to the amine feed with the exception that the concentration of heat stable salts has been reduced. No dilution of the amine is required. There is no effect on the operation of the amine unit. The amine unit's operation does not have to be modified in any manner when the electro dialysis unit is in operation.

The UCARSEP (Fig. 3) process can be operated in two distinct configurations. In the first, the amine charge can be neutralized as the HSAS build-up over time. Once the level of neutralized salts reach a desired maximum level the salt are removed with the electro dialysis unit. This method is generally utilized at sites were there is no permanent electro dialysis unit. In these case the UCARSEP mobile unit (Fig. 4) is used to remove the salts. As the capacity of this unit is far higher than the rate of accumulation of salt the system salt concentration can be rapidly reduced.

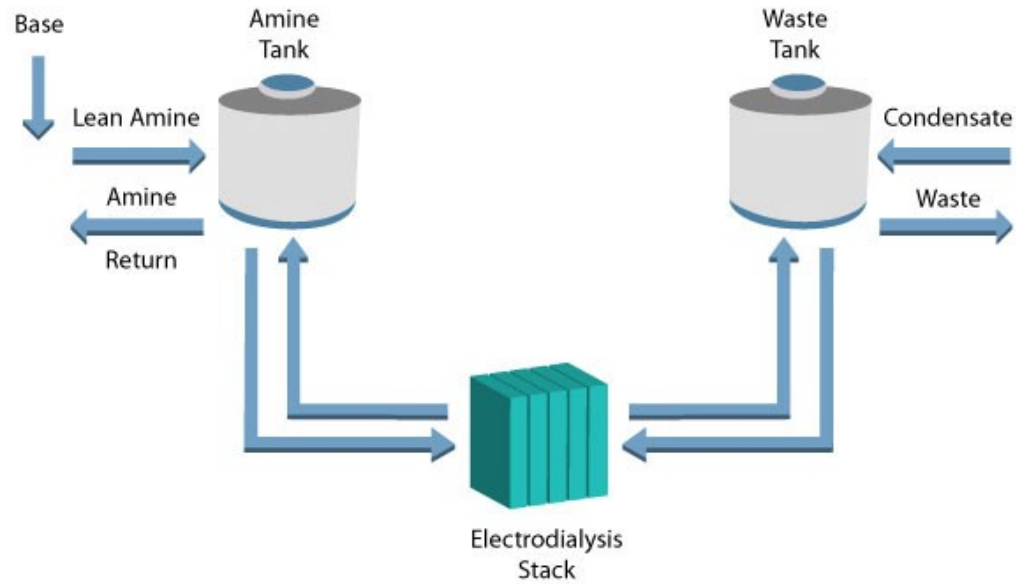


Fig. 3 - UCARSEP Process Flow Arrangement



Fig 4. – UCARSEP Mobile Electrodiolysis Unit

Base can also be added to the feed amine at the inlet of the electrodiolysis unit. The neutralized salts (base and heat stable anions) are then removed in the electrodiolysis unit. Very little residual base cation is returned to the amine system. This method is utilized for fixed units that are on site permanently.

In situations where no cations are to be removed the ElectroSep process (Fig. 5) can be utilized. In this process base is added directly to the electrodiolysis stack. Base anions are transferred to the amine solution by passing through a membrane. Base cations are transferred directly to the waste stream through a distinct membrane. No cations are added or removed from the amine stream. As there is no neutralization of the amine this process is

only practical for on site permanent units. This process while being more complex than the UCARSEP process does have the advantage of lower amine losses. Precautions must be made to avoid the slow build-up of cation in the amine unit.

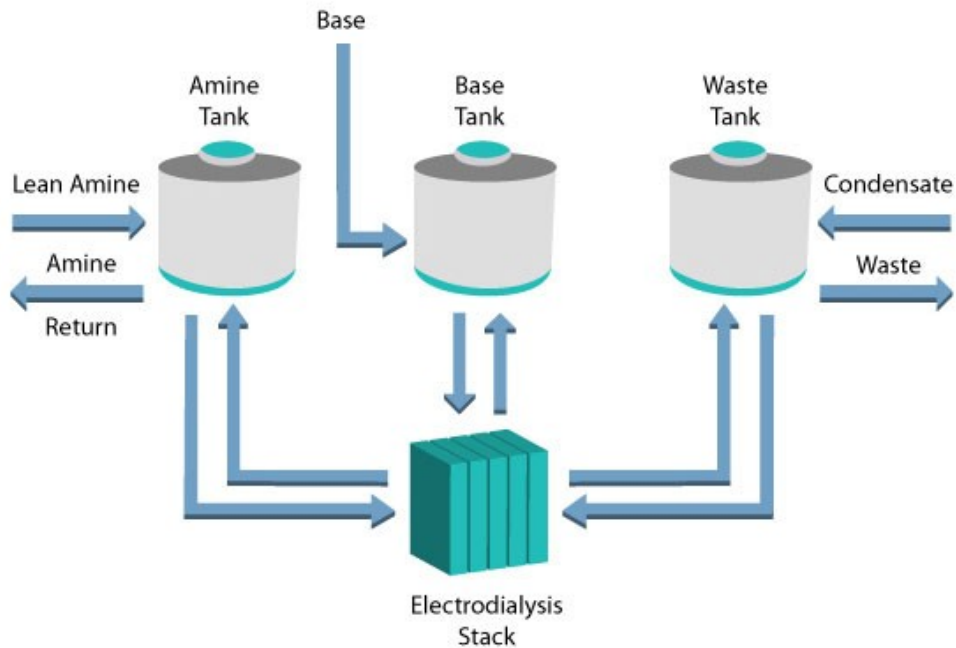


Fig. 5- ElectroSep Process Flow Arrangement

Operating Results

The UCARSEP mobile unit has been in operation for over 14 years. It has visited many refineries and gas plants throughout North America. The unit has proven to be reliable and when in operation does not require that the operation of the amine unit be modified in any manner. Set-up can often be completed in a single day. The only tie-ins are those shown in Fig. 4. No other tanks or modules are required. The waste stream in the vast majority of cases can be sent directly to the site's wastewater treatment system.

Fig. 6 is a shows typical operating on-stream time results. This performance was at a US Gulf Coast refinery.

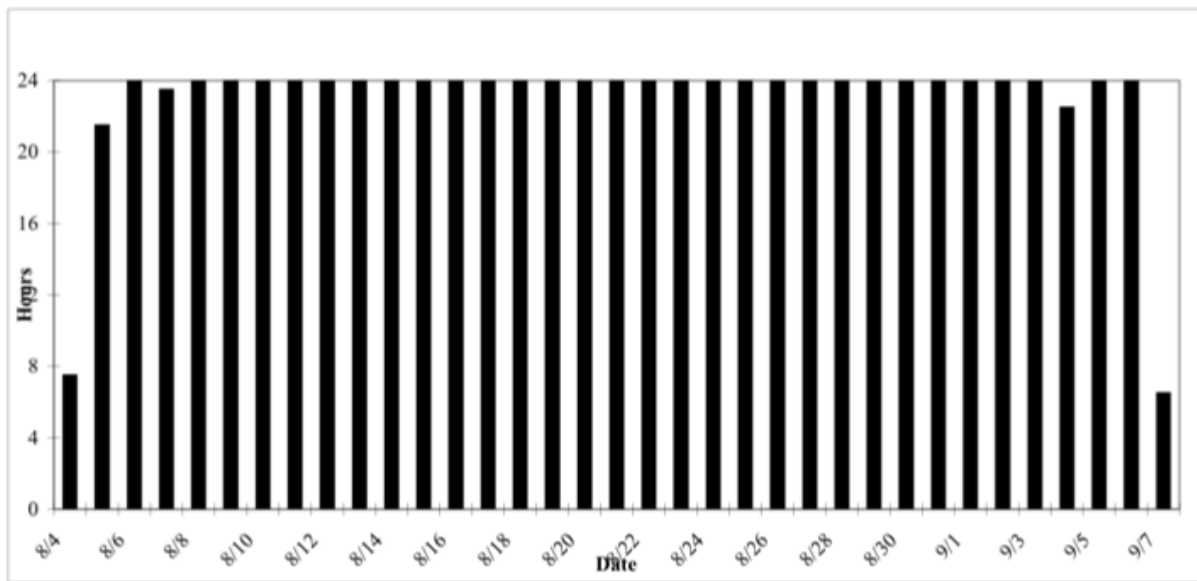


Fig. 6 - On Stream Time Results, UCARSEP Unit

The UCARSEP unit can be utilized to remove neutralized heat stable salts from pre-neutralized systems or the neutralization can be performed as the amine enters the process. Data taken from a Mid-Western refinery are given in Fig. 7. The total anion concentration and amine system sodium concentration over the period that the amine system was treated with the UCARSEP unit are given. Over a 12-day period total heat stable anion concentration was reduced from approximately 18,000 ppm to approximately 6,000 ppm. Lower anion concentrations could have been achieved, but would not have resulted in an improvement in system performance. As this was a refinery, the major anions present and removed were formate and thiocyanate.

The amine was neutralized at the tie-in point of the UCARSEP unit. The amine system sodium content before treatment commenced was just under 200 ppm. The sodium content in the amine increased slightly during the initial portion of the treatment to a maximum of 250 ppm and was reduced at the end of the treatment when the UCARSEP unit was operated for approximately 24 hours with no sodium addition. Final sodium content was just over 200 ppm, slightly higher than the initial concentration.

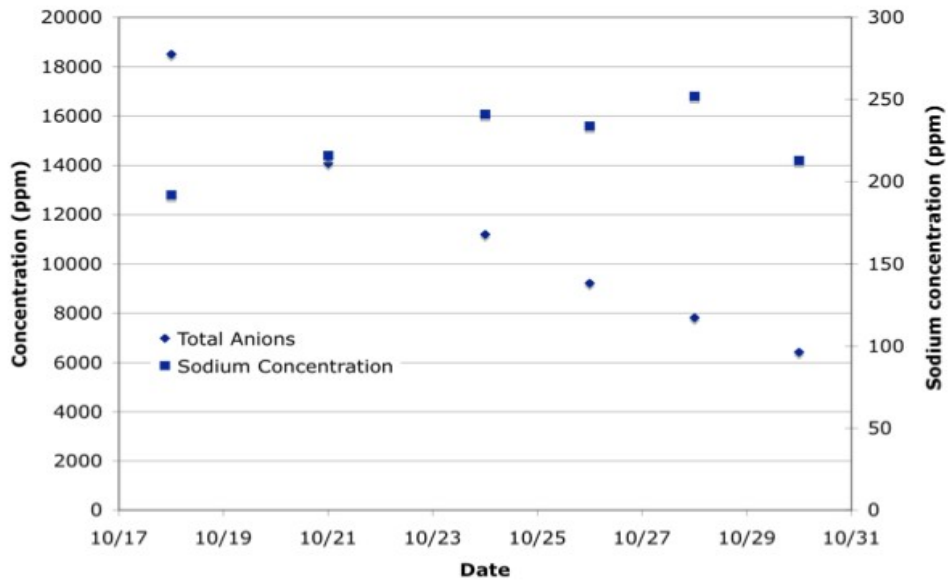


Fig. 7 – Anion and Sodium Concentration

In natural gas plants well treating fluids and anions in make-up water can enter the amine unit. Most anions are present in small concentrations and do not represent an operating problem. Chloride content though can be a major concern, as it can result in serious corrosion problems even at relatively low concentrations.

The UCARSEP unit has been utilized to remove chloride from amine streams where the overall anion concentration in itself did not represent any problems and was under control or low. A typical result is given in Fig. 8.

Total chloride content of the amine was reduced in a five day period from approximately 4,500 ppm to just under 500 ppm. Total heat stable anion concentration was reduced from 7,000 ppm to 1,200 ppm. These results also illustrated that electro dialysis is capable of reaching low overall anion concentrations if required.

Chloride anions are smaller than most other heat stable anions, such as for example formate, thiocyanate and sulfate. The relative removal rates of anions across the anionic membrane are dependent on the charge of the species and principally the molecular size and structure. Chloride anions are composed of a single atom and are less bulky than other heat stable amine anions. Chloride concentration was reduced by 89%, while overall heat stable anion concentration was reduced by 82%.

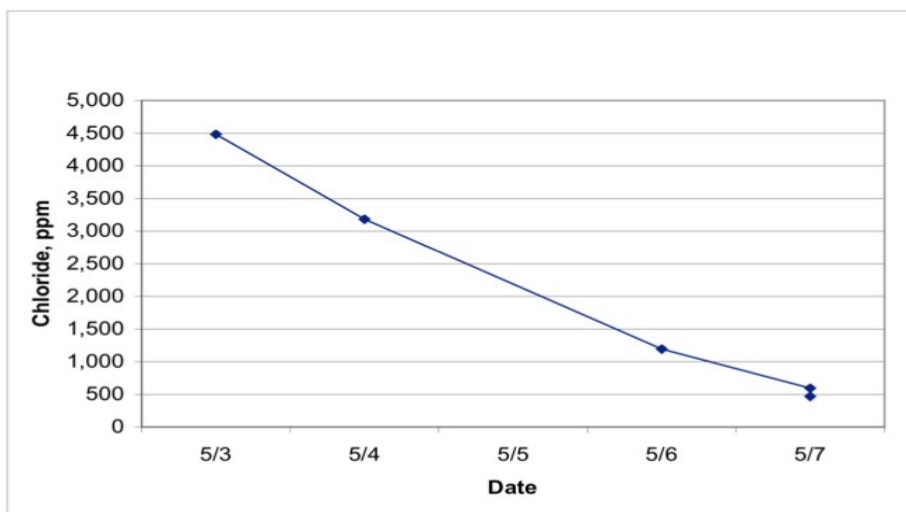


Fig. 8 – Chloride Removal from a Gas Plant Amine

Fig. 9 illustrates chloride removal at a Gulf Coast refinery. In this case initial chloride concentrations were approximately 1,200 ppm. Total heat stable anion concentrations were approximately 15,000 ppm. Chloride concentration was reduced to less than 100 ppm. Chloride levels of less than 50 ppm have been achieved. Overall heat stable anion concentration was reduced to less than 7,000 ppm, illustrating the preferential removal of the smaller chloride anion.

The UCARSEP process can also be utilized to remove cations from amine solutions. In situations when amine units were practicing amine reclamations methods that removed anions only, sodium concentrations often were found to increase over time. The UCARSEP unit was utilized to remove both sodium and heat stable anions. As the sodium atom is much smaller than the amine molecule, sodium removal is greatly favoured, over that of the amine molecule.

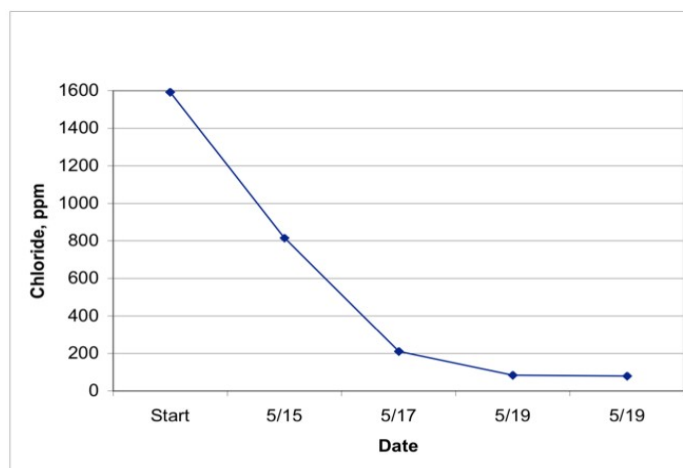


Fig. 9 – Chloride Removal from a Refinery Amine

The mobile unit is utilized primarily at sites that have pre-neutralized their amine system. Once the level of neutralized salts reaches a high level the unit mobile unit is reduces both anion and cation concentration in the amine.

This is illustrated in Figure 10. Both total anion and sodium concentrations are reduced at a large Gulf Coast Refinery. The primary heat stable anions are formate and thiocyanate.

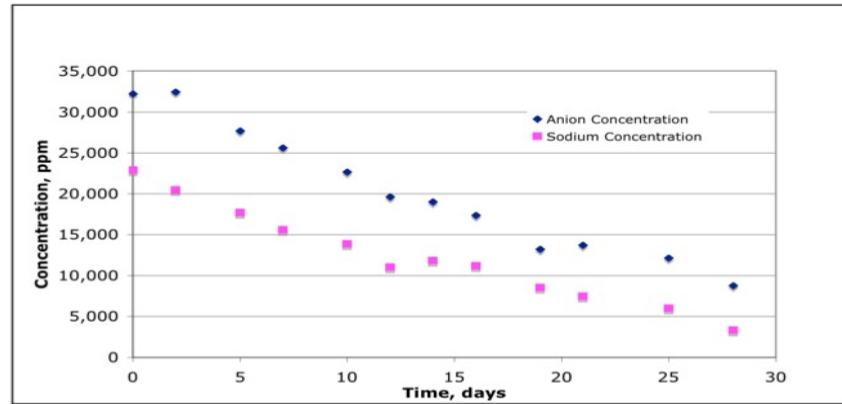


Fig. 10 – Anion and Cation Reduction in a Refinery

In an earlier paper Burns and Gregory¹ reported that typical amine losses represent approximately 2% of the amine inventory, which was slightly higher than some competing processes. This is the case when yard neutralization is practiced. When in-line neutralization is practiced amine losses are reduced significantly. Recent results when the amine feed is neutralized at the inlet of the unit show amine losses that are reduced by over 50%, resulting in overall amine recoveries in excess of 99%.

The ElectroSep process in which the amine is neutralized directly in the electro dialysis stack, result in another reduction of amine losses. Overall amine recoveries of 99.5% have been achieved.

CONCLUSIONS

Electrodialysis has proven over the past 14 years to be an effective method of amine heat stable salt control. Heat stable anions concentrations can be reduced to levels that are required for the proper operation of amine units.

Chloride, a particularly corrosive anion, is removed preferentially. Concentrations of less than 100 ppm have been achieved. In fixed units or when the mobile unit is operated with in-line neutralization, amine recoveries in excess of 99% can be achieved.

REFERENCES

1. D. Burns, R. A Gregory, "The UCARSEP™ Process For The On-Line Removal of Non-Regenerable Salts from Amine Units", Laurence Reid Gas Conditioning Conference, University of Oklahoma, Norman, OK, (1995)
2. P.C. Rooney, T.R. Bacon, and M.S. DuPart, "Effect of Heat Stable Salts on Solution Corrosivity of MDEA-Based Alkanolamine Plants", Laurence Reid Gas Conditioning Conference, University of Oklahoma, Norman, OK, (1997)
3. R. G. Asperger, H.J. Liu, J.W. Dean, "Accurate, Reproducible Measurement of Reduced Corrosion in Gas Treating Amine Systems After Application of Judicious Neutralization Techniques", AIChE Spring National Meeting, March (1995)
4. H.J. Liu, J.W. Dean, S.F. Bosen, "Neutralization Technology to Reduce Corrosion from Heat Stable Salts" NACE International, Corrosion Orlando, Florida March, (1995)
5. A.L. Kohl and F.C. Riesenfeld "Gas Purification", 4th ea., , Gulf Publishing Company, Houston, (1985), Chapter 2.
6. R. Gregory, M.F. Cohen, "Removal of Salt from Aqueous Alkanolamine Using an Electrodialysis Cell With an Ion Exchange Membrane" US Patent 5910611, (1999)
7. C. Byszewski, "Process For The Removal Of Heat Stable Amine Salts". US Patent 6517700, (2003)