



**Neutralization Technology to Reduce Corrosion
from Heat Stable Amine Salts**

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Abstract

Laboratory experiments have demonstrated the corrosivity of a contaminated N-methyldiethanolamine solution from a refinery can be reduced by adding caustic or a proprietary neutralizer. A model formic acid contaminated amine solution was shown to have similar behavior.

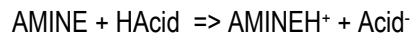
Laboratory studies have shown there is a definite decrease in corrosivity as the pH of the amine solutions increase. Three possible mechanisms for the observed pH corrosivity behavior are discussed.

Plant experience that demonstrates the usefulness of neutralization and a novel method for dissolved solids removal are presented.

Keywords: amine, alkanolamine, heat stable amine salts, corrosion, neutralization, reclamation, undissociated acid

Introduction

Amine solutions have been used for over 60 years to remove acid gas contaminants, usually H₂S or CO₂, by reactive absorption from a wide variety of process gas streams ¹, equation (1).



The acid gas is then desorbed from the amine solution in the regenerator by the reverse of equation (1). Corrosion in amine treating units has been a problem for plant operators and a topic for intensive study by corrosion engineers ²⁻⁵. Much attention has been given to the effects amine type, acid gas removal service and loadings and amine degradation products.

Heat stable amine salts (HSAS) have also been implicated in causing corrosion in amine gas treating units ⁴. HSAS are formed in the gas treating solution by the reaction of amine with acids, equation (1), forming salts that do not undergo the reverse of equation (1) under normal regenerator conditions. These acids mainly come from the process gas stream but can also be produced by oxidation of amines and other reactions in the amine solution. HSAS include formate, acetate, glycolate, propionate, oxalate, chloride, sulfate, thiosulfate, and thiocyanate. HSAS also impact the overall operating efficiency of the amine solution by reducing the amount of unprotonated amine. Only unprotonated amine will reactively absorb acid gases.

When corrosive or other detrimental amounts of HSAS accumulate in the solution remedial action must be taken. While there are a number of possible strategies, one that is easy to practice has been developed and incorporated into an overall Amine Management Program. This Amine Management Program includes neutralization of the HSAS with UCARSOL[®] DHM⁽¹⁾, a proprietary neutralizer. To lessen the possibility of operational problems when concentrations of anions reach levels high enough that solids precipitate, causing fouling, under deposit corrosion and erosion, the UCARSEP[®] Process^{(1) 6} can be used to reduce the concentration of anions to acceptable levels without a system shut down. This paper presents laboratory and plant data that demonstrate the concepts of the Amine Management Program neutralization of MDEA HSAS and removal of ash by proprietary electro dialysis.

Experimental Procedure

Test Solutions

Reagent grade chemicals were used when possible. A used proprietary N-ethyl-diethanolamine (MDEA) based amine (field) solution was obtained from a refinery system treating a cracked LPG stream. The chemical analysis is given in Table 1. The model amine solution was prepared gravimetrically to yield the following; 35 (wt%) virgin proprietary MDEA base amine, 5 wt% formic acid and balance liquid chromatography grade water. Both field and model amine solutions were neutralized to different HSAS levels with either 50 wt% sodium hydroxide or the neutralizer. Hydrogen sulfide was purchased as a mixture, 1.98 vol. % in nitrogen, from a specialty gas supplier. Hydrogen sulfide content of solutions was determined by iodimetric titration ⁷ and reported as mole per mol ratio to amine.

Corrosion Coupon Tests

Corrosion tests were conducted in 1 liter 304 stainless steel (UNS S31600)⁽²⁾ autoclaves equipped with an agitator and rated for 12.4 MPa (1800 psi) at 121°C (250°F) solution temperature. Autoclaves that previously contained sulfide solutions were not used for corrosion rate measurements of solutions that did not contain sulfide. Four mild steel (UNS G1018)⁽²⁾ corrosion coupons, 1.27 cm (0.5 in) X 2.54 cm (1 in), were installed at the bottom of the cell and isolated with Teflon holders to avoid any metal contact. The coupons were exposed to approximately 500 mls of test solution.

Once coupons and the test solution were in place, the autoclave was sealed. Atmospheric oxygen was removed by filling the autoclave with nitrogen to 138 kPag (20 psig) and venting to atmospheric pressure a total of five times, followed by pressuring to 690 kPag (100 psig) for one hour to ensure complete seal. Pressure was then released to atmospheric pressure prior to heating the test solution. When H₂S was needed, it was added after the pressure test with solution agitation to the desired loading, as determined by iodimetric titration. No additional fluid was added to the autoclave to make up for the small amount of liquid removed for analysis. The agitator was turned on at 200 rpm and heating initiated to a final temperature of 121°C (250°F) which was maintained for the 14 day test period. At the end of each experiment the autoclave was cooled to room temperature, and a N₂ purge applied before the autoclave was opened. Solution pH was measured at room temperature using an Orion Model 610 pH meter and an Orion combination glass electrode. Weight loss corrosion rates from the coupons were determined by following ASTM G1-90 Standard Practice ⁸ by the chemical cleaning option. Reported corrosion rates are the average of three or four individual coupon measurements.

Some of the coupons were analyzed by Fourier Transform Infrared Spectroscopy (FTIR), Energy Dispersive X-ray Spectroscopy (EDS), and Electron Spectroscopy for Chemical Analysis (ESCA) to identify surface scales.

Results

Model Solvent vs. Field Solvent

Similarity with low H₂S: Figure 1 gives corrosion rates versus HSAS content of the field solution and the model amine solutions without added H₂S. Both amines show very consistent results that corrosion rates decrease with decreased HSAS. At 12% HSAS the corrosion rate is 406 μm/y (16 mpy), at 9-10% HSAS the rate drops to 305 μm/y (12 mpy) and when neutralized to 6% or lower the rate is further reduced to 25 μm/y (1 mpy) or lower. Both the field and model amine solutions exhibit similar behavior.

Similarity with H₂S: The effect of H₂S loadings at a constant 12% formate HSAS level in field and model amine solutions is given in Figure 2. Again the behavior of both amine solutions is very similar.

Results Cont.

At 0 to 0.002 mole/mole H₂S loadings corrosion rates for both are from 381-406 μm/y (15-16 mpy), 0.01 mole/mole H₂S loading corrosion rates are reduced to 127-152 μm/y (5-6 mpy) and at 0.05 mole/mole H₂S loading corrosion rates fall to 51-76 μm/y (2-3 mpy). The reduction of corrosion rates with increased H₂S loadings indicates the iron sulfide corrosion product on the metal surface, as determined by FTIR, EDS, and ESCA, inhibits corrosion under these test conditions for both the field and model amine solutions.

The model amine shows very good quantitative consistency with the field amine, both having 12% formate HSAS, see Table 1. This suggests that the remaining 20% of HSAS in the field amine solution does not significantly contribute to the corrosion rate.

Effect of pH: Corrosion rates versus solution pH for the model amine with and without H₂S are given in Figure 3. Corrosion rates increase as solution pH values decrease, whether H₂S is present or not. It appears that as long as the amine solution has a pH above 9.5-9.6, corrosion rates are minimized. This also suggests that when these low acid gas content high HSAS amine solutions reactively absorb acid gases, the corrosivity of the solution will increase due to the lower pH of the rich amine solution.

Caution should be used in trying to generalize from this specific result to systems with different amines, anions, temperatures and concentrations. Work is in progress in our laboratories that will attempt to address these issues in a broader context.

Possible Mechanisms

The variation in corrosion rate observed as the amine solution pH is changed by adding alkali must be the result of either: 1) formation of a passivating reaction product film, or 2) change in cathodic polarization. Since iron formate salts are soluble, these can't be responsible for passivation. Other possibilities are discussed below.

Iron oxide film hypothesis: The formation of a protective iron oxide film is generally accepted as the most common mechanism for steel passivation. Usually conditions exist where an inhibitor is present that results in the formation of an insoluble ferrous salt. While amines don't form insoluble iron salts and the experiments excluded both inhibitors and oxygen, the formation of a protective oxide film can not be rigorously as there is a significant quantity of water present.

Weakened iron sulfide film hypothesis: Two papers^{9,10} discuss the inhibitive properties of some forms of iron sulfide. Both conclude that some forms of iron sulfide solids are more protective than others and in the aqueous systems worked with, claim the wrong kind of iron sulfide forms are produced when solution pH is above 6.2 and below 8.8-9.5. Since the cited work was done in purely aqueous media, it is difficult to completely accept that this is also the case in an amine solution. A major flaw of this hypothesis is the behavior of the model amine solutions that contain no sulfide.

Undissociated acid hypothesis: General acid corrosion of mild steel will be considered here and since the most common material of construction in amine units in refineries is mild steel, only corrosion iron will be considered.

Corrosion of mild steel in acidic (pH <7) aqueous media can be described by the following reactions:

Anode	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^{-}$	(2)
Cathode	$2\text{HX} + 2\text{e}^{-} \rightarrow \text{H}_2 + 2\text{X}^{-}$	(3)
Net Reaction	$\text{Fe} + 2\text{HX} \rightarrow \text{FeX}_2 + \text{H}_2$	(4)

Results cont.

In general, the aggressiveness of a medium relates to the strength of the acid HX, since it tends to affect the degree of cathodic polarization. In amine wetted areas of the scrubbing process, acid corrosion should not occur since the pH is always alkaline, and indeed in uncontaminated systems this is the case. However, some heat stable amine salts, such as formates, are slightly regenerable to the undissociated acid and amine at high temperatures. If this occurs especially under deposits or in crevices in heat transfer areas, acid corrosion may be significant.

In a gas treating solution, it can be shown from the definitions of the two equilibria involved that at a given temperature, the concentration of undissociated HA produced by a heat stable amine salt AmH^+A^- is:

$$[\text{HA}] = \frac{K_1}{K_2} \frac{[\text{AmH}^+]}{[\text{Am}]} [\text{A}^-] \quad (5)$$

where [] denotes concentration in moles/liter
HA is undissociated acid
 K_1 is the acid dissociation equilibrium constant for the protonated amine
 K_2 is the acid dissociation constant of HA
 AmH^+ is protonated amine
Am is free base amine
 A^- is the anion from acid HA

For the case of 5 wt% MDEA as the formate salt in 30 wt% MDEA, at a stripper temperature of 121°C (250°F) with no acid gas loading, the undissociated formic acid is calculated as (using 1.05 gm/l as the density and 119 as the molecular weight for MDEA):

$$\begin{aligned} [\text{FormicAcid}] &= \frac{10^{-7}}{1.07 \times 10^{-4}} \times \frac{0.05}{0.30} \times \frac{1050 \times 0.05}{119} \\ &= 6.87 \times 10^{-5} \text{ molar} \\ &= 3 \text{ ppm wt} \end{aligned}$$

While this may not seem high, in the context of corrosion inhibitors being effective at 20 ppm, it may be sufficient to produce corrosion. If corrosion does consume undissociated acid, it is immediately replaced by re-establishment of the equilibrium so that corrosion can proceed continuously.

Using the above relationships, amounts of undissociated formic acid were calculated and are plotted versus corrosion rate in Figure 4. The data for the field and model solvents were combined and categorized on whether or not sulfide was present. As was seen earlier, sulfide inhibits corrosion under these test conditions.

Work is continuing in our laboratories on other HSAS anions to further test these hypotheses. If the undissociated acid hypothesis is correct then other organic and inorganic acids with different acid pKa's should have corrosion rate versus solution pH profiles that are similar to the one obtained for formic acid but have different pHs where corrosion rates sharply increase. These pHs should also follow the same trend as the pKa of the acid. If the pH where corrosion rates rapidly increase is roughly the same for these other HSAS, then the mechanism has to be related to weakening of the protective film(s).

Results cont.

Neutralization Advantages

Comparison between the neutralizing agent and caustic neutralization: No discernible differences in corrosion rates were observed when the two amine solutions were neutralized with either caustic or the neutralizer. What has been observed in field practice is that plant personnel using caustic can more easily over neutralize the amine solution which results in poorer acid gas removal and in some cases rapid and catastrophic production of solids.

Both caustic and the neutralizer increase the amount of amine available in the circulated amine solution for acid gas removal.

The neutralizing agent was used to neutralize heat stable amine salts of an MDEA-based solvent in a second refinery. Figures 5 and 6 shows the before and after effects of neutralization on some operational measurements such as heat exchanger efficiency, pressure drop on tube sides of heat exchanger, and pressure drop in the absorber in a six month time period. Without using neutralization (Figure 5), the system experienced difficulties in maintaining steady operation conditions. With neutralization (Figure 6), the operation upsets were drastically reduced. Table 2 also gives the number of times remedial action (washing heat exchangers, absorber trays, and changing filters) was needed to correct an operational problem before and after neutralization with the neutralizing agent at this refinery. Remedial action was reduced after neutralization was implemented.

Electrodialysis Process

When the inorganic salts resulting from neutralization (not amine salts) accumulate to a certain level, fouling and foaming may occur due to solids precipitation. A clean-up of the solvent is required. There are a number of choices available to remove excessive amounts of dissolved solids such as, purge and make up, amine solution change out, ion exchange and electrodialysis.

Electrodialysis technology: The electrodialysis process uses specially selected ion exchange membranes arranged in an electric field to remove electrically charged species from the solution. Two types of ion exchange membranes are used simultaneously - one type selective to cations such as sodium, and potassium; the other type selective to anions such as chloride, nitrate, formate, acetate, oxalate, thiocyanate, phosphate, citrate, and sulfate. Figure 7 illustrates the separation of cations and anions by means of selective ion transport across permeable membranes under the influence of an electrical potential. Cation or anion permeable membranes allow concentration of the impurities in a "waste brine" stream.

HSAS have an amine molecule tied up in the protonated cation form. When salts are removed by this commercial process, the amine can be also removed. This increases the amount of amine lost to the brine solution. Ash salts are salts that have an inorganic cation. These salts are formed by adding the neutralizing agent or caustic to HSAS (neutralization) to release amine. Thus it is desirable to neutralize all HSAS prior to electrodialysis.

Advantages of the electrodialysis process: The electrodialysis process will typically be applied after heat stable amine salts neutralization with the neutralizing agent or caustic has resulted in ash levels of over 5 wt%. This process has successfully removed 10 wt% heat stable amine salts/ash salts down to less than 0.5 wt%.

Results cont.

Several features and advantages of this electro dialysis process are indicated as follow:

- Very low energy costs and solvent losses as compared to other separation technologies such as ion exchange and vacuum thermal distillation.
- The on-line process technology can be applied to a slipstream of the operating solution so that the amine unit does not have to be shut down while reclaiming.
- The flow to the electro dialysis unit is so small that it will not affect the regular operation conditions in the amine unit.

Case study of the electro dialysis process: Table 3 shows changes in solution analysis of an MDEA-based solvent with electro dialysis treatment. Formate was reduced from 58,000 ppm to 10,500 ppm; acetate from 4,000 to 2,400 ppm; thiocyanate from 21,500 to 900 ppm. The total anions were reduced from 83,000 ppm to only 13,800 ppm. Total ash salts were reduced from 11.6% to 1.6%. Heat stable amine salts remained almost constant and low enough to not cause any observed unit corrosion.

Conclusions

An Amine Management Program to resolve corrosion issues of HSAS in MDEA based amine gas treating units has been developed and demonstrated. Laboratory studies have shown neutralization of formic acid HSAS reduces the corrosivity of MDEA based amine solutions. Plant experience indicates the laboratory data can be extended to plant situations with MDEA base amine solutions. A novel method for removal of accumulated inorganic salts (ash) has also been presented.

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Table 1
Composition of Field MDEA Amine Solution Before Neutralization and HSAS
Contribution of Each Anion Present.

Parameter	Unit of Measurement	Found	% HSAS ^(a) Equivalent
Amine	Weight %	35	
H ₂ S	mol/mol	.002	
Formate	Ppmw	45,000	11.88
Acetate	Ppmw	5,000	1.01
Chloride	Ppmw	200	0.07
Sulfate	Ppmw	100	0.02
Oxalate	Ppmw	100	0.02
Thiosulfate	Ppmw	600	0.12
Thiocyanate	Ppmw	3,500	0.72
Total anion	Ppmw	54,500	
Total HSAS	Weight % ^(a)		13.84

(a) HSAS expressed as wt% MDEA

Table 2.
Neutralization of the Second Refinery MDEA Base Solution with the Neutralizing
Agent

Type of remedial action	6 months prior to neutralization	6 months after neutralization
Number of heat exchanger water washes	4	0
Number of absorber tray water washes	10	0
Number of particulate filter changes	16	5

Table 3
Plant Trial of Electrodialysis⁶ Salt Removal

	Before treatment	After treatment
Formate ppmw	57,747	10,474
Acetate ppmw	3,789	2,406
Thiocyanate ppmw	21,462	883
Total Anions ppmw	82,998	13,763
HSAS %	1.6	2.4
Total ash	11.6	1.6

Figure 1
Effect of formate HSAS on corrosion rate for field and model MDEA solutions

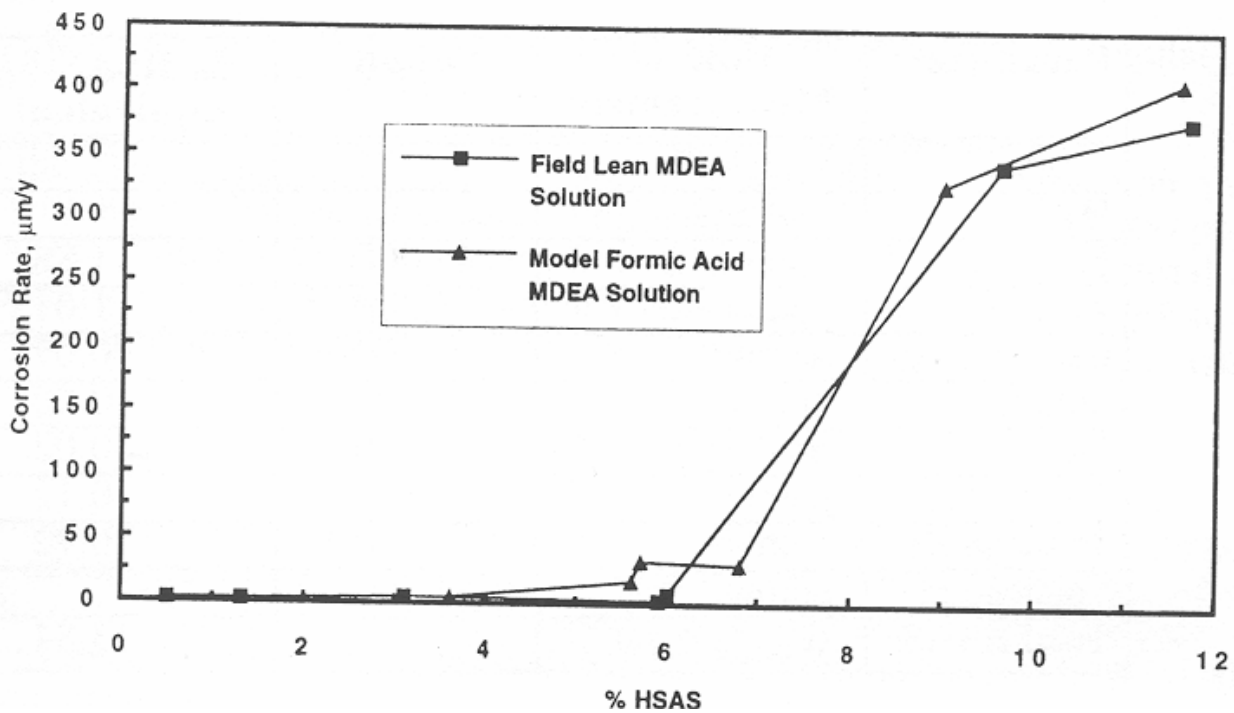


Figure 2
Effect of H₂S loading on field and model MDEA solution corrosion rates

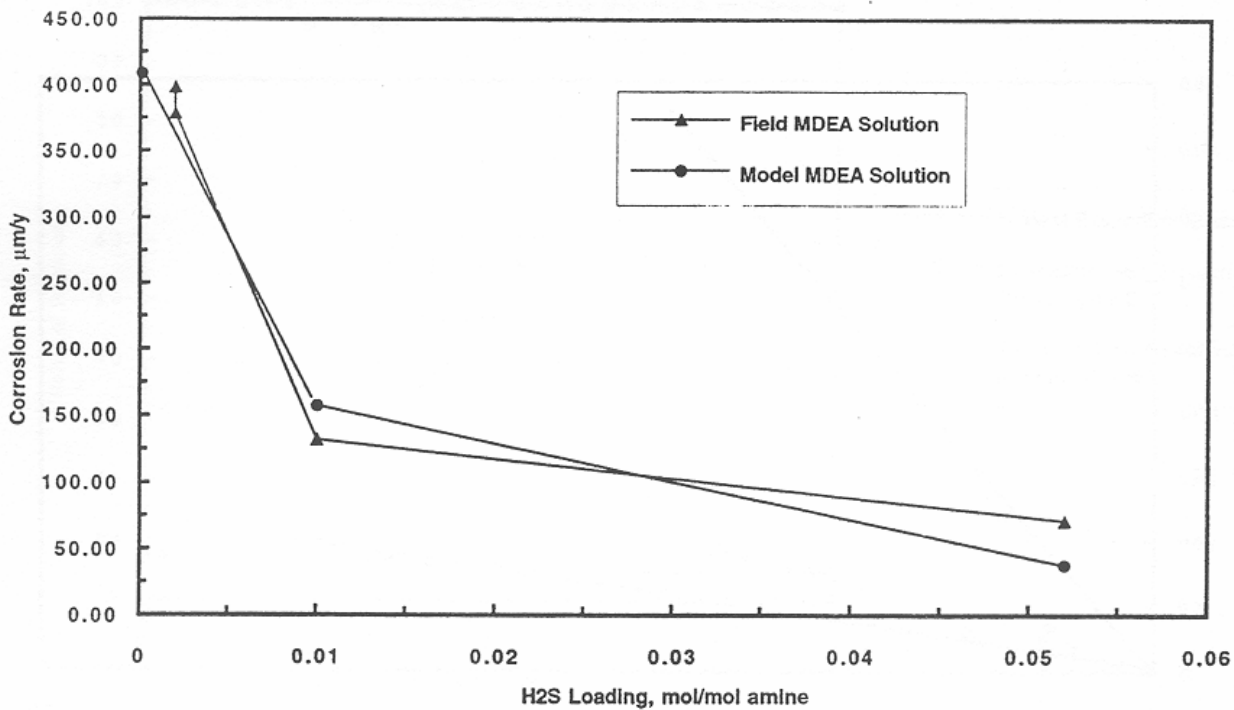


Figure 3
Effect of H₂S on model MDEA solution rate versus room temperature pH

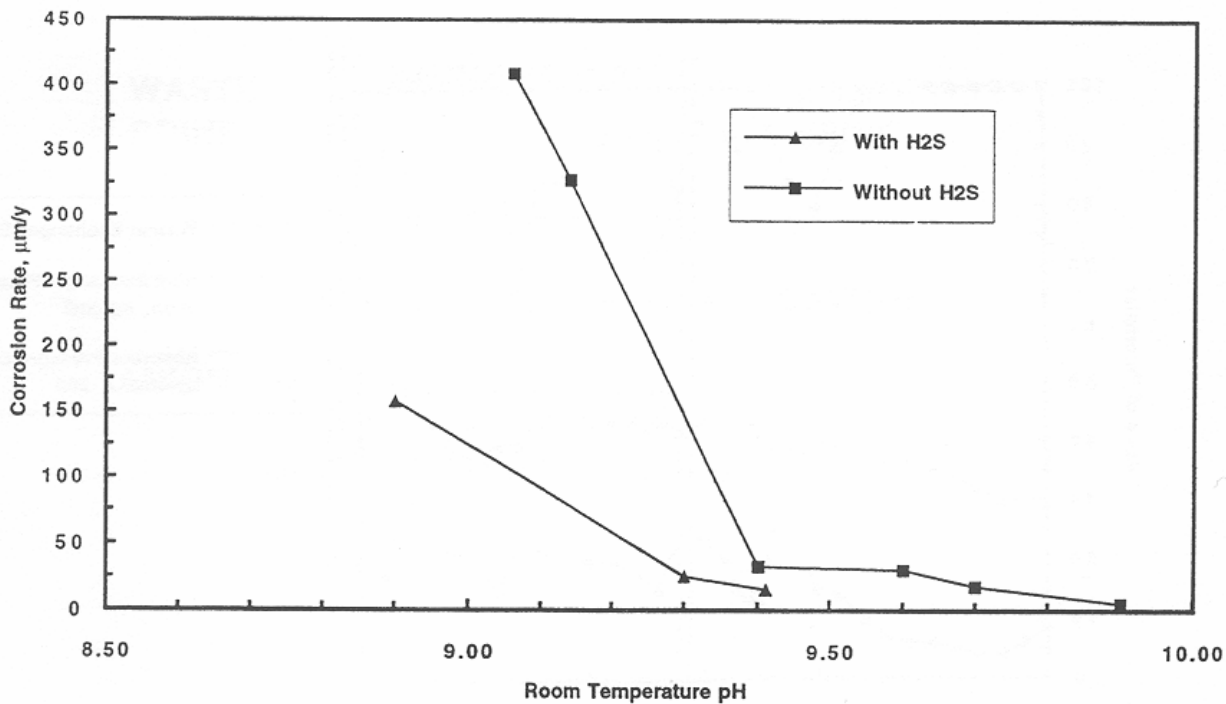


Figure 4
Relationship between corrosion rates and calculated undissociated formic content of MDEA solutions with and without H₂S present.

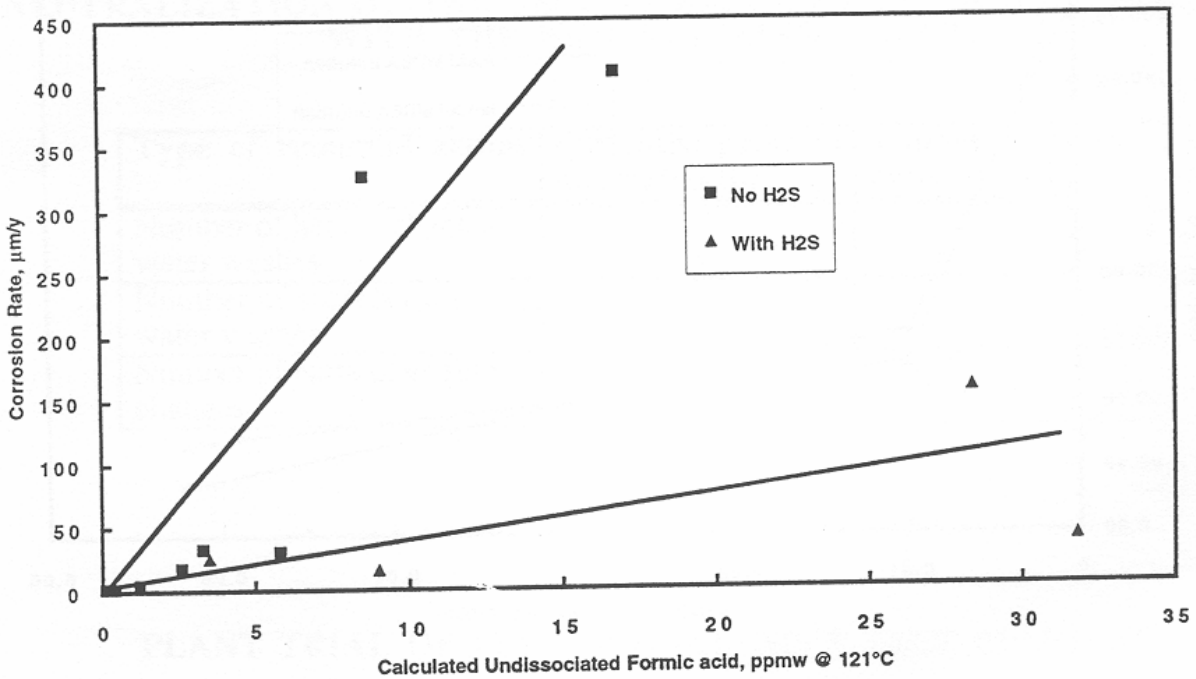


Figure 5
Plant operating parameters versus time before neutralization

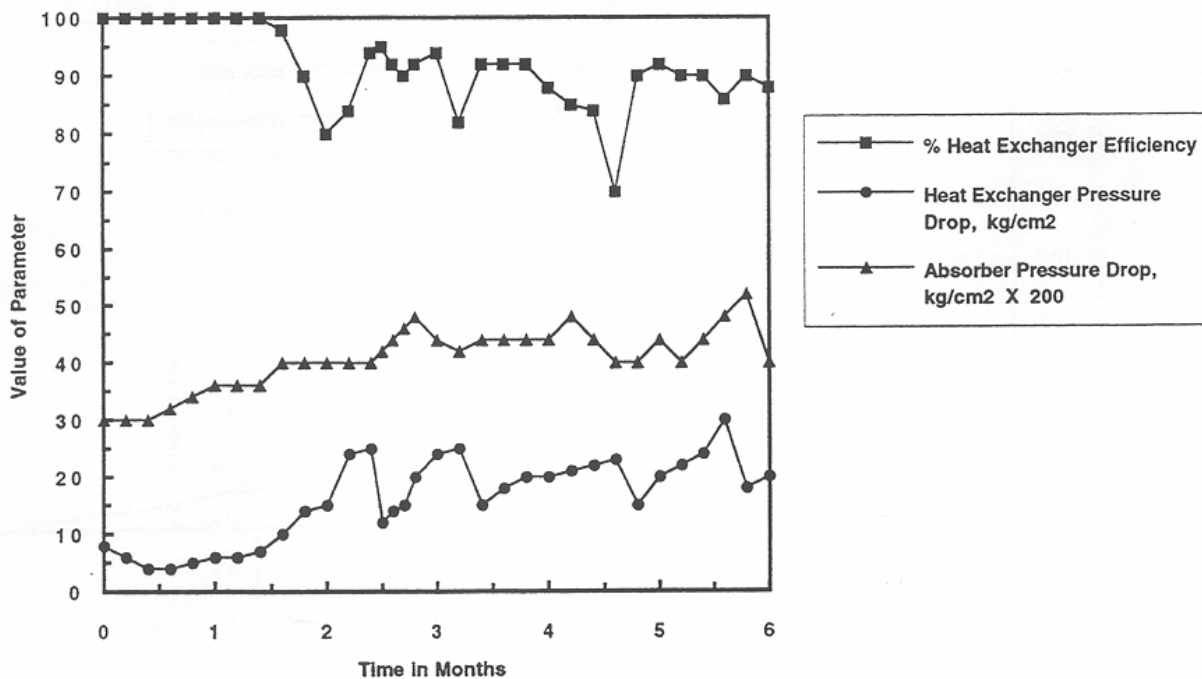


Figure 6
Plant operating parameters versus time after neutralization with the neutralizing agent

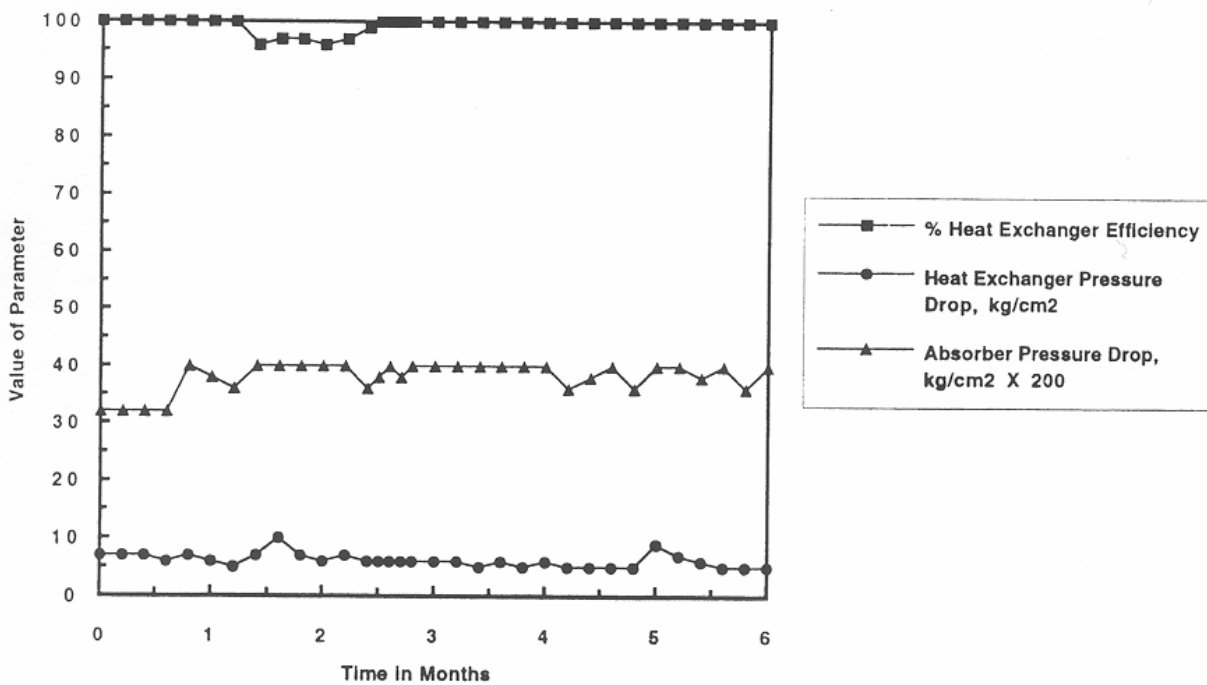
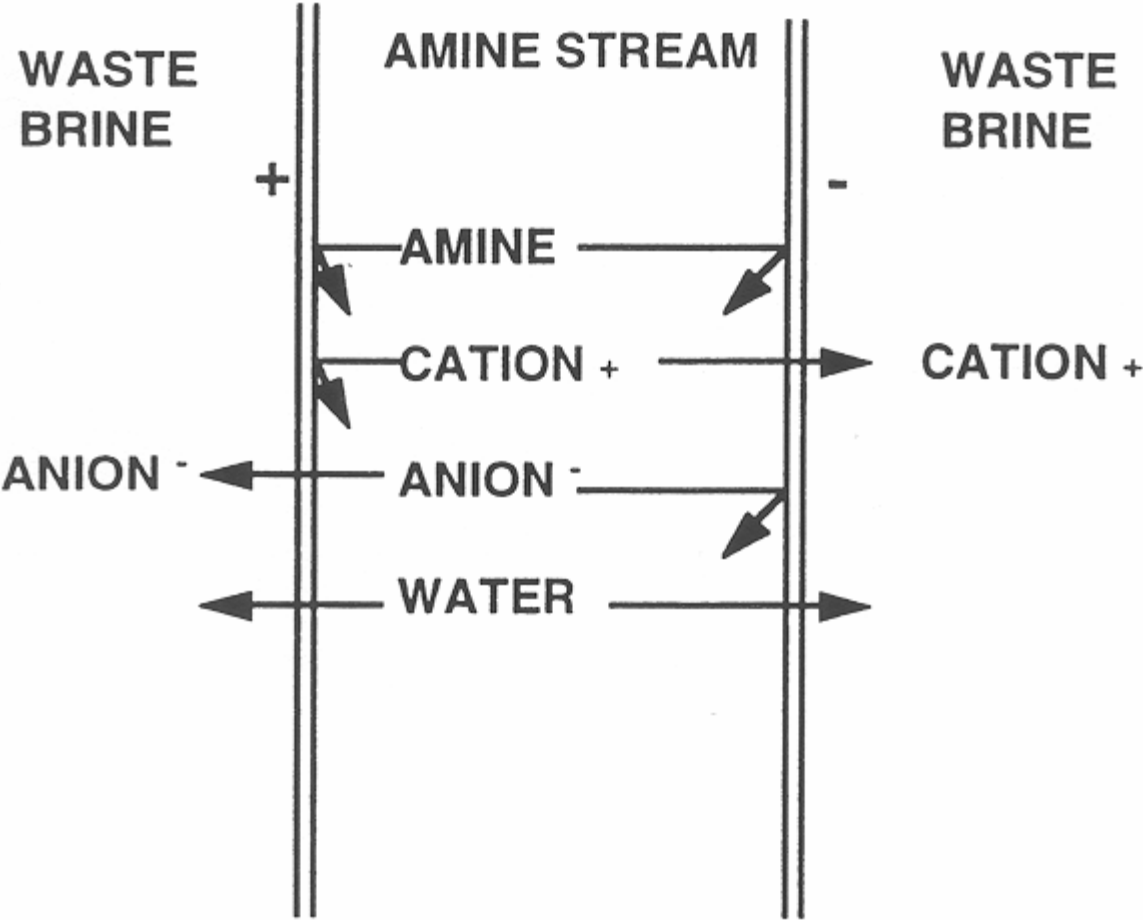


Figure 7
Schematic of the electro dialysis cell ⁶



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