Corrosion Management in Gas Treating Plants (GTP's): Comparison between Corrosion Rate of DEA and MDEA A Case Study in Sour Gas Refinery

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Abstract

In the past years with increasing gas demand, the possibility of debottlenecking and capacity increasing for the sweetening units were focused by replacing of Methyl Di-Ethanol Amine (MDEA) instead of Di-Ethanol Amine (DEA). During years, corrosion study in DEA and MDEA was done in sour gas treating plant. Corrosion subject in alkanolamine gas treatment plants has a special importance. Plant economics are negatively impacted by the loss of revenue due to unplanned corrosion caused plant outages and the cost for repair of the corrosion damages. In this research corrosion rate for lines and equipments in amine paths was investigated. Also the amount of heat stable salt (HSS) formation and amine degradation products were compared for DEA 34Wt% and MDEA 45Wt%. The rate of contaminations build up, especially amount of HSS and degradation products in different amines discussed, HSS anions increase the corrosive nature of the solvent, so removal of HSS; play a critical role in optimizing MDEA system performance and unit reliability. Moreover, some products as MDEA contaminants will be formed from degradation of the MDEA molecules during unit operations. The level of such contaminants must be monitor and control in MDEA system. Therefore, methods used to control and reduce impurities will investigate. Advantages and disadvantages of each method will discussed, the operational results achieved from amine treatment package including carbon bed, resin beds etc., that designed and built by ourselves to control the quality of amine during the operation an how useful was that, to reduce corrosion and foaming rate of amine, benefits and saving system created, will discussed in detail.

Keywords
Corrosion Management, Plant economics, Gas Treating plant, Contaminant removal

Introduction

In the past years with increasing gas demand, the possibility of debottlenecking and capacity increasing for the sweetening units were focused by replacing of MDEA instead of DEA. Sweetening solvent successfully was changed from DEA 34Wt% to MDEA 45Wt% in 2004[1] after 20 years experience. During years, corrosion study in DEA and MDEA was done in sour gas treating plant. Corrosion subject in alkanolamine gas treatment plants has a special importance. Plant economics are negatively impacted by the loss of revenue due to unplanned corrosion caused plant outages and the cost for repair of the corrosion damages. Many of the causes of amine plant corrosion have been identified and reported earlier Based on this experience (Bonis et al. 2004, Bitch et al. 1996, Rooney et al. 2000, Dupart et al. 1993).The design and operating practices of gas treating units are constantly updated and upgraded. Among those factors identified are choice of amine, acid gas, acid gas ratio, contaminants and operating conditions.

In this article has been tried to investigate comparative results of corrosion rate for lines and equipments in amine paths. Also the amount of heat stable salt formation and amine degradation products were compared for DEA 34Wt% and MDEA 45Wt%. The rate of contaminations build up, especially amount of Heat Stable Salts (HSS) and degradation products in different amines (DEA and MDEA) discussed, HSS are acid anions with a stronger acid strength than the acid gases. These anions bind to the useable amine and making amine unavailable for the acid gas absorption. HSS anions increase the corrosive nature of the solvent, so removal of heat stable salts; play a critical role in optimizing MDEA system performance and unit reliability. Moreover, some products as MDEA contaminants will be formed from degradation of the MDEA molecules during unit operations (such as DEA, MMEA). The level of such contaminants must be monitor and control in MDEA system. Therefore, methods used to control and reduce impurities will investigate. Advantages and disadvantages of each method will discussed, the operational results achieved from amine treatment package including carbon bed, resin beds etc. that designed and built by ourselves to control the quality of amine during the operation an how useful was that, to reduce corrosion and foaming rate of amine, benefits and saving system created, will discussed in detail.

Materials and Methods

Figure (1) shows main areas of an amine unitthat, the rate of corrosion must be measured by different methods of corrosion monitoring.In GTPcoupon corrosion testing system has been used during previous years, the rate of corrosion in the main equipment includes: Reboilers, lean/rich heat exchangers, pumps, contactors, regenerators and amine circulation paths were measured and analyzed formore than one hundred points for both DEA and MDEA solutions at the similar operating conditions.Laboratory analysis of the operating MDEA solution (after 18- 24 months of operation) was done by gas chromatography to determine the amount of HSS.

Performance and effectiveness of an anionic resin sample was studied in reducing HSS under laboratory conditions. In this work, an ionic resin bed was created and then 500 ml of amine solutions (about two years had been in operation) was passed through the resin bed; after passing each 100 ml of amine solution, the amount of chloride, acetate, formate and sulfate was measured by gas chromatography. Therefore, based on the results, the end of desalting operation and the ionic resin capacity was determined.

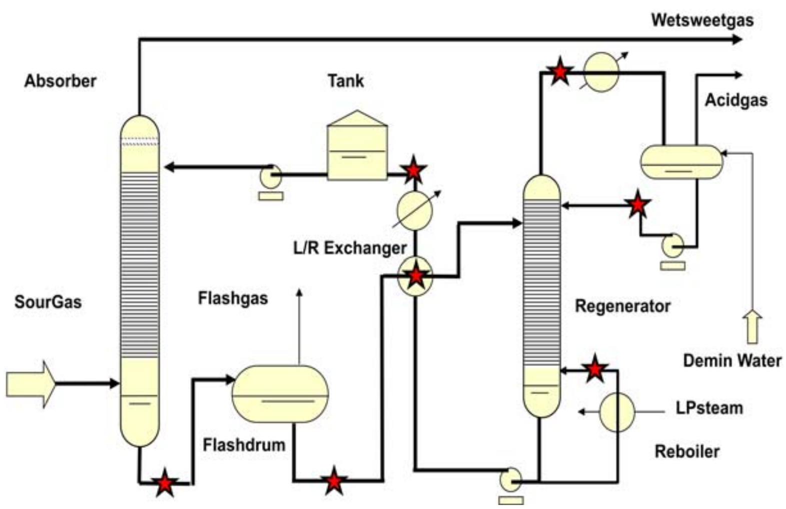

Figure 1: Main corrosion areas in a schematic amine process flow diagram

As we know, key factors including: type of amine and concentration, amine loading, temperature, contaminants , rate of oxygen that can be entered and inadequate design (too high flow rates) have influenced on corrosion in amine plants (Kohl 1997). Heat stable salts and degradation products play a main role on corrosion problems. The heat stable salts are essentially the reaction products of alkanolamines and the acids stronger than hydrogen sulfide (H_2S) and carbon dioxide (CO_2). These acids are usually introduced to the amine units with makeup water and feed gas streams or generated within the units by undergoing the chemical reactions with contaminants such as oxygen (O_2), carbon monoxide (CO), and sulfur dioxide (SO_2) .Table 1 shows5 common sources of anions and it is a guideline for maximum tolerable amount of HSAS in amine solution, as a rule of thumb; HSS shouldn't exceed 10% of the amine concentration (Shielan et al. 2008).

By nature, the heat-stable salts are non-regenerable under solvent regeneration condition. As such, they remain and accumulate in the absorbent throughout the plant. In this research, samples of amine with different life time were analyzed and measured the amount of contaminants for DEA and MDEA solutions. Then the effects of contaminants were evaluated on corrosion. Finally for reducing impurities, amine purification package designed and built in GTP.

Table 1: Heat stable salts, common sources for the anion

Anions	Source
Chloride	Makeup water/brine with inlet gas
Nitrate/Nitrite	Makeup water/corrosion inhibitors
Sulfate/sulfite	Sulfur species oxidation products
Thiosulfate	$2H_2S + O_2 = S_2O_3 + 2H_2O$/component in gas
Formate/oxalate	Acid in the feed gas/O_2 degradation
Acetate	thermal degradation
Thiocyanate	Reaction product of H_2S and CN
Phosphate	Corrosion inhibitors/phosphoric acid activated carbon

Based on scheduled program, after 24 months of operation time ,corrosion rate for amine pipe lines and equipments were measured for three similar gas treating units (Gtu1,Gtu3,Gtu5) for both DEA 34wt% and MDEA 45wt% at same operating conditions.

Measurement of DEA and MDEA corrosion

Locations of coupons in gas treating units were shown in table2 and the results of corrosion rate of coupons were illustrated in figure 2. Based on the results, corrosion in amine pipe lines and equipments can be divided in two areas (high corrosion zone and low corrosion zone) for DEA solution. High corrosion zone, including: reboilers and lean/rich exchangers have higher corrosion rate than the other equipments.

Table 2: Location of coupon in gas treating units

Coupon No.	1	2,3	4	5,6		7	8	9	10
Location	Contactor	Reboiler	L/R Exchanger	Amine cooler		Regenerator	L.A.Filter	Reflux	Flash drum

Methods of amine purification

There are currently a few commercially available reclaiming methods in the industry. Ion exchange, electro dialysis and vacuum distillation are the most preferential methods for MDEA solution reclaiming (Dupart et al. 1993). Caustic treatment of amine has been used for HSS problems, but this a temporary solution. This method can create many additional problems. The caustic treatment can form sodium salts, some with low solubility and some very corrosive (Kohl 1997, Shielan et al. 2008) Ion exchange and electro dialysis are not able to remove non-ionic compounds, so amines cannot be separated from each other, but vacuum distillation is able to remove certain amine compounds from each other. Under certain processing conditions, ion exchange and electro dialysis will remove the HSS anions only, leaving you with contaminants in the system. Vacuum distillation will not only remove all of HSS but also will remove all of the contaminants from the system. Batch processing has been found to be the most efficient way to reclaim amine solutions. The process of vacuum distillation is complicated and it needs many types of equipment such as tank, heat exchanger, distillation tower, flash tank etc (Bonis et al. 2004). Ion exchange process is an easy excellent method to reduce high HSS to extremely low levels.

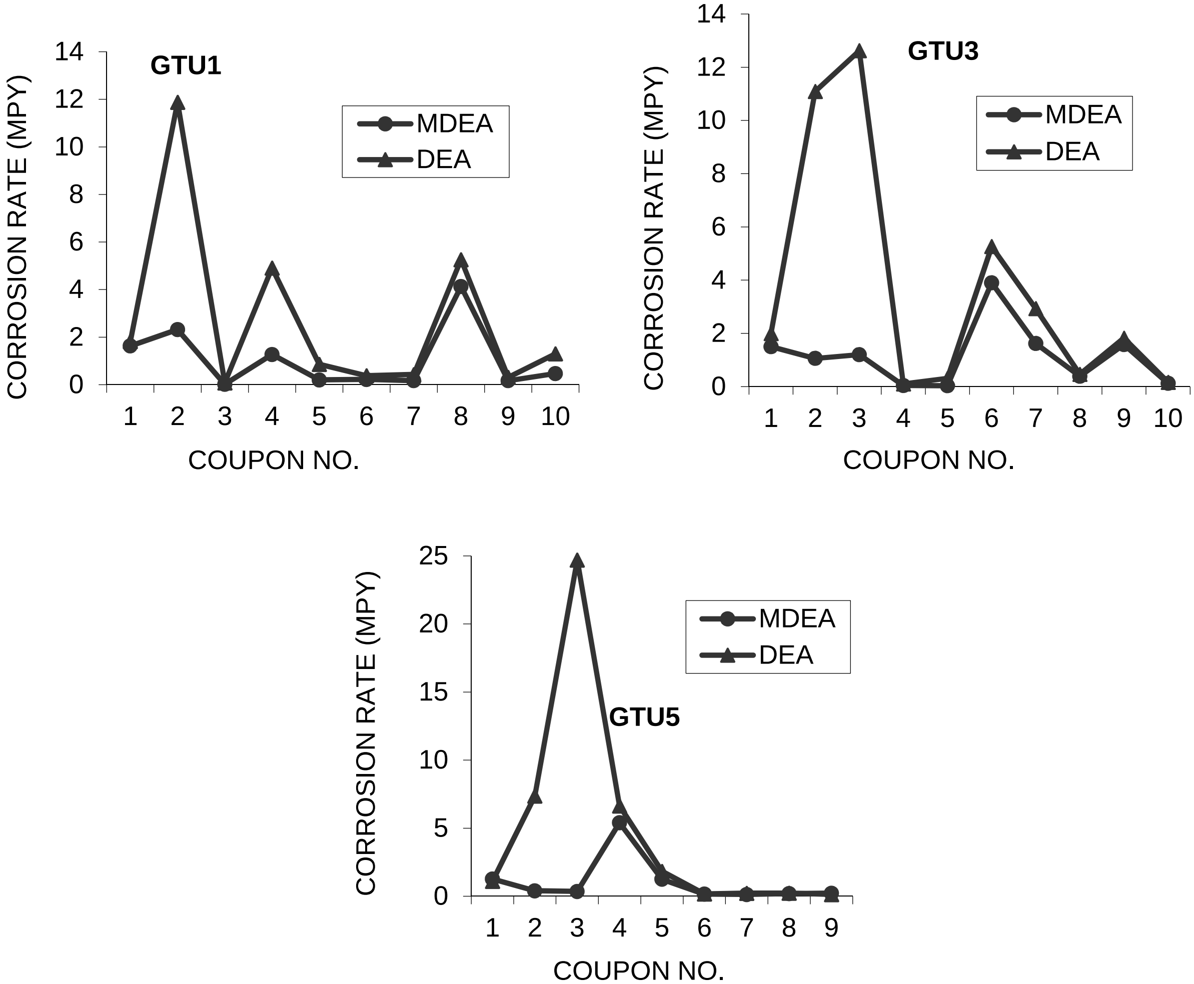

Figure 2: Corrosion rate for MDEA and DEA in GTU1, GTU3

Figure 3: Samples, left to right (used amine, after filter carbon, after resin bed)

Laboratory works and the results

Laboratory analysis of the operating MDEA solution (after 18- 24 months of operation) was done by gas chromatography to determine the amount of HSS. Table 3 shows the results.

Table 3: Laboratory analysis of operating MDEA solution

Sample	MDEA solution	Limits
GC – Titration (WT %)	0.7	N.A
THEED (WT %)	< 0.01	< 1.2
HSAS (PPMW) Neutralized	2.7	N.A
FORMATE(PPMW)	2100	500
GLYCOLATE(PPMW)	750	500
SULFATE(PPMW)	130	500
OXALATE(PPMW)	130	250
ACETATE(PPMW)	430	1000
BUTYRATE(PPMW)	310	N.A

N.A means not available.

Result showed a high level of HSS (especially formates) and low level of tri hydroxy ethyl ethylene diamine (THEED), a degradation product of DEA. Therefore, with regarding the corrosive nature of HSS, they should be removed from our plant solution to maintain the quality of solvent and the improvement plant corrosions. For evaluation the performance of an ionic resin in removal of HSS, resin bed was created in the laboratory and then 500 ml of amine was passed through the resin bed. After passing each 100 ml of amine, the amount of chloride, acetate, formate and sulfate were measured by gas chromatography. Laboratory results are in Table 4.

Table 4: The performance of typical ionic resin on HSS removal

Test	Unit	Acetate	Formate	Chloride	Sulfate
After passing the first 100 cc of MDEA solution	ppm	1.2	0.7	11.46	1
After passing the second 100 cc of MDEA solution	ppm	0.846	0.369	8.83	0.041
After passing the third 100 cc of MDEA solution	ppm	6.033	3.687	18.026	0
After passing the fourth 100 cc of MDEA solution	Ppm	395.4	405.8	528	0
After passing the fifth 100 cc of MDEA solution	ppm	553	915	733.45	0

Based on the results, if the amount of chloride controlled to less than 10 ppm in the treated amine, we will have been sure the other heat stable salts will be at very low level. This index can be used as the end point of amine desalting operation and the beginning time for resin regeneration. The results also show, for each volume of ionic resin (that use in our plant), four volume of amine can be treated by consideration the amount of HSS in the amine solution of sweetening units in GTP after about two years in operation. This fact was experienced in amine purification package in GTP.

Amine treating package and the result in Gas Treating Plant

For reducing impurities and removing HSS, a batch wise amine purification package designed and built in GTP, this package is in operation properly now. Anion resin beds and other equipments including carbon bed for removal of heavy hydrocarbons to prevent resin greasy, high capacity filters before and after beds, amine feed tank, amine treated tank, and filtration vessel and caustic solution tank were shown in figure 3.

Figure 3: Ion exchange for amine treating in GTP

There is the possibility of treating 6600 liters of amine solution by amine purification package per cycle and the amounts of chloride and heat stable salts will reduce extremely to a very low level. According to analysis and test results (Figure 4), after passing 6600 liters of amine solution, is necessary to regenerate the resin bed. The caustic solution with 3 wt% is used for resin regeneration.

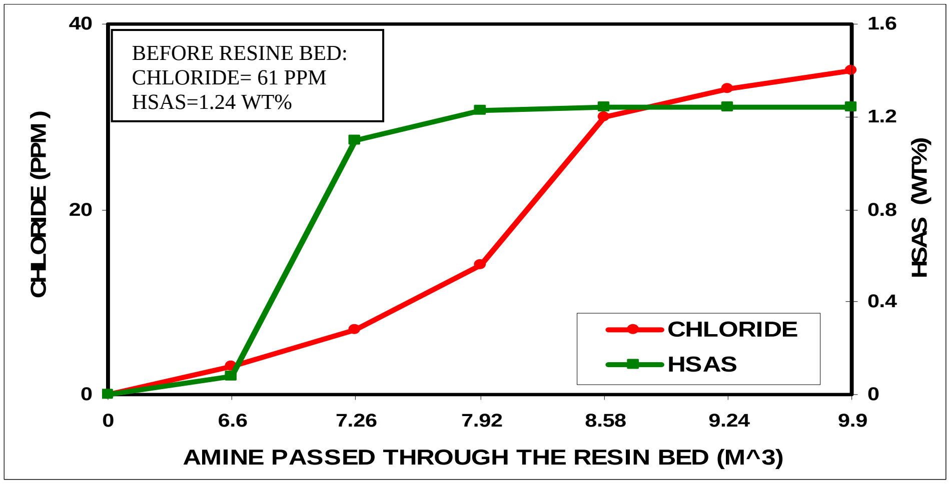

Figure 4: Amine flow through bed using anion resin in S.G.P.C

Results and Discussion

The results also show that corrosion rate of equipments for MDEA are less than DEA (especially for high corrosion zone). Temperature is one of the most important parameters that effect on the corrosion rate, process fluid temperature in reboilers and lean/rich exchangers is higher than the other parts in amine circulation path. As it was shown in the figure3, all of the points in high corrosion zone are related to equipments that mentioned above. Heat stable amine salts (HSAS) and amine degradation products play an important role in corrosivity of alkanolamine, so it is necessary to control them in amine solutions. Recommended limit of individual species of heat stable salts were shown in table 5 (Shielan et al. 2008, Rooney et al. 1997).

Table 5: Recommended limit of HSAS and degradation products in DEA and MDEA solution

	DEA	MDEA
HSAS(Wt% Solution)	<1.2	<1.2
THEED(Wt% Solution)	<1.5	<2.5 MDEA Fragments
Bicine (Wt% Solution)	<1	<0.4
Formamides (Wt% Solution)	<3	----

By reaction between amine molecules and other components in the feed gas (O_2, Cl and etc except H_2S and CO_2), heat stable salt such as: sulfate, Format, chloride, acetate, oxalate and etc will form. Laboratory result showed heat stable salts will form in both MDEA and DEA solutions. Amine degradation products are high molecular weight compounds. By reaction between amine and other component, (especially CO_2), degradation product will form. THEED (Tris-hydroxyethyl ethylene amine) and Bicine are the known degradation products of second and third amine type. In this study, four samples with different life time were analyzed for DEA 34wt% and MDEA 45wt% , the amount of HSS and degradation products were indicated. Results are shown in Table (6).

Table 6: samples analysis for amine solutions

SAMPLE	MDEA after 18 month	MDEA after 6 month	DEA after 6 month	DEA after 18 month	Limit[7,8]
GC – Titr (Wt %)	0.7	0.16	1.9	2.9	----
THEED (Wt %)	< 0.01	< 0.01	4.5	7	< 1.2
HSAS (ppmw) Neutralized	2.7	2.1	2.1	4.3	----
Formate (ppmw)	800	350	325	700	500
Glycolate (ppmw)	750	210	80	150	500
Sulfate (ppmw)	130	30	30	35	500
Oxalate (ppmw)	130	35	85	90	250
Acetate (ppmw)	430	130	560	1200	1000
Butyrate (ppmw)	310	70	70	70	----

The results indicate that the difference between the titration and gas chromatography (G.C.) for DEA is 5 times more than MDEA. Also Analysis results of amine solutions clarifies that heat stable salts and amine degradation products are accumulate for both MDEA and DEA during operation. Based on the results, the amount of neutralized HSAS for DEA solution (after one and half year operation) is 59% more than MDEA. Moreover, results show, contaminants will form more in DEA than MDEA solution during processing of sour gas. The main degradation product of DEA solution (THEED) is much more than MDEA for the analyzed samples. From the results can be understood that the amount of HSAS in MDEA after 18 month exceed from allowable limitation must be separated.

Conclusion

Corrosion in alkanoleamine gas treating units can be controlled and minimized by proper amine selection. Corrosion rate for amine circulation equipments and pipe lines are more sever in DEA 34wt% compared with MDEA 45wt% solution(particularly for high corrosion zone). Heat stable salts and amine degradation products increase the corrosive nature of the solvent and formation of them in DEA are more than MDEA. The major degradation product of the second and third amine type is THEED and accumulation of it in DEA is much more than MDEA. Due to the unit reliability and decreasing the corrosive nature of the solvents, it must be monitored and controlled the amount of HSS and degradation product in the gas treating plants during operation. The control of HSS in MDEA is important while both HSS and degeradation products are concern in DEA. Based on laboratory results and operational data from amine purification package(carbon bed, resin bed, filters etc.), the following items can be in to consideration by regarding the amount of HSS in amine sweetening solution (approximately two years after the operation) in GTP. It is possible to reduce HSS to extremely low levels in amine solution by using the ion exchange process. The amount of chloride in treated amine can be used as an index for the end point of amine desalting operation and the beginning time for resin regeneration these tests can be done easily. For each volume of ionic resin (in this case study), four volume of amine can be purified. Our experience emphasis, carbon bed is very profitable to prevention of resin greasy and longtime life of resin.

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Biography

Reza Mesgarian is a Head of Quality Control in NIGC, Iran. He has 14 years experience in the process and plant optimization in gas treating, sulfur recovery, natural gas liquid recovery and distillation. Mr. Mesgarian is a member of International Gas union (IGU) and has a BS degree in chemical engineering from Tehran university and a MS in chemical engineering from Technical and Science University, Tehran, Iran.