

# Amine Gas Sweetening System Problems Arising from Amine Replacement and Solutions to Improve System Performance

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## Abstract

This paper includes the significant on-site experience of the authors related to problems faced in amine systems with fresh amine and their possible solutions in phases #2&3 of South Pars gas complex. The amine system was designed as a closed circuit system with the primary objective of removing  $H_2S$ ,  $CO_2$ , and other acidic components from gaseous hydrocarbon streams. Amine plant operational problems such as excessive foaming, intense corrosion and capacity reduction are observed in gas sweetening unit. Heat stable salt (HSS) accumulations were found to be one of the main reasons for corruptions. Since there are no MDEA purification facilities in phase #2&3, it was decided to replace old MDEA solution with fresh MDEA. However, there are some problems that many plants have experienced after amine replacing or construction. In this paper, practical strategies with experimental data were proposed to overcome these problems.

**Key words:** Amine Replacement, HSS, MDEA, Corrosion, Degradation, Regeneration

## Introduction

The amine treating unit is of great importance in gas processing and refinery operations. The amine plant now attracts increasing attention due to high pressure for environmental compliance and quality of  $H_2S$  and  $CO_2$  removal. Two major problems representing a significant threat to an amine gas treating plant are corrosion and instability of operation, resulting in unscheduled upsets and outages [1]. High corrosion rates, typical for a number of amine plants, as well as of stainless steel, usually attributed to chloride, create serious safety concerns. High corrosion leads to high repair costs, potential environmental implications, and lost production. The results of a survey conducted by the National Association of Corrosion Engineers (NACE) indicate that 60% of total 24 amine plants surveyed experience stress corrosion cracking in the amine absorbers [2]. A similar survey by the Japanese Petroleum Institute reported a 72% occurrence of cracking at amine gas treating facilities [2]. Carbon steel corrosion is often attributed to the amine contaminants, which cannot be stripped and thereby accumulate in the amine solution. These contaminants include metals from the unit equipment, specific ions that interfere with the absorption, amine

degradation products and amine by-products in the form of heat stable salts present. These heat stable amine salts in the solution reduce the amount of amine available for gas treatment, thereby reducing the unit's productivity. Heat stable salts (HSS) also cause corrosion problems and lead to a higher foaming tendency of the solution [3]. Foaming in the absorber columns, higher amine losses, absorber tower pluggage, heat exchanger fouling, shortened amine filter life, and overall unit instability, affect performance of the sulfur recovery unit. Removal of the HSS from the circulating amine will help to improve the performance of the amine unit, decrease maintenance and filter replacement costs, and foaming [4]. Periodic amine clean-ups, either on-site or off-site, ion exchange, vacuum distillation, electro dialysis, and periodic reclaiming, are ways for providing a solution for HSS accumulation [5, 6].

To prevent severe problems and HSS removal in phases #2&3 of SPGC, it was decided to replace old amine with fresh amine. However, there are some problems many plants have experienced after amine replacing or construction. In this paper, practical strategies with experimental data were proposed for solving these problems.

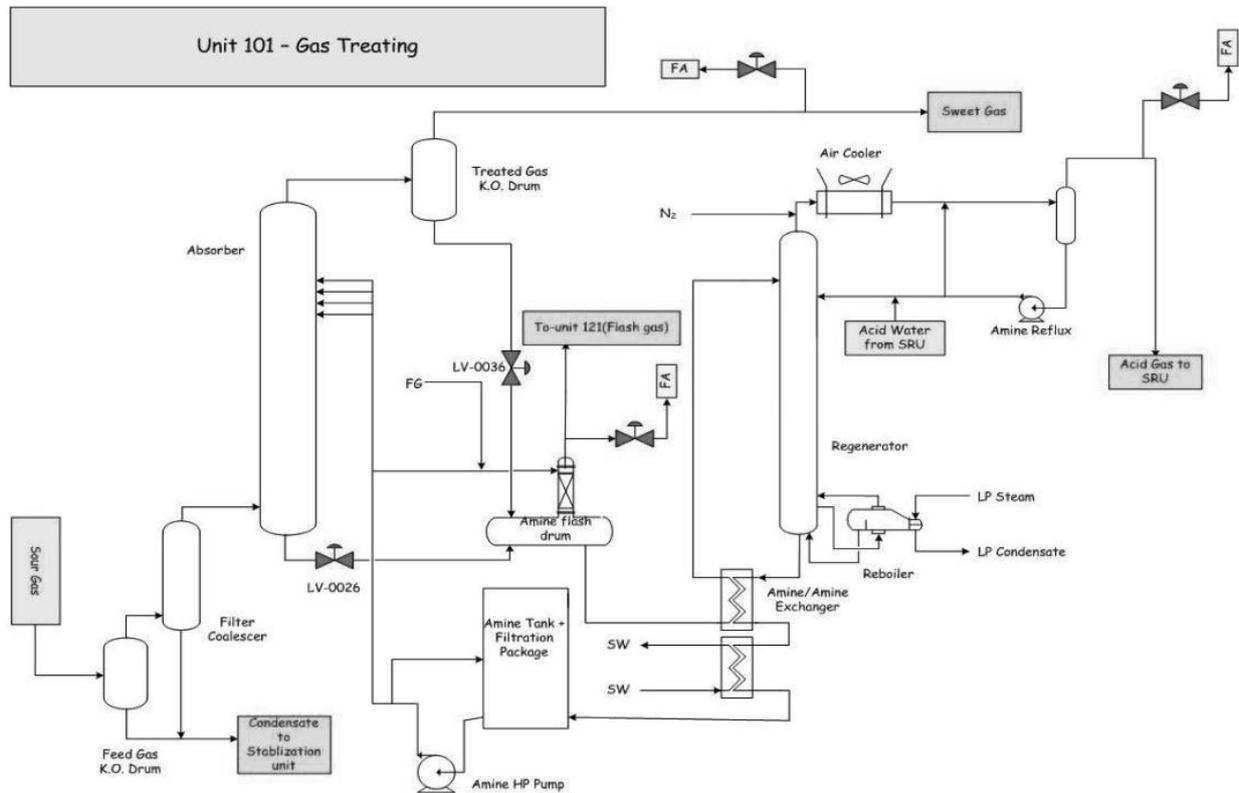


Figure 1- Gas Sweetening Unit.

**Experimental**

Amine plant operational problems, such as excessive foaming, intense corrosion and capacity reduction are observed in gas sweetening unit that lead to amine replacement (fig. 1).

**Corrosion**

The major problem with the amine unit was corrosion (fig. 2,3).

According to the inspection report, max corrosion rate of gas sweetening unit was 10.5 mpy in 2009, which was a very high corrosion rate compared with to previous years. It is noted that the refinery’s goal is to keep the corrosion rate below 10 mpy. Some samples were taken from used MDEA. Analysis results for these samples are given in Table 1.

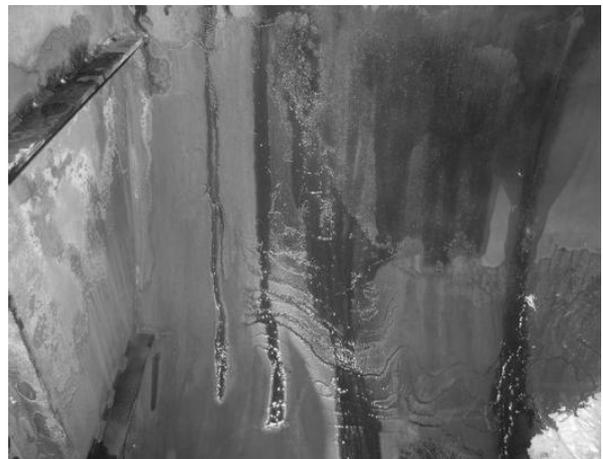


Figure 2- Corrosion sign in reboiler train#1

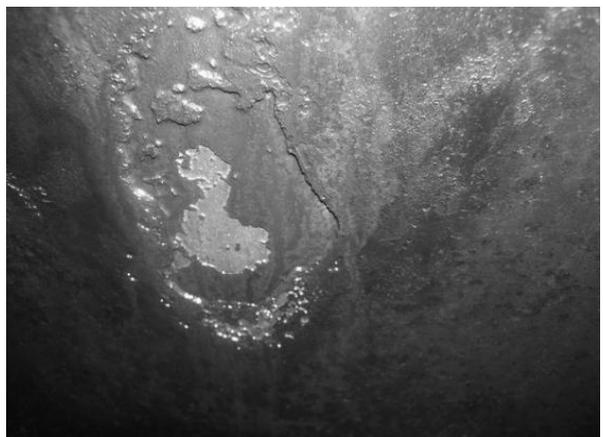


Figure 3- Corrosion sign in reboiler train#2

Table 1- Old MDEA analyze results in gas train 1, 2

| Test                  | Unit             | Train1    | Train2    |
|-----------------------|------------------|-----------|-----------|
| MDEA                  | wt%              | 44.9      | 45        |
| Chloride              | g/l              | 0.4       | 0.2       |
| Sulfate               | mg/l             | 41        | 32        |
| Total Acidity         | mg KOH/ g sample | 3         | 2.7       |
| H <sub>2</sub> S as S | ppm              | Trace<1.0 | Trace<1.0 |
| H <sub>2</sub> O      | mass%            | 36.6      | 40.1      |
| Na                    | ppm              | 51        | 39        |
| Ca                    | ppm              | 5.8       | 5.2       |
| Fe                    | ppm              | 1.6       | 3.4       |
| Cr                    | ppm              | <1.0      | <1.0      |
| Ni                    | ppm              | <1.0      | <1.0      |

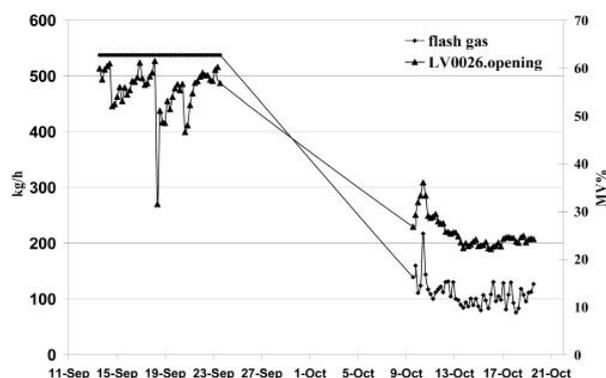
Also, some samples were taken from gas sweetening units' scales during 2009 shut down period. Result of analysis are shown in table 2. Results showed that scales mainly contain corrosion products and hydrocarbons.

**Table 2-** Scale analysis result in gas trains during 2009 shut down.

|                                     | Absorber | Regenerator | Reboiler |
|-------------------------------------|----------|-------------|----------|
| Ca <sup>2+</sup> (W %)              | Trace    |             |          |
| Mg <sup>2+</sup> (W %)              | Trace    |             |          |
| Cl(W %)                             | 0.38     |             |          |
| Acid in Soluble (W %)               | 1        |             |          |
| Total Fe (W %)                      | 25.91    | 45          | 39.2     |
| Loss At 600°C (W %)                 | 60.18    |             | 19.5     |
| S <sup>2</sup> (W %)                | Trace    | Trace       | Trace    |
| Na <sup>+</sup> (W %)               | 0.2      |             |          |
| CO <sub>3</sub> <sup>2-</sup> (W %) |          | Trace       | Trace    |
| SO <sub>4</sub> <sup>2-</sup> (W %) |          | 20.98       | 41       |

### Flash gas

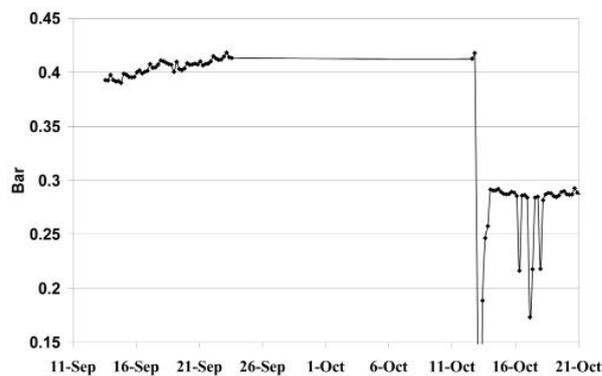
Operation parameters have shown signs of excessive foaming. Amount of outlet flash gas from flash drum after absorber tower was high and opening of LV0026 (bottom absorber level valve) a sign of flash gas was increased, too. This is clearly shown below (fig.4).



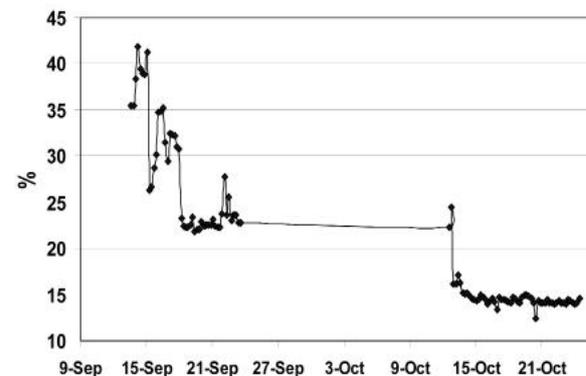
**Figure 4-** Flash gas form flash drum and LV0026 opening

### Absorber Differential Pressure (DP)

Before 2009 overhaul absorber DP in gas train was increasing gradually and caused amine carry over from absorber to treated gas K.O drum. This means there is foaming in absorber. Therefore, to prevent risk of tray failure, feed to absorber was reduced in order to meet max allowable DP across the tower. During overhaul lots of scale was found over trays. After overhaul opening of LV0036 (bottom sweet gas K.O drum level valve) a sign of carryover and PDI-0026 (Absorber DP) decreased (fig 5, 6). LV0036 opening reduction shows that amine carryover was reduced after overhaul. These indicate foaming has reduced in amine loop. DP reduction can be related to the cleaning of scales over the tower trays, too. DP of absorber before overhaul reached 0.41 barg and decreased down to 0.28 barg after overhaul and tray cleaning.



**Figure 5-** DP of amine absorber



**Figure 6-** Bottom sweet gas K.O drum level valve

### H<sub>2</sub>S of sweet gas

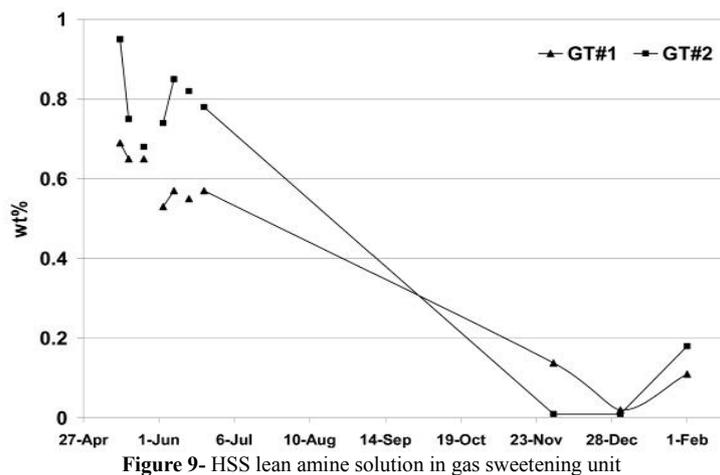
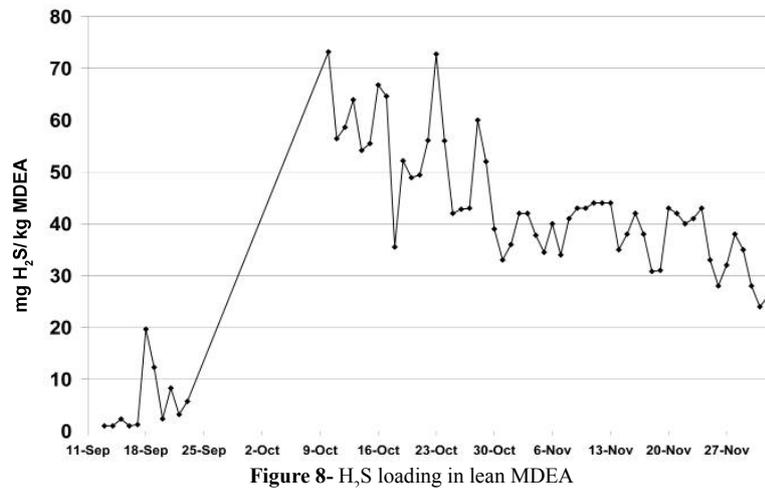
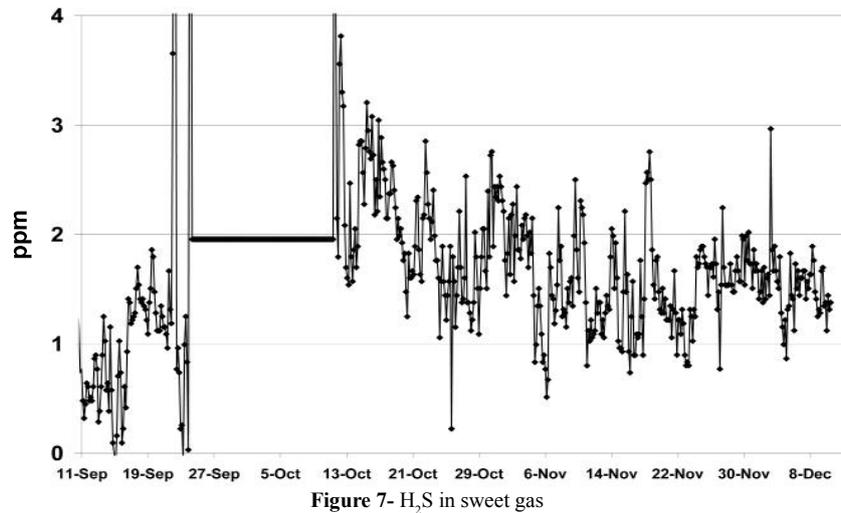
H<sub>2</sub>S content of sweet gas was within acceptable range before amine replacement, but it was high after MDEA replacing because H<sub>2</sub>S loading of fresh MDEA was considerably higher than that of old MDEA as a result of acid assisted regeneration phenomena. By taking some actions, such regeneration, top temp increasing and amine flow decreasing, sweet gas H<sub>2</sub>S content dropped back to the spec range (fig7).

### H<sub>2</sub>S loading

After start up of the H<sub>2</sub>S unit loading of the lean fresh MDEA was considerably higher than old MDEA while all operating parameters were the same as before (Fig.8).

This is a problem many plants have experienced after amine replacing. What is happening is a result of loss of heat stable salts in old amine solution. Actually, the acids that make these salts improve the regeneration of the MDEA because they will preferentially drive off the H<sub>2</sub>S from the lean amine solution, leading to a lower lean loading than it would get with pure MDEA. This phenomenon is known as "acid assisted regeneration". (fig.9).

Another reason for high H<sub>2</sub>S loading can be higher loading CO<sub>2</sub> by fresh amine, which can affect the regenerator tower performance and lead to increased H<sub>2</sub>S loading. As the fresh amine begins to form heat stable amine salts, solvent starts to reach lower and lower lean loadings for the same regeneration conditions. It should just let natural incursion rate of salts solve the problem.



However, there are some actions that have been taken to decrease amine H<sub>2</sub>S loading. These actions are:

1. Decreasing amine flow rate from 155 down to 140 m<sup>3</sup>/h in order to increase MDEA residence time in regenerator.
2. Increasing regenerator top temperature set point from 98 to 105 °C in order to have better amine regeneration and H<sub>2</sub>S loading decrease.

As we know, the higher the temperature, the higher the amine degradation rate. As mentioned above, amine flow rate was decreased. If amine flow rate is lower, it can provide suitable regeneration temperature with lower regenerator bottom temperature. In conclusion, by taking these actions, amine degradation due to more regeneration temp is reduced. So, amine flow rate was declined after amine replacing (see fig10).

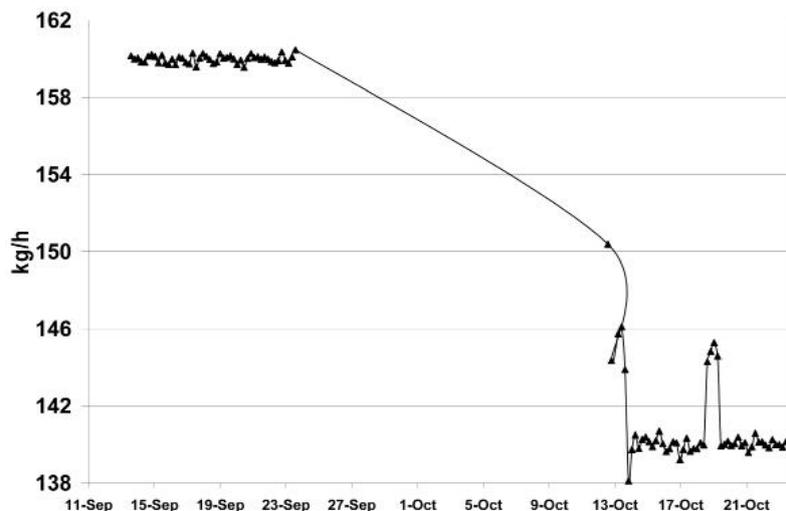


Figure 10- Amine flow rate in gas sweetening unit

### Regenerator Bottom Temperature

In order to prevent formation of primary or secondary amine in MDEA solution, the reboiler temperature shall not rise above 132 °C even for a short time [7], while according to the trends of reboiler temperature, this value exceeds frequently before amine replacement. This high temperature could be due to the presence of MEG in amine loop. This event is very harmful. Because high temperature can cause amine degradation leading to acid causing corrosion. In fact, heat stable salts are formed when amines react with acidic components other than  $H_2S$  and  $CO_2$  in the inlet gas to the amine absorber. According to the amine expert documents this problem can occur when the salt stability decreases in the point where some disassociations take place in a site- specific location in the unit. Corrosion occurs when that disassociation creates a corrosion cell with metal in the system. Other problems are caused by chelating effect of some of the organic acids, which are formed. They can hold the iron in solution rather than allowing it to form a protec-

tive film on the metal, resulting in areas of fresh metal where corrosion is more likely [8]. As mentioned, to decrease amine  $H_2S$  loading, regenerator top temperature is increased from 98 to 110°C to improve amine regeneration. However, top temperature increase aligns with bottom temperature increase. In order to prevent formation of primary or secondary amine in MDEA solution, the reboiler temperature shall not rise above 132°C because this high temperature leads to amine degradation. Amine degradation products (results of chemical modification of alkanolamines) promote corrosion by complexing iron. That complex iron enhances the corrosion in amine systems in the same manner as HSS. Regenerator bottom temperature is kept below 132°C by amine flow reducing from 155 to 140  $m^3/h$ . Lower amine flow rate increases MDEA residence time in regeneration loop and as a result decreases  $H_2S$  loading so that it could be possible to decrease top temperature from 110 to 105°C and consequently bottom temperature to less than 132°C in order to prevent degradation.

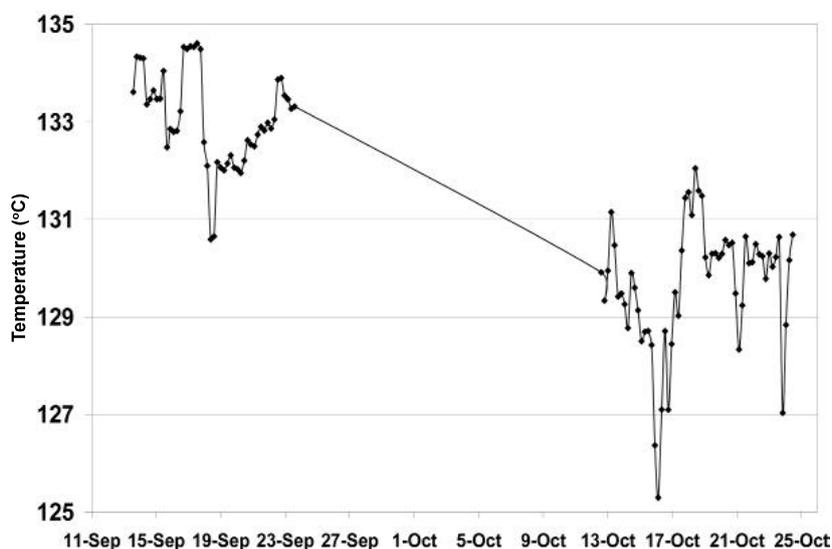
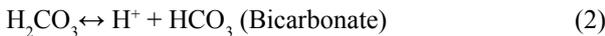
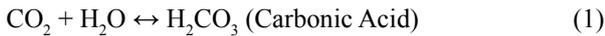


Figure 11- Bottom regenerator temperature in gas sweetening unit

### CO<sub>2</sub>% in Acid Gas to SRU

There was found a high MEG concentration in amine loop in lab tests. After amine replacement in constant amine concentration water was substituted for MEG. So, water content in fresh amine increased. The reaction between the amine and CO<sub>2</sub> is a bit more complex because CO<sub>2</sub> absorption can occur via two different reaction mechanisms. When dissolved in water, CO<sub>2</sub> hydrolyses to form carbonic acid, which in turn slowly dissociates to bicarbonate. The bicarbonate then undertakes an acid-base reaction with the amine to yield the overall reaction (Eq.1-4) shown below:



Tertiary amines must react with CO<sub>2</sub> via the slow CO<sub>2</sub> hydrolysis mechanism discussed earlier [9]. For MDEA, since the CO<sub>2</sub> reaction with water to form bicarbonate is slow while H<sub>2</sub>S reaction is fast, it is generally felt the H<sub>2</sub>S reaction is gas phase limited while the CO<sub>2</sub> reaction is available for CO<sub>2</sub> absorption, MDEA products yield significant selectivity toward H<sub>2</sub>S relative to CO<sub>2</sub>. It may be possible that water concentration increase in amine helps to increase CO<sub>2</sub> reaction with amine. Thus,

CO<sub>2</sub> concentration increases in acid gas and is followed by H<sub>2</sub>S by concentration decrease (Fig12). It has been shown that H<sub>2</sub>S concentration in acid gas was decreased after amine replacement which can confirm this hypothesis. Also, this is possibly related to absorption increase with fresh MDEA compare with used MDEA. To decrease CO<sub>2</sub> absorption, it is recommended to change feed tray from 27 to 25.

### TSS of lean amine solution

Trends in fig.13 show that Total Suspended Solid (TSS) has been increased after shut down and amine replacement. Because during overhaul cleaning and washing of gas sweetening unit equipments and piping were not done due to time limitation. It's recommended to perform washing before loading new amine and put amine filtration packages in service before gas sweetening unit start up.

### Antifoam consumption

After amine replacement, antifoam injection rate was decreased from 11 to 6 Lit/hr. Thus, antifoam consumption has decreased considerably with amine replacement.

### Results and Discussion

Since amine plant operational problems, excessive foaming, and intense corrosion are observed in gas sweetening

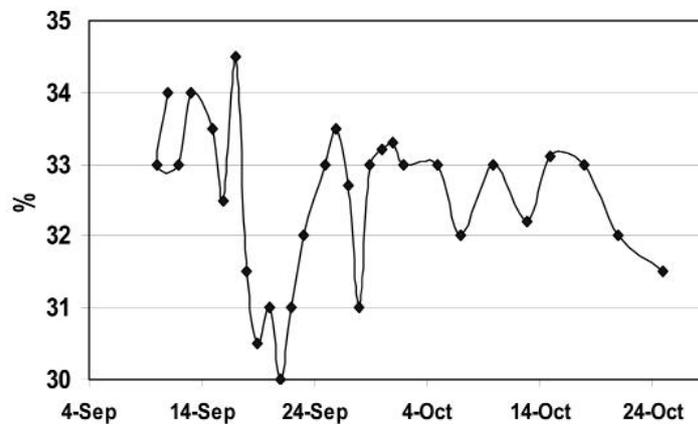


Figure 12- H<sub>2</sub>S concentration in inlet sulfur recovery unit

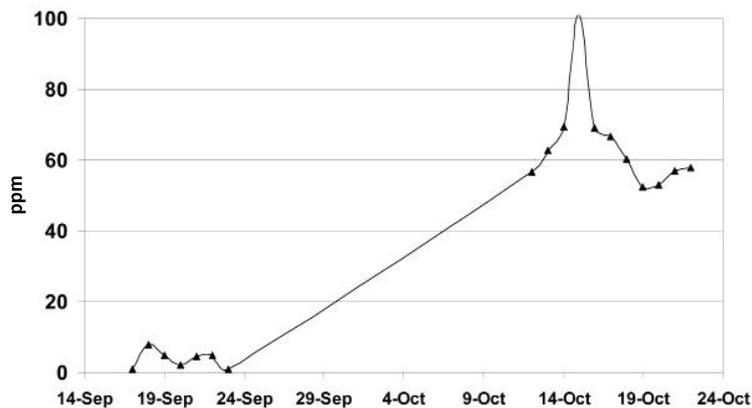


Figure 13- Total suspended solid in lean MDEA

unit, it was decided to replace old MDEA solution with fresh one. There are some problems, which many plants have experienced after amine replacing or construction [10].  $H_2S$  content of sweet gas was high after MDEA replacing because  $H_2S$  loading of fresh MDEA was considerably higher than old MDEA, a result of acid assisted regeneration phenomena. To decrease amine  $H_2S$  loading, amine regenerator temperature increased from 98 to 110 °C for better amine regeneration. However, top temperature increase aligns with bottom temperature increase. In order to prevent formation of primary or secondary amine in MDEA solution, the reboiler temperature shall not rise above 132 °C because this high temperature leads to amine degradation. Amine degradation products (results of chemical modification of alkanolamines) promote corrosion by complexing iron. The complex iron enhances the corrosion in amine systems in the same manner as HSS. Regenerator bottom temperature is kept below 132 °C by amine flow reducing from 155 to 140 m<sup>3</sup>/h. Lower amine flow rate increases MDEA residence time in regeneration loop and as a result  $H_2S$  loading decreases so that it would be possible to decrease top temperature from 110 to 105°C and consequently bottom temperature less than 132°C in order to prevent from degradation.

### Conclusion

Amine degradation causes the formation of heat stable salts (HSS) that can lead to corrosion. The amine unit performance begins to deteriorate as the HSS level increases and the performance absorber and regenerator becomes less stable. Therefore, to overcome this problem, old amine was substituted with fresh amine in phases#2&3 of SPGC. Some useful suggestions can be used in other sweetening plants by replacing amine. One of the most important results of amine replacement is improvement performance of the unit, reduction of antifoam use, and probable decrease of maintenance cost because of severe corrosion. Although installation of a continuously operating HSS reclaimer allows amine plants to ensure consistent reliable gas treating.

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