Mini Review

Effect of hydrogen sulfide concentration in circulated amine solution on the treated gas in gas treatment plant

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INTRODUCTION

Natural sour gas present in a deep beneath the earth’s surface. Its composition contains mainly of methane (C1), small amounts of hydrocarbon gases such as (C2-C5), C6+ as liquid condensate and nonhydrocarbon gases such as carbon dioxide, nitrogen, and hydrogen sulfide. Khurmala Gas Treatment Plant (GTP) is located in Southwest Erbil-Kurdish region 60 km from Erbil city. It has 60 wells distributed around three wells zones named: North, Middle and South wells stations as shown in Figure 1.

Each group of wells send oil and gas to the Central Process Station (CPS), where CPS complex is responsible for separating impurities coming with oil and gas (sludge and non desirable condensates) with production of heavy acid gases (large content of hydrogen sulfide-H$_2$S and carbon dioxide CO$_2$)

and desalted crude oil for refining. The laboratory analysis has showed that the Khurmala natural sour gas, in normal conditions, has huge quantities of H$_2$S (3.5%) and CO$_2$ (5%) as mentioned in Table 1.

Therefor it cause 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 (Abdulrahman et al., 2015) (Machenzie et al., 2006).

Table 1. Typical sour gas composition feeding GTP

| Composition       | Mole Percentage |
|-------------------|-----------------|
| Methane           | 76%             |
| Ethane            | 9.50%           |
| Propane           | 3.40%           |
| Iso-Butane        | 0.30%           |
| n-Butane          | 1.20%           |
| Iso-Pentane       | 0.50%           |
| n-Pentane         | 0.40%           |
| Carbon Dioxide    | 5%              |
| Hydrogen Sulfide  | 3.50%           |
| Nitrogen          | 0.20%           |
To prevent those problems, the sweetening process must have, to catch at least 99.5% minimum of \( \text{H}_2\text{S} \) through a physical absorption by using aqueous alkanolamine solution such as 50% of Methyldiethanolamine (MDEA), according to the design unit of Khurmala gas treatment plant this solvent can catch 50% of \( \text{CO}_2 \) also, the composition of sweet gas can be seen from Table 2.

Table 2. Typical sweet gas composition feeding GTP.

| Composition     | Mole Percentage |
|-----------------|-----------------|
| Methane         | 82%             |
| Ethane          | 9.50%           |
| Propane         | 3.40%           |
| Iso-Butane      | 0.30%           |
| \( \text{n-Butane} \) | 1.20%          |
| Iso-Pentane     | 0.50%           |
| \( \text{n-Pentane} \) | 0.40%       |
| Carbon Dioxide  | 3%              |
| Hydrogen Sulfide| 0.02%           |
| Nitrogen        | 0.20%           |
| Water vapor content | 0.01%   |

That’s means \( \text{H}_2\text{S} \) enter to GTP 3.5% mole and it is reduced into Sweet/dried gas to maximum 194 ppm. In this order of ideas, natural gas has a significant role in the recent world development especially for Iraq/Kurdish region who is interested to use its natural resources to get energy independence.

The MDEA as used in Gas Treatment Plant utilizes selectivity of the chemical for \( \text{H}_2\text{S} \) in Preference to \( \text{CO}_2 \) in no equilibrium situation. The reaction of \( \text{H}_2\text{S} \) with MDEA is very fast by proton transfer as is the case with other commonly used amines.

\[ \text{H}_2\text{S} + \text{R}_2\text{NCH}_3 \leftrightarrow \text{R}_2\text{NCH}_4^+ + \text{HS}^- \]

**Description of the Research**

Sweetening process taken in Khurmala GTP is shown from the Figure 2, sour gas is passing through the absorber to produce sweetened gas by using special alkanolamine (Methyldiethanolamine – MDEA) to catch acid loading, this amine with high level of acid gas dissolved in it (rich amine) is regenerates to be used again in a close circuit process, as can be seen, top of absorber, regenerator tower, flash drum and condensers are under extremely corrosion process, it is important to mention GTP is mainly carbon steel constructed so, corrosion rate will be expected to be high and must be controlled to avoid lack of production due to shutdowns by this cause. The most commonly used chemical solvent for \( \text{H}_2\text{S} \) removal is MDEA. Using of methyldiethanolamine can give us better \( \text{H}_2\text{S} \) absorption than carbon \( \text{CO}_2 \) absorption. Typical amine gas sweetening processing block diagram unit represented by Figure 2.

\( \text{CO}_2 \) firstly reacts with water to form bicarbonate. It is the formation of the bicarbonate which is generally the slow reaction which limits the \( \text{CO}_2 \) reaction to less than equilibrium values at short contact times.

\[ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+ \]

The bicarbonate then undertakes an acid-base reaction with the amine to yield an overall \( \text{CO}_2 \) reaction:

\[ \text{CO}_2 + \text{H}_2\text{O} + \text{R}_2\text{NCH}_3 \rightarrow \text{R}_2\text{NCH}_4^+ + \text{HCO}_3^- \]

Because of that step (carbon dioxide react with water to form bicarbonate), it may be assumed that the reaction of \( \text{H}_2\text{S} \) with MDEA will be in gas phase limited while the \( \text{CO}_2 \) reaction is liquid phase limited (Mark of Schlumberger, 2016) (Douglas et al., 1987) (West, 2008).

The rich solution with absorbed \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) exits the absorber at the bottom and flows into a flash tank. The flash tank is operated at a much lower pressure than the absorber, allowing dissolved light hydrocarbons to be released. Before entering the regenerator, the solution is preheated by heat exchange with the lean solution.

![Figure 2. Schematic of simplified gas sweetening plant (GTP)](image-url)
coming out of the regenerator. In the regenerator, steam generated in the reboiler is used to strip the acid gases from the rich solution. The regenerated lean amine is then recycled back to the absorber.

**SUMMARY OF THE RESEARCH**

One of the objectives of this research is to determine absorbed hydrogen sulfide gas concentrations in an aqueous MDEA stream, the result of this method may be linked to a control system and to founding a desired \( \text{H}_2\text{S} \) loading in the lean amine, this is more important to improve regeneration process because of the stripping process is incomplete, and it causes to reduce the efficiency of amine to remove \( \text{H}_2\text{S} \) from natural sour gas, so, to maximize this efficiency the amine regeneration process must effectively possible. Then if the data is out of the limit of the desired value then the system either informs the operator who then manually directs a corrective response or else the system automatically orders the corrective response. Another objective of this research is to make a relationship between \( \text{H}_2\text{S} \) in lean amine with Treated Gas when all the samples have taken at the same condition 3.5\% \( \text{H}_2\text{S} \) and 5\% of \( \text{CO}_2 \) and same flow of the feed. The control system then compares the \( \text{H}_2\text{S} \) loading in lean amine and treated gas to have an \( \text{H}_2\text{S} \) in treated gas under the range of the specification (Universal Oil Processing, 1981).

**RESULTS AND DISCUSSION**

A high precise method is used for the determination of dissolved hydrogen sulfide concentration in lean amine by oxidation with the standard iodine solution 0.05 M in acidic medium apparent hydrogen. If thiosulfate is present, is also titrated an included \( \text{H}_2\text{S} \) in the calculation.

**SUMMARY**

For a solution containing more than 100 grain of \( \text{H}_2\text{S} \) per gallon or where better precision is required. A portion of amine sample is pipette into an acidic water solution containing an excess standard iodine solution. The excess of iodine is back titrated with standard sodium thiosulfate solution using starch as indicator.

Precision method: Pipette 1 mL sample into a 250 mL Erlenmeyer flask containing a magnetic stirring bar and 100 mL of water with the viscous sample, rinse the pipette with water and add the rinsing into the flask and then Pipette a 1 mL of HCl, and add approximately 2 mL of starch indicator solution. The solution titrated with standard iodine solution until reach a blue color which means the endpoint.

The procedure followed involved 23 samples of lean amine and 23 samples of treated gas which all of them were taken at the same operation condition 94 MMSCF/D of feed which contains 3.5\% \( \text{H}_2\text{S} \) and 5\% \( \text{CO}_2 \).

Shimadzu Gas Chromatography coupled with Pulsed Flame Photometric Detection (GC-PFPD) as shown from the Figure 3.

**PFPD**

It is almost new detection that can be used in analytical chemistry, it invented about 30 years ago. It uses a flame like its namesake, PFPD came from the improvement of old FPD, FPD was generally used for detection S and F only, but PFPD has the capability and enhanced to detect N, As, Sn, Se, Ge, Te, Sb, Br, Ga and selective detection of sulphur and phosphorus.

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*Figure 3.* Shimadzu Gas chromatography, Model-2014 GC-PFPD and helium as carrier gas used to detect \( \text{H}_2\text{S} \) in Treated in ppm level.
The basic of PFPD working depends on the flame source and combustible gas flow, hydrogen and air used as a mixture of combustible gases with the sample components which are in a continuous flow into the flame chamber, the combustible gas is also fed separately. Firstly the ignited flame is propagated back to the flame chamber and terminated in few milliseconds because of the pulsed flame can’t be continuous in the combustor holder small hole. Then the continuous gas flow makes additional ignition in few hundred milliseconds, the emitted light transferred to the photomultiplier tube through the glass filter and detected (American Standard for Testing and materials, 2010) (Stevens et al., 1969) (Kientz and Verweij, 1987) (Godoi et al., 2003). PFPD diagram can be seen from the Figure 4.

Due to the fact that H$_2$S is highly corrosive gas in nature. The products of dissociation of H$_2$S gas is aggressive and can catalyze the electrochemical reactions, especially the dissolution of Fe to form iron sulfide FeS, therefore the study of H$_2$S concentration in both lean amine and treated gas is more important to have a monitored and highly effective regeneration system and preventing the problems causing by H$_2$S in treated gas. The relation between H$_2$S in both lean amine and treated gas represented by Figure 5.

Figure 3 explained the relation between H$_2$S concentration in both lean amine and treated gas. It is obvious that with the increase of H$_2$S loading in lean amine solution the value of H$_2$S concentration in treated gas is also increased due to the decreasing of lean amine catching capacity by more protonated amine ions (R$_2$NH$_3^+$).

\[
H_2S + CH_2H(C_2H_4OH)2 \rightarrow HS^- + CH_2N(C_2H_4OH)H^+
\]

The greater the concentration of protonated amine ions (CH$_2N(C_2H_4OH)H^+$), the greater will be the concentration of H$_2$S in treated gas, there is a direct proportional relationship between them (Nielsen et al., 1995) (Snowdon, 2001) (American Standard for Testing and Materials, 2003).

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