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Development Design of Amine Sweetening Unit Plant of Natural Gas

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Abstract: *In addition to reduced equipment sizes, lower circulation rates, and greater overall amine concentration, selective amines have become more popular for gas sweetening. Selective amines absorb H₂S from CO₂ through thermodynamic or kinetic processes. Selective amine mixtures may enable a small quantity of CO₂ to remain in the treated gas. Plant capacity margins for selective amine units are frequently small. Increasing the acid gas concentration or throughput might result in sweet gas that does not fulfill CO₂ specifications. Increasing the amine concentration, employing combinations of amines, and altering the lean amine temperature were explored since adding new equipment may be costly. Compared to increasing reboiler or pumping capacity, these factors need little or no extra capital.*

Keywords: *Amine, Sweetening, Natural Gas, Plant, Development, CO₂, Design, H₂S*

I. INTRODUCTION

The literature has extensively explored amine unit optimization. Selection of amines (Polasek and Bullin, 1984), plant configuration (Polasek et al., 1983), and amine-water or other physical solvent mixes (Polasek et al. 1992; Okimoto, 1993). The authors acknowledge the value of preferential amines in the gas sweetening sector.

Selective amines prefer H₂S over CO₂. Many writers believe that this preference arises from variations in solubility, reaction speeds, or both (Barth et al., 1981, Cornelissen, 1982, and Danckwerts, 1979). The rate of reaction for CO₂ reduces with substitution on the nitrogen group, therefore primary amines react quicker than secondary and tertiary amines (Bullin et al., 1982). Because H₂S reacts so quickly, equilibrium is essentially attained for all amines. Primary amines are too rapid for selective commercial sweetening units; nevertheless, secondary and tertiary amine selective units are commonly constructed to harness this potential.

The introduction of selective amine treatment units increased plant efficiency. The industry embraced this new technology quickly due to its economic benefits. In normal operation, methanolamine (MEA) and diglycolamine (DGA) absorb CO₂ as fully as H₂S. Di-tertiary amines such as DEA, DIPA, and MDEA are selective amines best used at high pressure (> 300 psi, 20 kPa). To increase selectivity using selective amines, researchers examined low molecular weight sterically hindered amines with selectivity comparable to MDEA (Sartori and Savage, 1983).

Selective amines allow for smaller equipment and circulation rates. Denny Law (1994) recently reported how employing MDEA mixes reduced the predicted tray count for an acid gas standard. The CO₂ absorption by extra trays may actually raise H₂S content in the sweetened gas. Adding stages seems to increase CO₂ absorption, displacing H₂S. Because selective amines have lower reaction temperatures than non-selective amines, regeneration takes less energy and smaller reboilers. Selective amines seldom create caustic salts.

The use of selective amines, particularly MDEA, has spawned a new industry of "specialty" amines. Companies including BASF, Dow, Huntsman Chemical, Shell, and Union Carbide produce MDEA-based specialized amines to boost or "customize" the amine's sweetening capabilities. Shell combines sulfolane with MDEA or DIPA to generate Sulfinol, which enhances mercaptan and COS removal (Okimoto, 1993). Increasing the performance of these "specialized" amine units has been documented. Huffmaster and Nasir (1995) compare circulation rate and steam usage in amine and Sulfinol plants.

Numerous seminars and articles have addressed amine unit efficiency. Keller et al. (1995) report an industry conference that reviewed amine process operations, issues, and solutions.

This study found that amine losses, solution contamination, and off-spec products were the main causes of inefficient units. Surprisingly, the amine type had no effect on efficiency or operability of MEA, DEA, and MDEA units.

Abry and Dupart (1995) provide great advice for improving amine plants using historical data. According to the authors, this process knowledge helps regulate and avoid disturbances. Away from design circumstances, the authors explain how this plant data may be utilized to improve the facility's performance. The optimization in this reference used a lower intake gas flow rate with the same acid gas content. With larger concentrations of acid gas components, their analysis proved impractical and maybe unduly optimistic. Concerned about amine unit efficiency, most current work discusses employing plant data or proprietary "specialty" amines. This is incredibly helpful yet incomplete information. Few recent research discuss process simulators in amine unit optimization. This is concerning as amine sweetening simulations get more accurate. Engineers may utilize these technologies to identify optimal plant operating parameters. An optimization study may look at alternate amines, amine mixes, absorber equilibrium phases, or regenerator reboiler duties. In an active facility, acquiring plant data for different amines or equilibrium phases is difficult. But process simulation can readily study these situations.

This research uses the TSWEET® process simulator. This program's accuracy has been shown for single amines (MacKenzie et al., 1987) and amine combinations (Spears et al., 1996). There are two acid gas models: Kent and Eisenberg (1976) and NRTL (Chen and Evans, 1986). All simulations and computations in this work employed the NRTL model. Other sites provide details on the program's calculations (Bullin et al., 1981).

II. AMINE UNIT BASIC OPERATION

Although there are several amines and amine sweetening plant combinations, the basic mechanism is almost universal. To save money, several sophisticated facilities use series and parallel layouts.

Figure 1 shows a basic amine treatment plant. In the absorber, sour gas meets lean amine solution moving down the column. The amine solution absorbs the H₂S and CO₂ from the acid gas, while the sweet gas exits for processing. The rich amine is transported to a flash tank, where absorbed hydrocarbons vaporize. The lean/rich exchanger heats the rich amine to 377.7K (220°F). It is then stripped at low pressure to remove dissolved hydrocarbons and some water. The energy necessary to remove the amine is the total of sensible heat, absorption, and latent heats. Optimal stripping requires high pressure stripping columns to raise the reboiler temperature (Kohl and Riesenfeld, 1985). But do not surpass the amine decomposition temperature. The stripped or lean amine is returned to the lean/rich exchanger to cool. A pump raises the pressure over the absorber column. A heat exchanger then cools the lean solution before returning it to the absorber. The incoming lean amine is generally 322.2K (120°F).

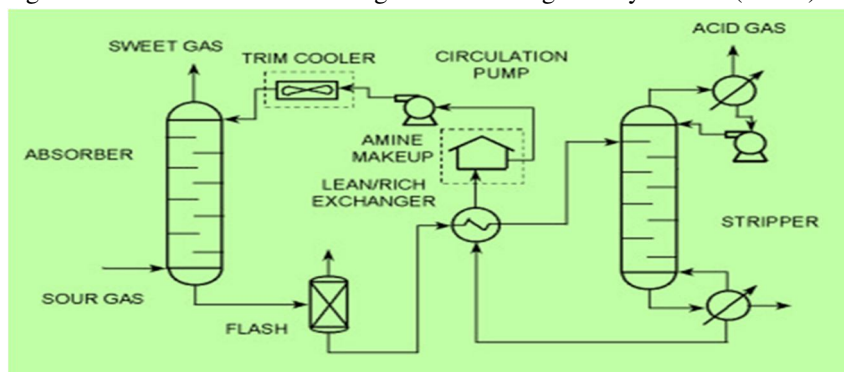


Fig. 1. Schematic Plant diagram for amine sweetening

EXAMPLE FACILITY

Table 1. Bryan Gas Plant Design and Operation, 1994

	Inlet Gas			Sweet Gas	
	Flow Rate MMSCFD	H ₂ S ppm	CO ₂ mole %	H ₂ S ppm	CO ₂ mole %
Design	35	0.1	2.91	nil	0.35
Operating	26	7	3.50	nil	0.42

Table 1 displays the facility's design and current operating characteristics. The operators were worried that the sweet gas exceeded CO₂ specifications, so they made alterations. Spears et al. (1996) explain the facility and how the process simulator TSWEET fits the plant data for DEA and MDEA/DEA. 0.35% CO₂ is the design parameter. Figure 2 compares simulation results to plant data for a 32 wt% DEA solution and a 32 wt% DEA/13 wt% MDEA combination. This value provides a benchmark for simulation accuracy.

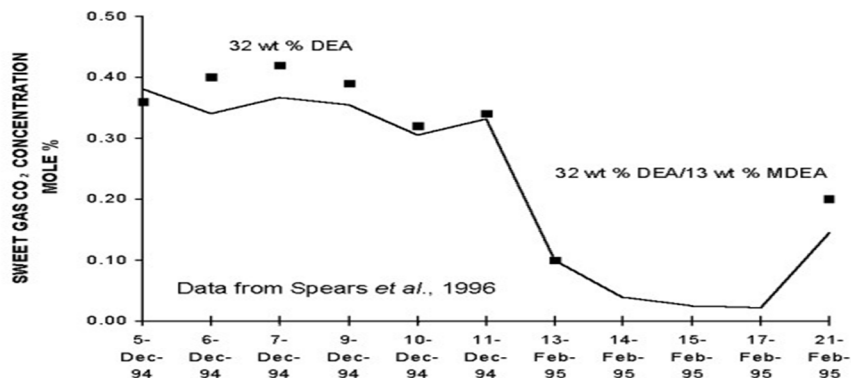


Fig. 2. Data from plants and TSWEET findings for CO₂ content in sweet gas for single and mixed amines.

The simulator was used to study amine concentration, mixed amine system, and lean amine temperature. These variables may be changed without adding new equipment or increasing current equipment. If the facility is presently at capacity, raising circulation rates, stripping steam, or the number of equilibrium stages may need capital expenditure.

Bullin et al. (1989) address MDEA CO₂ removal temperature. This study examines a low and high CO₂ intake gas stream. Boosting the trim cooler temperature from 311 to 328K (100 to 130°F) enhanced CO₂ absorption in both situations. As the solubility decreases, the amount of CO₂ absorbed decreases. It seems that the maximum temperature is dependent on amine concentration, incoming acid gas concentration, and contactor acid gas absorption. Sadly, no comparable statistics were available at the time.

The sample facility detailed here is not indicative of general circumstances, since there is no such thing as a "general case" in gas processing. Each instance must be evaluated individually owing to the diverse circumstances and needs of gas processing plants. Engineers cannot control certain factors like incoming gas flow rate and composition. Moreover, each sweetening unit's goal may vary depending on the final destination of the sweetened gas. A facility's incoming gas composition and flow rate may be same. One facility may be able to sneak as much CO₂ as feasible whereas another may have rigorous CO₂ concentration limits. H₂S must be accomplished in any instance. Each of these equipment should be developed differently to maximize the goal.

A. Concentration of Amine

The amine concentration may be increased easily. However, rust makes this impractical. Due to high primary and secondary amine concentrations, the lean/rich exchanger and reboiler suffer from significant corrosion. Figure 3 displays CO₂ and H₂S concentrations as a function of amine weight percent. The process variables DEA, DIPA, and MDEA were kept constant.

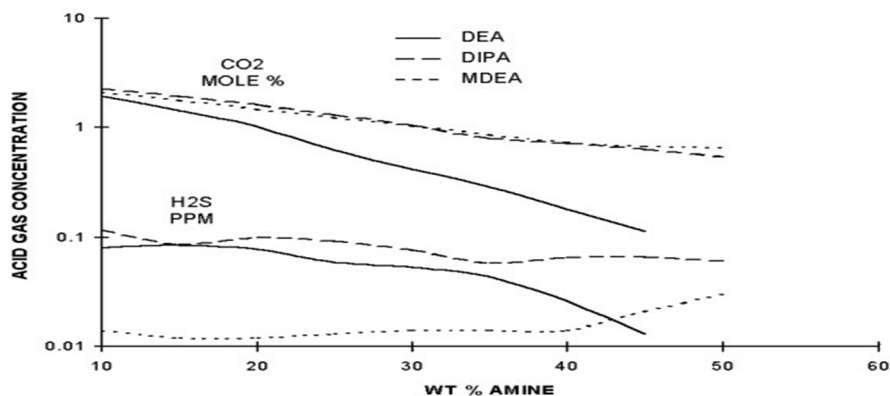


Fig. 3. Calculated findings for CO₂/H₂S concentration in the sweet gas for DEA, DIPA, and MDEA as a function of amine weight % amine.

With rising DEA content, CO₂ and H₂S concentrations declined. With rising amine concentrations, CO₂ concentrations declined while H₂S concentrations remained stable. The extra CO₂ these amines absorb tends to displace the H₂S. For all amines examined, the H₂S content was well within specification.

According to Figure 3, DEA at 40% or more is necessary to remove the acid gas. At such concentration, DEA tends to take up a lot of acid vapors, potentially caustic. Increasing the amine concentration is not an option here.

B. Mixtures of Amine

Since increasing concentration of a single amine could not fulfill the CO₂ standard, amine combinations were investigated. A 30 wt% DEA solution is shown in Figure 4 with the CO₂ content in the sweet gas changing when MDEA is added. H₂S concentrations were significantly below specification. All other process variables were kept constant. Because MDEA is less corrosive than DEA, larger amine concentrations may be employed. The facility met specification with 5% MDEA; 10% MDEA provided a safety buffer. It may seem counterintuitive to add an amine renowned for sliding CO₂ to boost CO₂ pickup. However, adding MDEA raises overall amine levels.

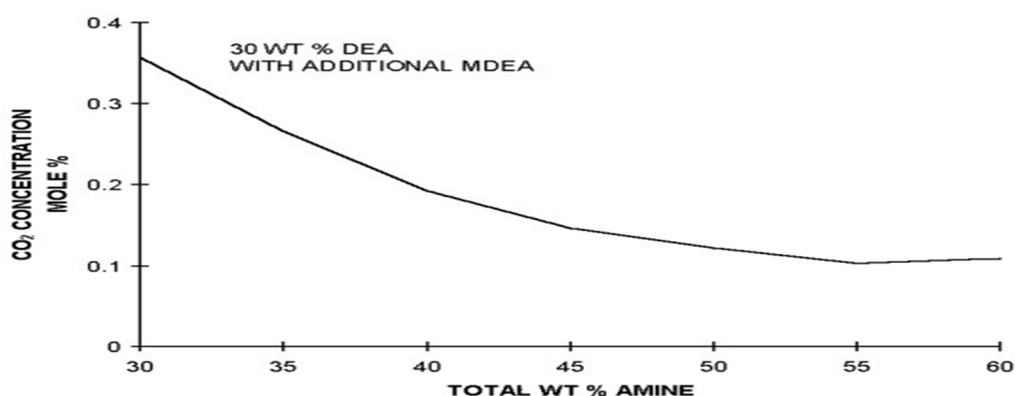


Fig. 4. Calculated findings for CO₂ concentration in the sweet gas for DEA/MDEA mixture

Figure 5 shows the concentration of CO₂ in DEA and DEA/MDEA mixtures. Assumed 12/94 input circumstances for DEA; dashed line 2/95 input conditions. The slope of the pure DEA line is larger than the slope of the MDEA/DEA combination, indicating that DEA alone has a stronger propensity to absorb CO₂. Using MDEA enhances amine concentration and reduces heat of absorption while being less corrosive.

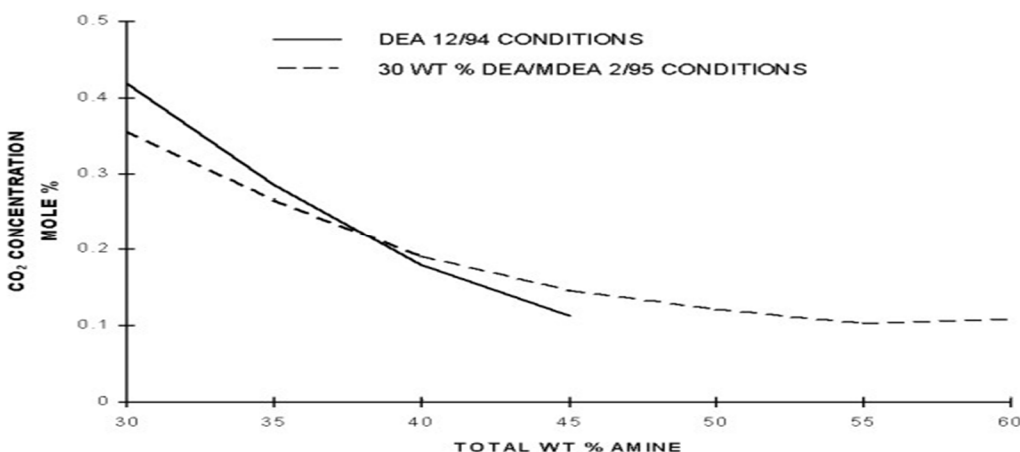


Fig. 5. Comparison between calculated findings for CO₂ concentration in the sweet gas for DEA and DEA/MDEA mixture

C. Temperature of Trim Cooler

Use thermodynamic equilibrium and kinetic absorption competition to sweeten selected amines. The temperature of the lean amine seems to affect CO₂ absorption. This may be critical for eliminating CO₂ from the intake stream. Figure 6 depicts the Bryan gas plant data as a function of lean amine temperature.

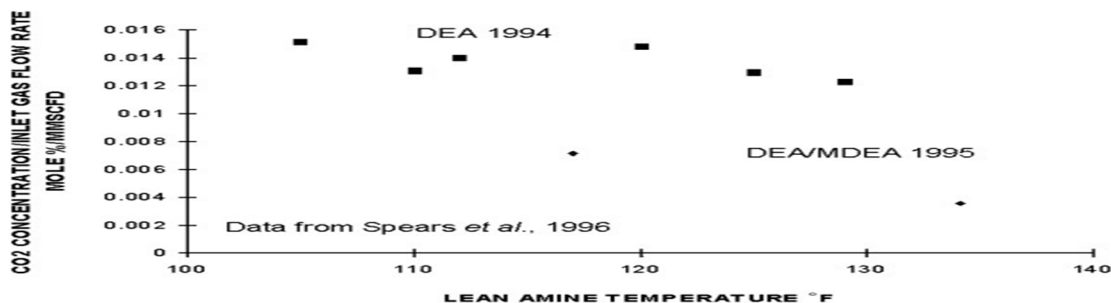


Fig.6. CO₂ content in the sweet gas per unit volumetric flow rate of intake gas for single amines and amine combinations

So, for a given volume of intake gas flow rate, Figure 6 depicts CO₂ concentration in the sweet gas per volume inlet gas flow rate. Data shows that trim cooler temperature affects selective amine CO₂ absorption. Also, at 314-331K (105-135°F) temperatures, the CO₂ content in the sweet gas falls as the lean temperature rises. To test how lean amine temperature influences CO₂ composition in sweet gas, the simulator kept all other process variables constant. Adjustments are made to duty in the lean amine cooler, as well as amine and water makeup.

On the other hand, DEA (32 wt%) has a higher acid gas concentration in the sweet gas (Figure 7). Due to diminishing solubility, the concentration of H₂S grows monotonically with colder temperature. The H₂S specification is met at 336K (145°F) lean amine temperatures. The sweet gas CO₂ concentration is lowest at 322K (120°F) lean amine temperature. The kinetic effect increases with temperature, while solubility decreases. After a certain temperature, solubility trumps kinetics. Notably, the CO₂ concentration never falls below 0.35 mole percent.

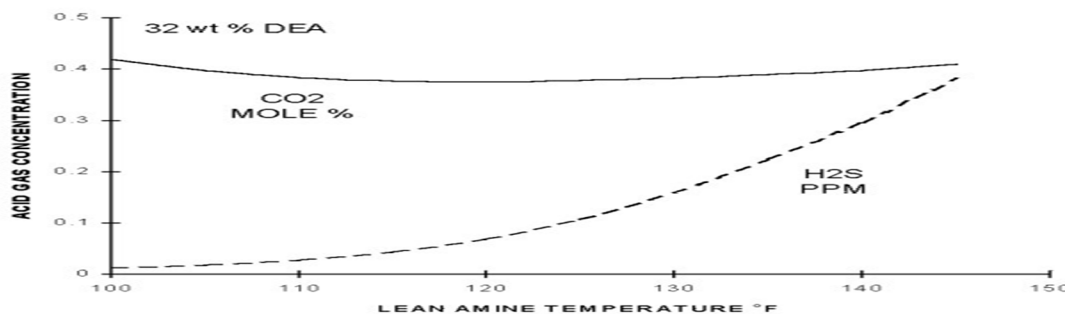


Fig.7. Calculated CO₂ and H₂S proportions in the sweet gas as a procedure of lean amine temperature for 32 wt % DEA

From 311 to 336K (100-145°F), Figure 8 shows the comparison of DEA, DIPA, and MDEA at 32 wt%. Dat DIPA and MDEA are more selective or kinetically regulated than DEA. From 311 to 327K (100 to 130°F), MDEA exhibits a 40% reduction in CO₂ concentration. Notably, the 32 wt% DIPA and MDEA cross at 322K (120°F). DIPA absorbs more CO₂ than MDEA at lower temperatures but less at higher temperatures. Nevertheless, neither MDEA nor DIPA at 32 wt% absorb enough CO₂.

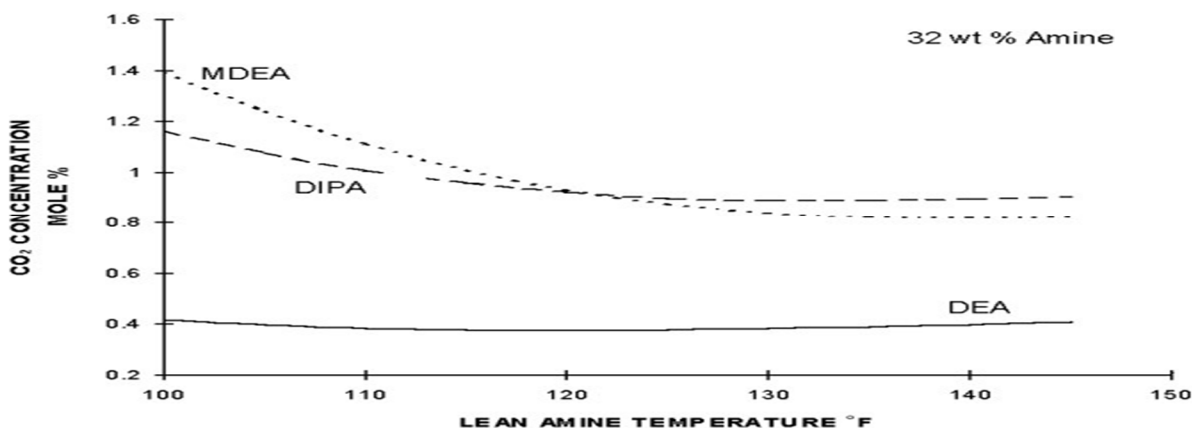


Fig. 8. Calculated CO₂ concentrations in the sweet gas versus lean amine temperature for DEA, DIPA, and MDEA at 32 wt %

Water and amine losses should rise with lean amine temperature. Amine losses increased from 311 to 333K (100 to 140°F) for DEA, DIPA, and MDEA. Figure 9 shows that water losses rose by a factor of 6. The simulator findings show that most water loss happens in the absorber when the sweet gas departs saturated. Minimal flash tank and stripper losses

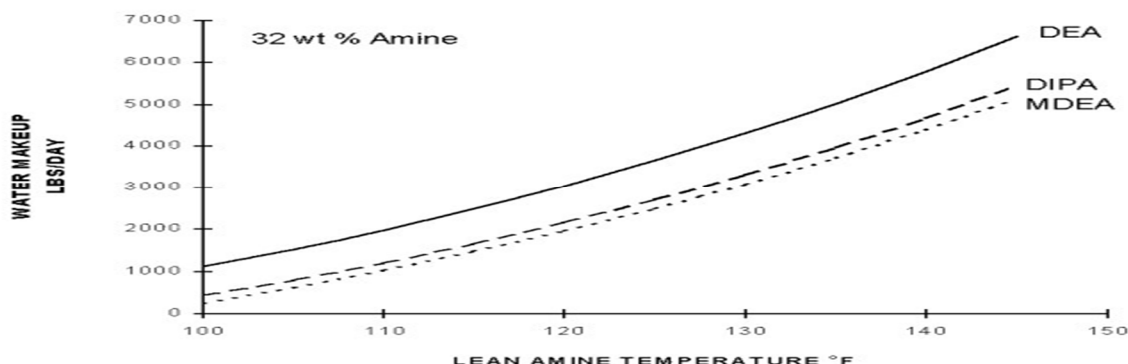


Fig. 9. Calculated water makeup vs. lean amine temperature for 32 wt % DEA, DIPA, and MDEA

Next, amine mixes and lean amine temperatures were explored. The starting point was 30% DEA. The MDEA concentration was raised to 30% with the same circulation rate. From 311 to 336K (100-145°F), the lean amine temperature. The CO₂ concentration in the sweet gas was the main worry as the single amine concentrations met the H₂S criteria. Increasing the MDEA concentration in the solution reduces the CO₂ content in the sweet gas. Additional MDEA after 25% wt% seems to have minimal impact on CO₂ uptake. Less clear, however, is the influence of wt % MDEA on the minimum CO₂ concentration in the sweet gas. The lowest concentration of DEA is at 322K (120°F). The lowest is 319K (115°F) with 5% MDEA. The lowest temperature rises with MDEA content.

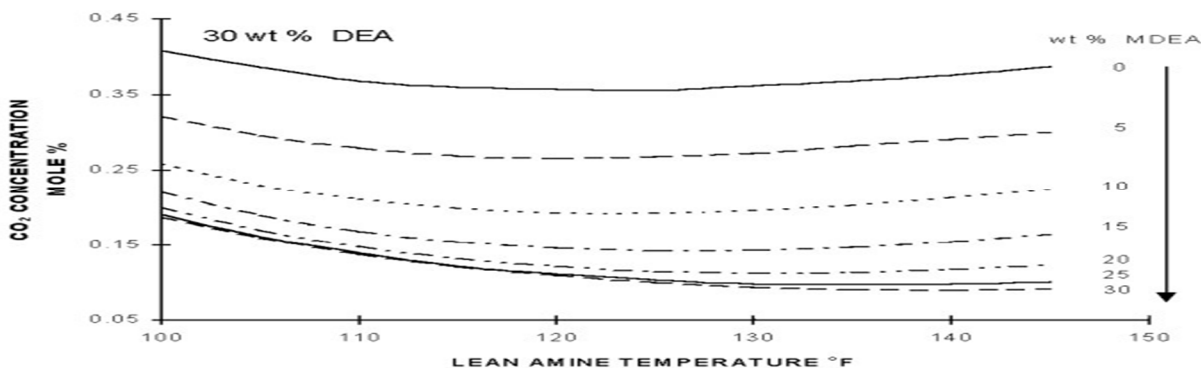


Fig.10. Calculated CO₂ concentrations in sweet gas for 30 wt % DEA based on lean amine temperature and wt % MDEA

This research focused on the influence of lean amine temperature on selective amine CO₂ pickup, although the reverse may be investigated. The operator may enhance CO₂ slip by lowering the lean amine temperature or precooling the intake gas.

III. GENERAL GUIDELINES

Using the knowledge from this situation, certain generalizations or rules may be made for other institutions. Use the most selective amine (MDEA) at low concentration and flow rate to slip as much CO₂ as possible while meeting H₂S specifications. Use as few theoretical equilibrium phases and as low a temperature as feasible. Because CO₂ absorption is kinetic, reducing contact time and temperature tends to increase CO₂ slip. The H₂S specification affects solution concentration, flow rate, and equilibrium phases. It also increases H₂S solubility. This kind of facility is reasonably stable when the incoming gas composition rises in CO₂. Due to the lower heat of absorption and lower circulation rates required by selective amines, non-selective amine facilities tend to be oversized. If the goal is to reach a specified CO₂ standard, the situation becomes more complex. The base or stock answer is the first variable. If the amine is a secondary amine like DEA, it should be concentrated. Ingesting more amine picks up CO₂. But watch out for corrosion restrictions. If the unit employs a single amine, an amine mixture may be used to increase the concentration. Adding MDEA raises the amine content and limits corrosion. Due to MDEA's decreased absorption heat, issues with undersized reboilers are uncommon.

If the base or stock solution is MDEA, the only amine combination to select is MEA or DEA. These amines boost CO₂ uptake but have greater absorption temperatures and are more corrosive than MDEA. Undersized reboilers may cause issues. Finally, raising the lean amine temperature enhances CO₂ pickup, but only to a point. Amount of CO₂ uptake and amine concentration affect this temperature. Heat reduces H₂S uptake and increases amine and water losses. They must be checked.

IV. CONCLUSIONS

The ultimate purpose of amine sweetening is to manufacture goods of high quality at low cost. It has created selective absorbents that remove H₂S when CO₂ is present. Selective amines reduce circulation rates, reboiler sizes, and responsibilities while achieving H₂S requirements. Due to changes in intake composition or higher throughput, several operators now exceed the CO₂ standard in sweet gas streams. Complying with the process equipment limits is the most economical and desired option.

The amine sweetening unit was analyzed using TSWEET for amine concentration, amine mixes, and lean amine temperature. Increasing amine concentration is beneficial if it does not exceed corrosion limitations. It seems that using amine combinations would increase CO₂ uptake for DEA and MDEA based solutions. Finally, using selective amines like DEA, DIPA, and MDEA, the lean amine temperature may be changed to reduce CO₂ content in the sweet gas. The improvement depends on amine concentration but may reach 20%. As a consequence, lesser H₂S collection and greater water losses from the absorber occur.

To accomplish the H₂S criterion, the engineer should use the most preferential amine at the lowest concentrations and circulation rate feasible. Cold absorber temperatures promote CO₂ slip and H₂S pickup. The issue becomes more complex if the goal is to reach a specified CO₂ concentration. Consider raising the amine concentration or employing amine mixes.

It may be necessary to adjust equipment size. Increasing the temperature of the selective amines boosts CO₂ pickup. Inlet gas mix and loading affect maximum temperature. Water and amine losses rise with temperature, but H₂S uptake decreases.

V. ACKNOWLEDGEMENT

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