

EFFECT OF SOLVENT CONTAMINANTS ON AMINE SELECTIVITY¹

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ABSTRACT

There are two types of contaminants in amine treating solvents that affect selectivity: those that react with the acid gases being removed, and those that do not. Both types of contaminants can have marked effects, both beneficial and detrimental, on gas treating selectivity.

If the contaminant in an MDEA solution is reactive towards CO₂, it may result in very significant loss of selectivity. Examples of reactive contaminants include DEA and MMEA, which may be co-produced when MDEA is manufactured or formed as a degradation product of MDEA within the amine system. It will be shown that although DEA does not usually cause much selectivity loss, it can seriously skew measured vapor-liquid equilibrium data. MMEA is a more serious reactive contaminant because of its very fast reaction kinetics with CO₂. Even in small concentrations, MMEA can ruin selectivity. We will show examples of this effect in both a tail gas treating unit (TGTU) and acid gas enrichment (AGE) unit.

Non-reactive contaminants such as heat stable salts (HSS) are reported to accelerate corrosion of carbon steel. However, in the present context of amine selectivity, they can affect treating in both positive and negative ways. Phosphoric acid is a substance that is sometimes purposely added to MDEA in 1000s of ppmw concentrations to promote solvent stripping. Other HSSs are naturally occurring and can have the same beneficial effect, or they can harm selectivity depending on concentrations and process conditions.

This paper uses a series of case studies to address the effect of common amine contaminants, both reactive and nonreactive, on selectivity in tail gas treating and acid gas enrichment units.

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Introduction

Amine solvents circulating in a closed loop will inevitably contain contaminants. These contaminants can come from various sources including undesired reactions in the process, contaminated fresh amine make-up, and many others. The presence of contaminants can have a significant effect on the process. Sometimes the effects are positive (e.g. strong acidic contaminants acting as H₂S stripping promoters), and sometimes they are negative (e.g. reactive amine contaminants drastically increasing CO₂ pickup in a selective treating process). This paper will examine the impact that different types of contaminants can have on the selectivity of an amine solvent.

Selectivity

Selective treating is the process of removing H₂S from a gas stream while forcing CO₂ to slip through the absorber column. Selectivity is an important process objective when removal of H₂S is more important than removal of CO₂. For example, in a Tail Gas Treating Unit (TGTU) the gas stream contains both H₂S and CO₂. Removal of H₂S is required to stay below stack emissions limits. In contrast, absorption of CO₂ in a TGTU is not desired because absorbed CO₂ ends up being recycled to the front of the Sulfur Recovery Unit (SRU) where it consumes part of the plant's hydraulic capacity.

Designing for Selectivity

Designing a unit to meet selective treating goals requires detailed knowledge about the alkaline solvent and the mass transfer processes taking place in the absorber column. Since both H₂S and CO₂ are acid gases with similar acidity, the process design for a selective treating absorber column must exploit mass transfer rate differences between the two acid gases. **Figure 1** summarizes the mass transfer resistances occurring at the gas-liquid interface in acid gas absorption. H₂S absorption is usually dominated by vapor phase resistance because resistance in the liquid phase is all but eliminated by the nearly instantaneous aqueous proton transfer reaction kinetics. In contrast, the relatively slow hydrolysis reaction kinetics of CO₂ usually causes the liquid-phase mass transfer resistance to dominate its absorption rate, especially for tertiary and hindered amines. Absorber columns are designed to take advantage of this difference between the dominant mass transfer resistances of H₂S and CO₂ to absorption.

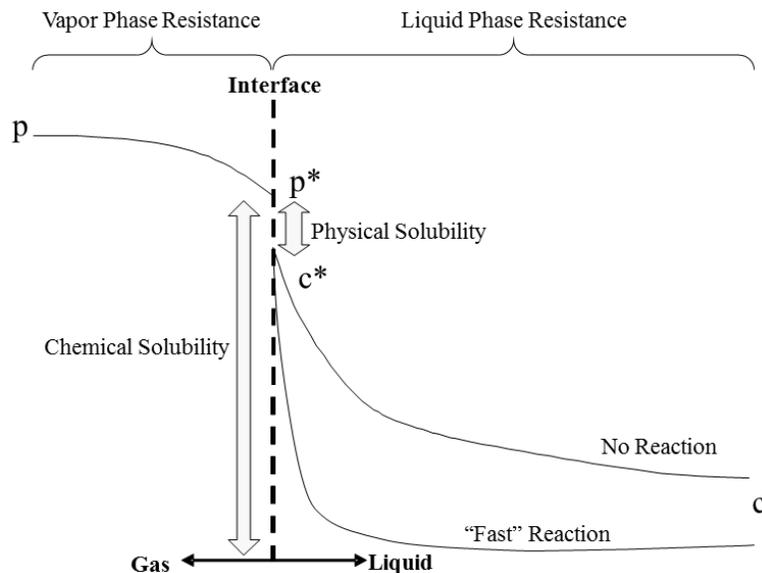


Figure 1 – Two-film mass transfer resistance of acid gas absorption

Selectivity is affected by solvent chemistry—the focus of this paper—but it can also be influenced by absorber hardware design. Absorber internals can be designed to encourage vapor phase mixing and minimize liquid phase mixing, for example, by using packing or by operating trays in the spray regime both of which will naturally increase selectivity for H₂S absorption. TGTU absorbers usually operate in a lean-end pinch condition with respect to H₂S. An H₂S lean-end pinch allows the treated gas to obtain H₂S equilibrium at the top of the absorber, before the slower absorption rate of CO₂ has had time to proceed very far.

In addition to influencing hardware design, the objective to treat selectively also affects solvent selection decisions. Specifically, the chosen solvent should slow the absorption of CO₂, which is why tertiary or hindered amines are typically used in this service. Since selectivity depends on slow pickup of CO₂, any contaminants which increase the CO₂ pickup rate will adversely affect the performance of the unit.

Contaminated solvents, the focus of this paper, are quite capable of preventing an operating unit from achieving its design objectives¹⁶. For example, if a unit's design is based on perfectly pristine amine then the operation of that unit will have to keep the solvent pristine, meaning that routine and frequent solvent analysis and hygiene will have to be emphasized.

Amine Contaminants

Circulating amine solvents can become contaminated in several different ways, for example:

- Supposedly pure amine purchased from a supplier can contain contaminants cogenerated during amine manufacture.
- Ineffective cleaning of trucks or rail cars between loads can contaminate pure, manufactured amine when it is delivered to the plant.
- Contaminants can be inadvertently added to the solvent stream in the operating plant through contaminated make up water, line up errors, carryover from upstream nonselective treating units, etc.

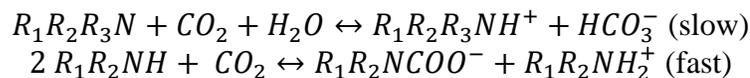
- Contaminants can form in the circulating amine from amine degradation and other chemical reactions.

Regardless of their source, contaminants can be divided into two broad categories based on how they behave in solution: reactive and non-reactive.

Reactive Contaminants

A contaminant is considered “reactive” if it can react directly with CO₂. Examples of typical reactive contaminants found in MDEA streams are DEA and MMEA. DEA and MMEA can be generated during MDEA manufacture⁸ or they can form in-situ through unintended side reactions. For example, it has been demonstrated⁴ that SO₂ breakthrough events can result in DEA and MMEA formation in TGTU solvents.

In operating columns, reactive contaminants increase the absorption rate of CO₂. The acceleration comes from faster CO₂ reaction kinetics in the liquid phase, e.g. carbamate forming reactions of primary and unhindered secondary amines proceed faster than the relatively slow CO₂ hydrolysis reaction:



As discussed later, faster chemical consumption of CO₂ effectively reduces the liquid phase mass transfer resistance by creating a steeper concentration gradient between the interface and the bulk liquid.

In addition to operating plants, laboratory studies and research projects could also be affected by MDEA contaminants. While laboratories are typically free from operating upsets such as SO₂ breakthroughs, reactive contaminants can still find their way into the laboratory since they can be created in the MDEA manufacturing process. It is not unusual for a laboratory study to obtain neat solvent from a commercial source and use it “without further purification”, and sometimes even without further analysis. While the presence of reactive contaminants would not be expected to affect H₂S VLE measurements very much, the impact on CO₂ VLE measurements is more pronounced. As shown later in Case Study 1, the measured partial pressure of CO₂ above a contaminated solvent at low CO₂ loadings could easily be 50% lower than the partial pressure which would exist over the equivalent, pure MDEA solution.

Non-Reactive Contaminants

Nonreactive contaminants considered here are strong acid anions, otherwise known as Heat Stable Salts (HSSs). HSSs come from many sources. For example, they can be created in process upsets⁸, they can come from process feed streams such as make-up water, or they can be added intentionally to enhance stripping. The effects of HSSs range from beneficial to detrimental depending on their concentration and specific process details. At moderate concentrations in non-reactive amine streams, HSS act as stripping promoters that effectively reduce lean loadings. At higher concentrations, HSSs accelerate corrosion and reduce the solvent’s capacity to absorb acid gases by binding or neutralizing some of the amine⁵.

HSS can also indirectly affect selectivity by degrading MDEA into DEA and MMEA^{3,8}. In other words, the non-reactive HSS contaminants can lead to the formation and accumulation of reactive contaminants which, in turn, adversely affect the selectivity of the solvent.

Simulating the Selective Treating Process

In order to investigate the quantitative impact of amine contaminants, we will look at three case studies. These case studies were built in the Version 6.2 of ProTreat[®] process simulator which is uniquely suited to investigate selective treating phenomena. As described above, selective treating works by exploiting differences in *mass transfer rates* between H₂S and CO₂. When contaminants reduce selective treating performance, they do so by increasing *the absorption rate* of CO₂. Since ProTreat is a mass transfer rate based simulator, it automatically predicts the impact of contaminants on mass transfer rates without requiring the user to anticipate how efficiencies, HETPs, or any other lumped parameter will change in response to composition changes in the solvent.

Contaminants largely affect selective treating by increasing the CO₂ absorption rate. A mass transfer rate based model calculates CO₂ absorption according to Equation 1.

$$N_{CO_2} = k_G a (P_{CO_2} - P_{CO_2}^*) = k_L a E_{CO_2} (C_{CO_2}^* - C_{CO_2}) \quad \text{(Equation 1)}$$

Where N_{CO_2} = Flux of CO₂ from vapor to liquid phase
 k_G = Vapor phase mass transfer coefficient for CO₂
 a = Interfacial area between vapor and liquid phases
 P_{CO_2} = Partial pressure of CO₂ in the bulk vapor phase
 $P_{CO_2}^*$ = Partial pressure of CO₂ at the vapor liquid interface
 k_L = Liquid phase mass transfer coefficient for CO₂
 E_{CO_2} = Enhancement factor for CO₂
 $C_{CO_2}^*$ = Liquid phase concentration of CO₂ at the vapor liquid interface
 C_{CO_2} = Concentration of CO₂ in the bulk liquid phase

The enhancement factor for CO₂ is a calculated parameter which is a function of the relative speeds of diffusion versus chemical reaction. By increasing the reaction kinetics with CO₂, reactive contaminants increase the enhancement factor and therefore increase the absorption rate of CO₂. This effect follows naturally from a mass transfer rate based model, which is therefore able to *predict* the impacts of amine contamination.

Case Study Parameters

When performing a quantitative study of contaminated amines, we must decide how far to take the contamination. In other words, “How contaminated is the contaminated amine?” The lower bound of contamination is obviously zero, i.e. no contamination. However, the upper bound is not as easy to set.

A contaminated amine stream could contain a wide variety of contaminants in many different concentration ranges within a real process. For the purposes of this paper, we consider two types of “contaminated” amine: MDEA contaminated with DEA, and MDEA contaminated with a 2:1

mixture of DEA and MMEA. The 2:1 ratio is based on experimentally measured values in a TGTU system after an SO₂ breakthrough event⁸. Various levels of contamination are considered as described in the individual case studies.

Case Study 1: Vapor-Liquid-Equilibrium Data

Laboratory studies producing acid gas-amine VLE data are potentially subject to amine contamination because some contaminants can be present even in fresh amine straight from the manufacturer. As discussed elsewhere¹², significant amounts of DEA and MMEA can be present in supposedly pure MDEA.

This case study is carried out at 104°F. The “pure MDEA” solvent is 35 wt% MDEA. The composition used for “contaminated MDEA” was generated by replacing 1% of the MDEA with a 2:1 molar ratio of DEA:MMEA. This is a relatively small amount of contamination, but we will see that it can have a significant impact on CO₂ VLE at low loadings.

Figure 2 and **Figure 3** below show the difference in equilibrium partial pressure of acid gas over a pure MDEA solution compared to a contaminated MDEA solution. **Figure 2** shows that there is significant deviation of CO₂ partial pressure at low loadings while the impact on H₂S partial pressure is minimal. **Figure 3** quantifies the impact: Contaminated MDEA could reduce the CO₂ partial pressure by 50% at low loading (< 0.01 mol / mol), whereas H₂S partial pressure is changed by < 5%.

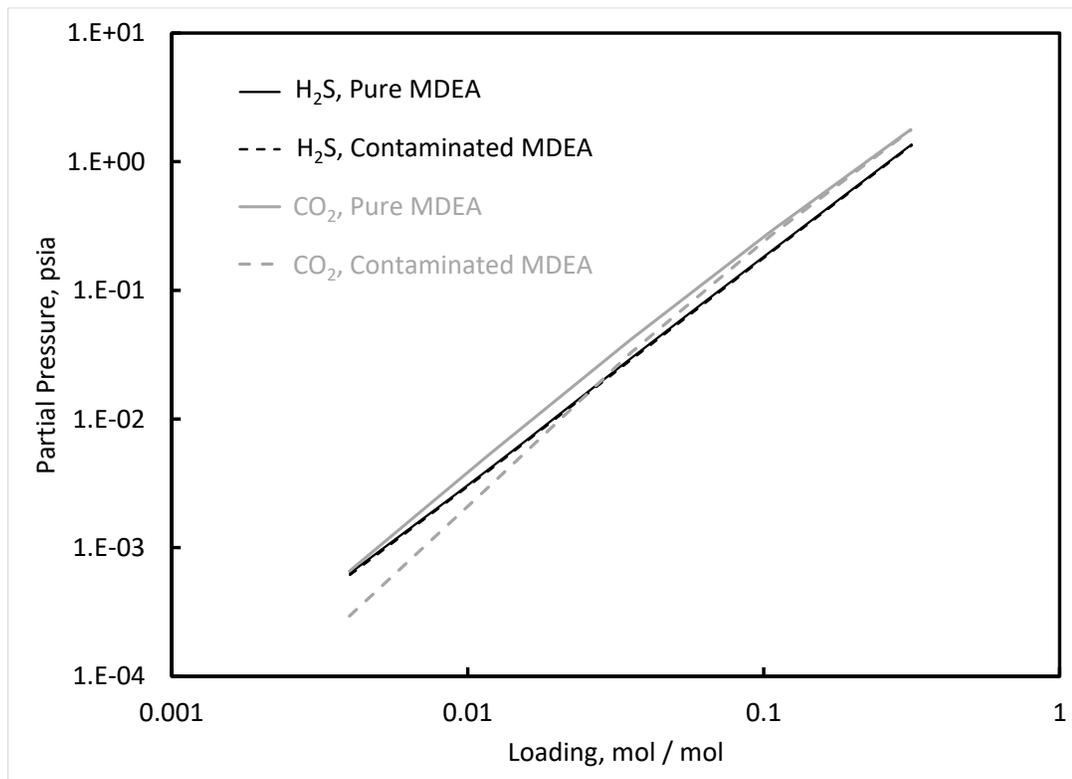


Figure 2 – Equilibrium partial pressure over pure MDEA and contaminated MDEA at 104°F

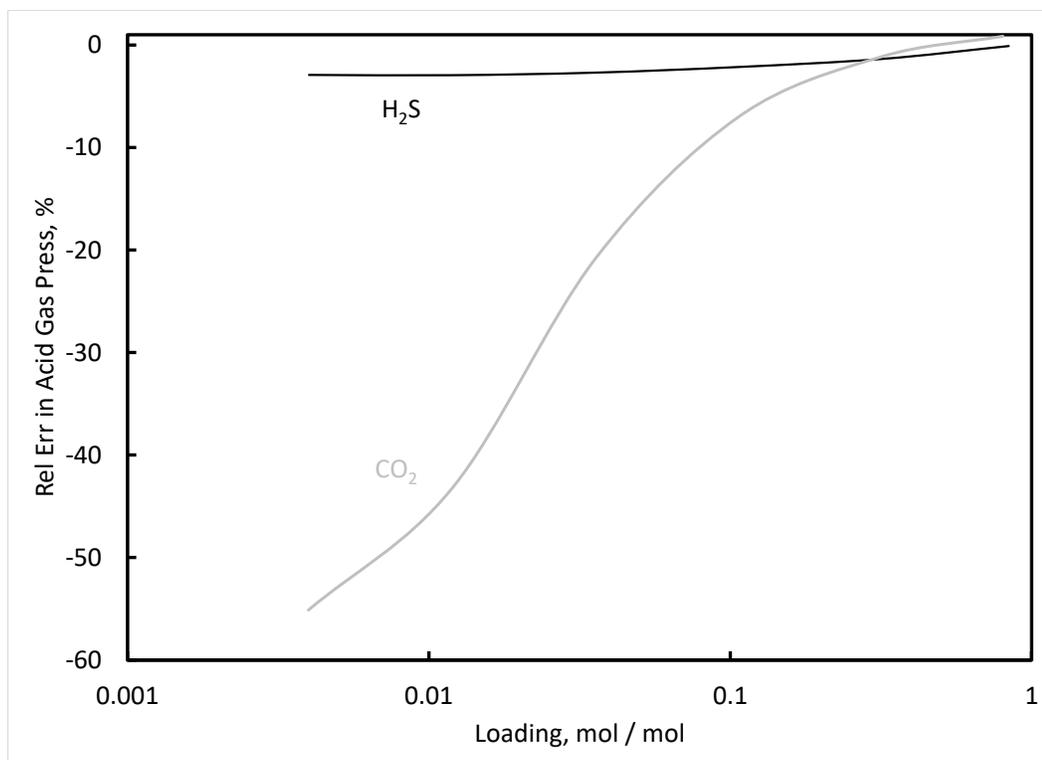


Figure 3 – Effect of MDEA Contamination on VLE. Difference in equilibrium partial pressure over 35 wt% MDEA vs 34.68 wt% MDEA / 0.21 wt% DEA / 0.07 wt% MMEA at 104°F

The CO₂ partial pressure reduction shown in **Figure 3** is quite profound for such a small level of contamination. Therefore, unless the MDEA used in laboratory studies is quite pure, serious error in the VLE data may be present. Twelve publications from the last two decades that report experimental acid gas VLE results for MDEA systems were arbitrarily selected and reviewed for amine purity (see **Table 1**). The purpose of examining the chemical purity of these studies is not to question the validity of the results, but rather to emphasize that VLE experiments rarely use pure MDEA. None of these studies used pure MDEA; the question is what the residual was. If the balance was secondary amines, the measured VLE data could be discrepant by a wide margin, depending on the exact contaminant. Based on the simulation results from this paper, it is recommended that future VLE analyses quantify the contaminants, especially secondary amine degradation products, present in the MDEA starting material to provide greater confidence in the results. This is especially important when the VLE data include low loading CO₂ values.

Table 1 - Solvent purity of published MDEA VLE studies

| Reference | Reported MDEA Purity |
|--|----------------------|
| Xu et al. (1998) ¹⁷ | Chemically Pure |
| Sidi-Boumedine et al. (2004) ¹⁴ | ≥ 99.7 wt% |
| Huttenhuis et al. (2007) ⁶ | ≥ 99 wt% |
| Silkenbäumer et al. (1998) ¹⁵ | ≥ 99 wt% |
| Ali & Aroua (2004) ¹ | ≥ 98.5 wt% |
| Ermachkov et al. (2006) ⁴ | ≥ 98.5 wt% |
| Ma'mun et al. (2005) ¹¹ | ≥ 98.5 wt% |
| Kamps et al. (2001) ⁷ | ≥ 98 wt% |
| Kuranov et al. (1996) ⁹ | ≥ 98 wt% |
| Addicks et al. (2002) ² | Not Reported |
| Lemoine et al. (2002) ¹⁰ | Not Reported |
| Park & Sandall (2001) ¹³ | Not Reported |

Case Study 2: TGTU

Our second case study demonstrates the impact of DEA and DEA/MMEA contamination on a TGTU in a SRU. The case study is based on a closed-loop absorber and regenerator simulation built in ProTreat[®]. A summary describing the case study set up is shown below in **Table 2**. The base case solvent has MDEA with a typical amount of HSS. The case study replaces incremental amounts of MDEA with DEA or DEA + MMEA. For cases with DEA + MMEA, the two contaminants were added at a constant DEA:MMEA molar ratio of 2:1.

Figure 4 shows the results of the case study. As non-reactive MDEA is replaced with reactive DEA / MMEA, the CO₂ slip is incrementally reduced. Lower CO₂ slip in a TGTU absorber means that more CO₂ will be recycled to the front of the SRU where it will ultimately reduce the capacity of the SRU by occupying hydraulic capacity.

By comparing the CO₂ slip curves, it can be seen that there is a significant difference between the DEA-only contamination and the DEA/MMEA contamination. CO₂ slip gradually falls as DEA replaces MDEA. In contrast, the CO₂ slip falls steeply as DEA and MMEA contaminants accumulate together. The presence of MMEA strongly reduces CO₂ slip because of its rapid reaction kinetics.

At first glance, the effect of reactive contaminants on H₂S treating seems counter-intuitive. How can adding a reactive contaminant make the amine do a *better* job at H₂S removal? The answer lies in the fact that this TGTU absorber operates in a lean-end pinch condition for H₂S. As shown in **Figure 5**, the interaction between CO₂ and H₂S results in lower lean loading of H₂S. Since the absorber is lean-end pinched, lower lean loading of H₂S will translate directly to a lower concentration of H₂S in the treated gas.

Table 2 - Description of Case Study 1 - TGTU

| Feed Gas | | Absorber | |
|------------------|--------------|--------------|---------------|
| Composition | | Packed Depth | 20 ft |
| Water | 8.4 mol% | Packing Type | 2" Pall Rings |
| Hydrogen Sulfide | 1.7 mol% | Diameter | 9.5 ft |
| Carbon Dioxide | 3.5 mol% | % Flood | 63 % |
| Hydrogen | 2.8 mol% | | |
| Nitrogen | 83.6 mol% | | |
| Temperature | 111°F | | |
| Pressure | 15.9 psia | | |
| Flow rate | 28.16 MMSCFD | | |

| Solvent | | Regenerator | |
|-------------|------------|-----------------|---------------|
| Circulation | 641 gpm | Wash Trays | 4 |
| MDEA | 37 wt% | Stripping Trays | 26 |
| Thiosulfate | 3,316 ppmw | Pressure (top) | 31.8 psia |
| Formate | 1,448 ppmw | Reboiler Duty | 40.8 MMBTU/hr |
| Sodium | 1,517 ppmw | | |

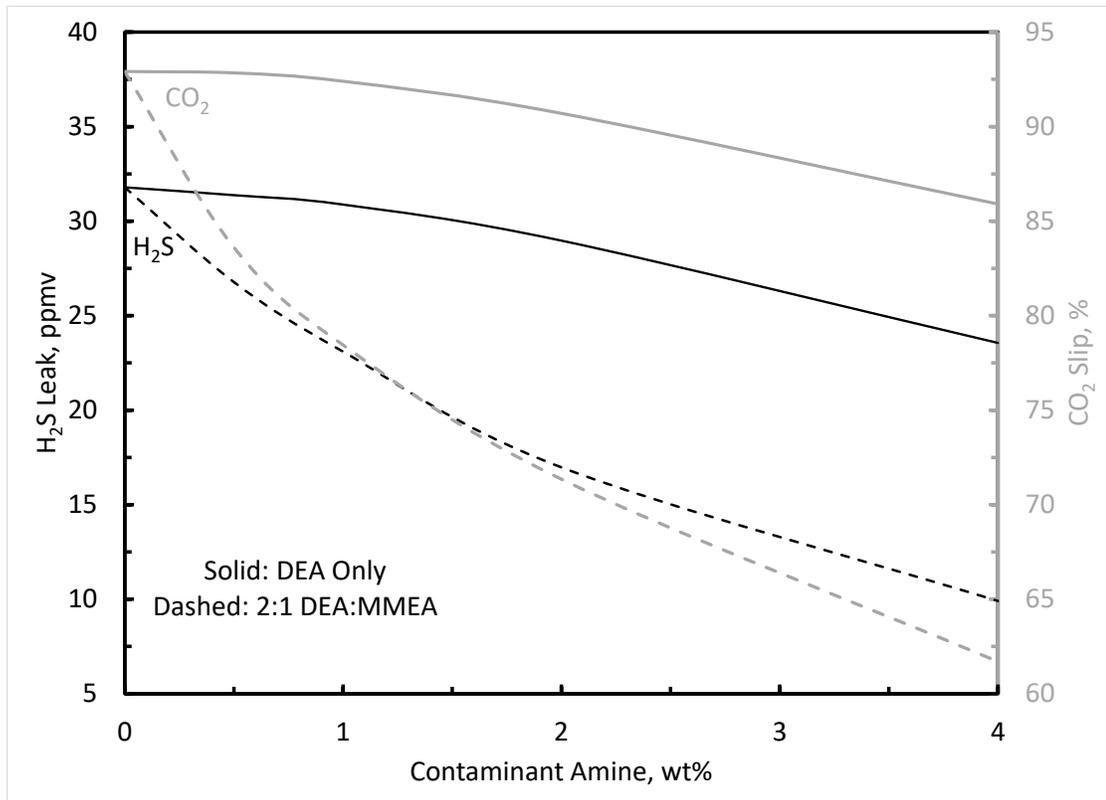


Figure 4 – Impact of reactive contaminants on TGTU performance (lean-end pinched wrt H₂S)

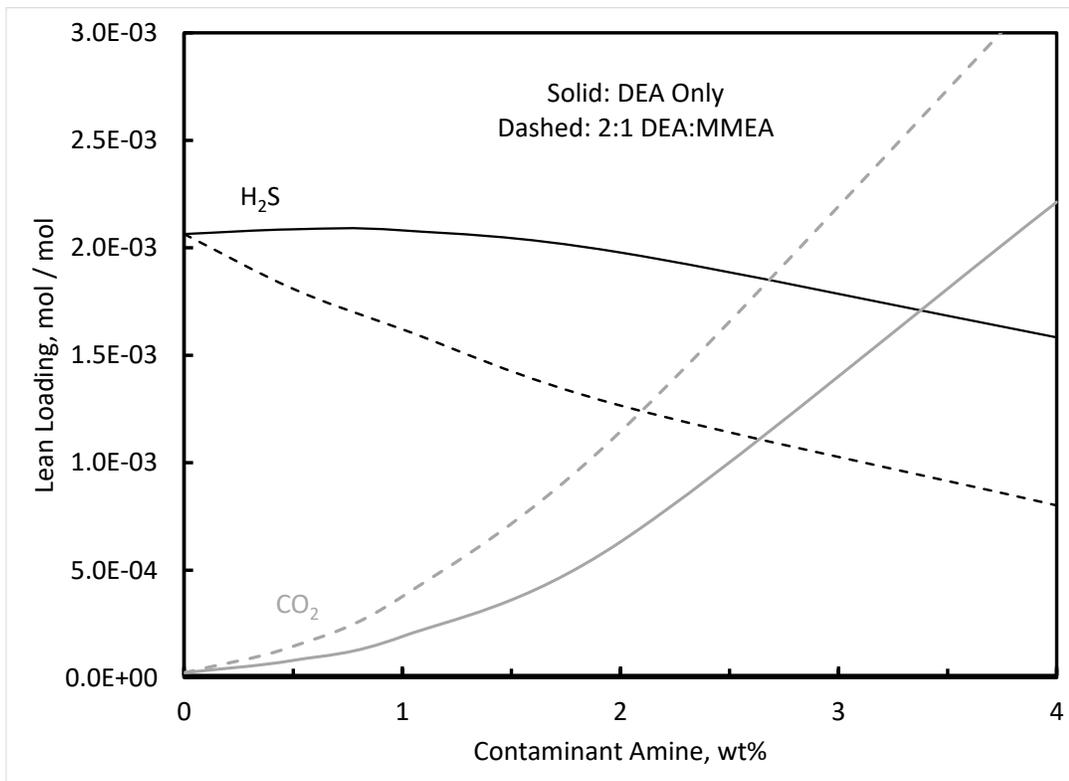


Figure 5 – Impact of reactive contaminants on TGTU lean loading

Case Study 3: AGE Unit

Our third and final case study demonstrates the impact of DEA and DEA + MMEA contamination on an Acid Gas Enrichment (AGE) unit. The AGE unit's objective is to produce a concentrated H₂S stream to feed to an SRU. Selective treating has obvious value in an AGE: every molecule of CO₂ that gets picked up by the amine will be fed to the downstream SRU where it will take up valuable hydraulic capacity. The case study is based on a closed-loop absorber and regenerator simulation built in ProTreat[®]. The case study set up is summarized in **Table 3**. Similar to the previous TGTU Case Study, the base case solvent has MDEA with a typical amount of HSS. Also similar to TGTU Case Study, we will replace incremental amounts of MDEA with DEA or 2:1 DEA:MMEA.

Results of the case study are shown in **Figure 6**. Just as in Case Study 2, CO₂ slip is incrementally reduced as the concentration of reactive DEA + MMEA is increased. Also, it can clearly be seen that MMEA is a much more potent CO₂ absorption promoter than DEA.

In contrast to the TGTU absorber, the AGE absorber is not lean-end pinched. Absorption of H₂S is controlled by the mass transfer rate; in other words, significant driving force for H₂S absorption exists everywhere in the absorber. The consequence of being mass transfer rate limited is shown by the black lines in **Figure 6**. The AGE absorber will pick up less H₂S and more CO₂ if the amine is contaminated.

As shown in **Figure 7**, the presence of reactive contaminants has a significant impact on the temperature profile in the absorber. The warmer temperature bulge is caused by faster absorption of CO₂, which has an exothermic reaction with the solvent. Because CO₂ is a stronger acid than H₂S, the faster CO₂ absorption also results in an elevation of H₂S back pressure. The warmer temperature bulge and increased back pressure cause the H₂S absorption to shift from mass transfer rate limited (no contaminants) to rich end pinched (with contaminants). These changes in the absorber operation are responsible for undesirable changes in the absorption of both CO₂ and H₂S.

Figure 8 shows the meaningful practical impact of contaminated amine in this AGE unit. As reactive amine contaminants accumulate in the circulating amine, the enriched gas will contain a higher concentration of CO₂ and a lower concentration of H₂S. If the AGE unit design is based on pristine MDEA then the accumulation of reactive contaminants could pose a real risk to the unit's ability to achieve its expected performance.

Table 3 - Description of Case Study 2 – AGE Unit

| Feed Gas | | Absorber | |
|------------------|--------------|-----------------|--------------|
| Composition | | Trays | 12 |
| Water | 5.8 mol% | Tray Passes | 2 |
| Hydrogen Sulfide | 7.5 mol% | Diameter | 8.6 ft |
| Carbon Dioxide | 84.8 mol% | % Flood | 70 % |
| Methane | 0.9 mol% | | |
| Ethane | 0.9 mol% | | |
| Temperature | 120°F | | |
| Pressure | 29.7 psia | | |
| Flow rate | 25.43 MMSCFD | | |
| Solvent | | Regenerator | |
| Circulation | 1250 gpm | Stripping Trays | 30 |
| MDEA | 45 wt% | Pressure (top) | 25.8 psia |
| Thiosulfate | 3,000 ppmw | Reboiler Duty | 275 MMBTU/hr |
| Formate | 1,500 ppmw | | |

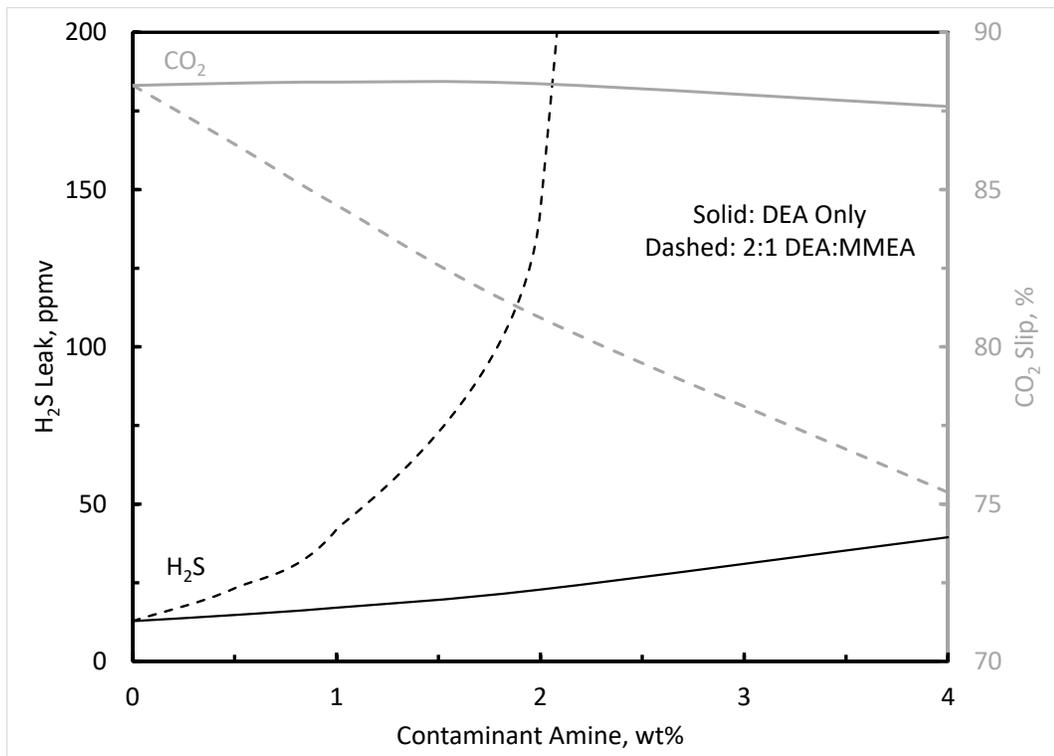


Figure 6 - Impact of reactive contaminants on AGE performance (mass transfer rate limited wrt H₂S)

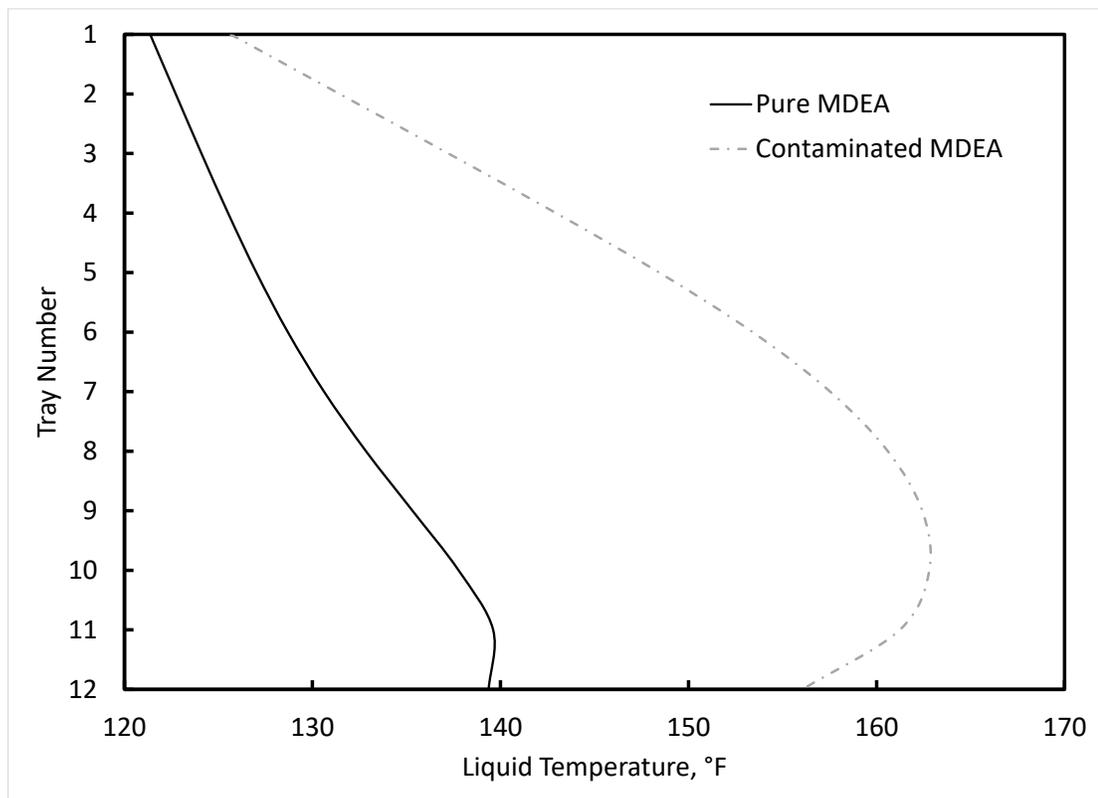


Figure 7 – AGE Absorber Temperature Profile with 37 wt% pure MDEA compared with Contaminated MDEA where 4 wt% MDEA was replaced with DEA:MMEA in a 2:1 molar ratio

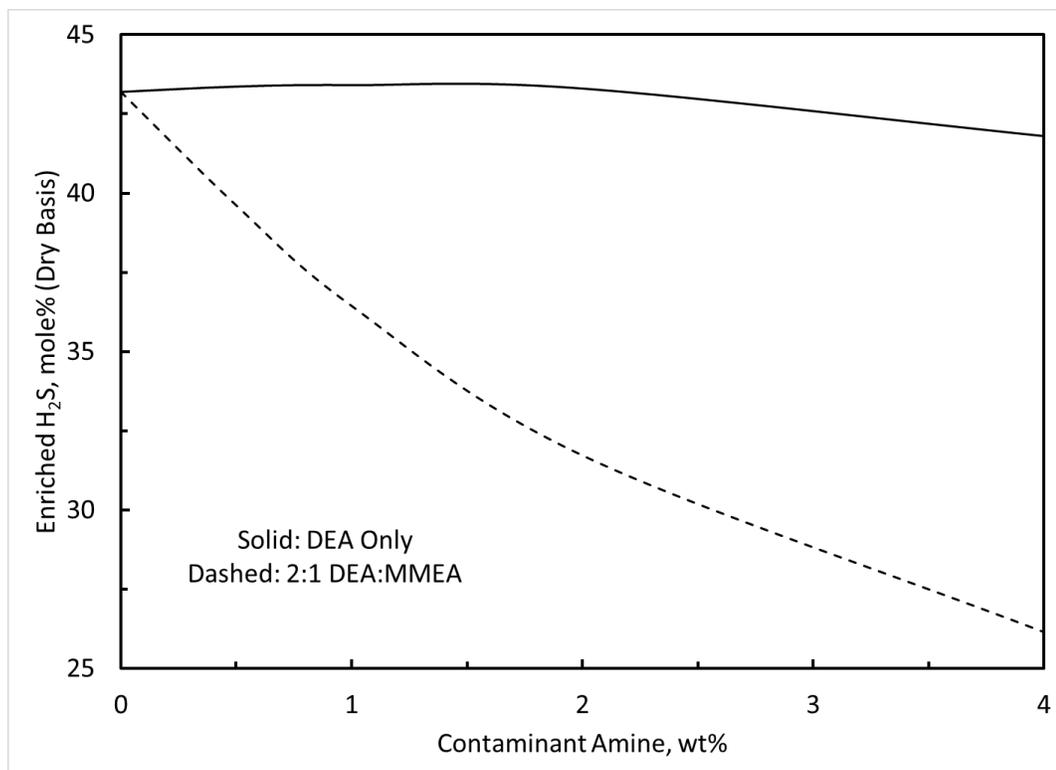


Figure 8 - Impact of reactive contaminants on enriched gas from AGE Unit. H₂S is diluted by additional CO₂ pickup caused by reactive amine contamination.

Conclusion

This paper has shown the real impact that reactive amine contaminants DEA and MMEA can have on selective pickup of H₂S in MDEA units. As discussed, selectivity is an important parameter because it affects unit design and operation. Understanding how common contaminants influence selectivity will help designers and operators achieve their process goals. As demonstrated in other publications^{3,8}, the presence of non-reactive contaminants can lead to the formation and accumulation of reactive contaminants.

We have shown that replacing only 1% of MDEA with a 2:1 molar ratio of DEA:MMEA can reduce equilibrium CO₂ partial pressure by 50% at low CO₂ loadings (~0.01 mol/mol). The impact of reactive contaminants on VLE of CO₂ at higher loadings and on VLE of H₂S is less pronounced. Confirmation of MDEA purity must be considered for VLE laboratory studies, especially if the study emphasizes treating to low CO₂ partial pressures (< ~0.1 psia CO₂ partial pressure).

In operating plants with closed solvent loops, the impact of reactive contaminants will depend on the operating regime of the plant. The impact on H₂S absorption can be positive or negative. If the absorber is lean end pinched with respect to H₂S, as in our TGTU case study, then reactive contaminants might *increase* H₂S treating effectiveness by reducing H₂S lean loading. (The corresponding increase in CO₂ pickup outweighs any benefit of better H₂S absorption, so the net impact of reactive contaminants is undesirable.) On the other hand, if the absorber is mass transfer

rate limited or rich end pinched, as in our AGE case study, then reactive amine contaminants can reduce H₂S treating effectiveness.

In all cases, the presence of reactive contaminants in an MDEA solvent will increase the pickup of CO₂. Both the TGTU and AGE case studies demonstrate that while both DEA and MMEA increase CO₂ absorption, MMEA is a much more potent contaminant in this regard.

Selectivity is a balancing act between competitive acid gas pick up rates. As demonstrated in the case studies, selectivity can be affected by changes to VLE, absorber temperature bulge, reaction kinetics, and other factors. Therefore a mass transfer rate model is required to correctly predict selectivity. Version 6.2 of the ProTreat[®] simulator was used to generate the case studies presented in this paper.

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