

SIMULATING MERCAPTANS AND COS REMOVAL

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detail a new model for carbonyl sulfide
(COS) absorption into amines based on
mass transfer rates and reaction kinetics.

Natural gas, refinery gas and hydrocarbon liquid streams such as propane (LPG) need to be cleaned of carbon dioxide (CO_2), hydrogen sulfide (H_2S) and other sulfides such as carbonyl sulfide (COS) and mercaptans (RSH). Failure to adequately do so will cause LPG, for example, to fail a copper-strip test. Even LPG that passes the copper strip test can fail later in the presence of water if there is residual COS, because of the gradual hydrolysis of COS to CO_2 and H_2S . This article discusses a new model for COS absorption into amines based on mass transfer rates and reaction kinetics. This is the first time that any commercial

software has been able to accurately simulate COS removal from gas streams.

Amines have excellent H₂S removal characteristics, but they are notoriously poor solvents for other trace sulfur species that are less acidic, such as COS and mercaptans. Until now, no simulator has been able to model COS and mercaptans adequately. For mercaptans, the basic problem appears to be insufficient, inaccurate phase equilibrium data. Almost all of the public domain mercaptans solubility data is academic in origin and this may explain the paucity of mercaptans data. Very few academic institutions welcome researchers who deal with mercaptans – academia is generally ill-equipped to handle them safely and risks fogging up campuses. Good-quality data is hard to come by. For COS, one of the main issues has been that simulators have ignored its reactive nature in aqueous amine solutions, treating its chemistry in an over-simplified way as a purely physically-dissolved, non-reacting solute. COS absorption rate is thus wrongly computed because the calculations fail to account for the absorption rate enhancement that

Table 1. Typical lean loadings of H₂S and CO₂

Loading	MEA	DGA®	DEA	MDEA	MDEA + Pip
H ₂ S	0.01	0.01	0.005	0.001	0.001
CO ₂	0.1	0.1	0.08	0.001	0.1

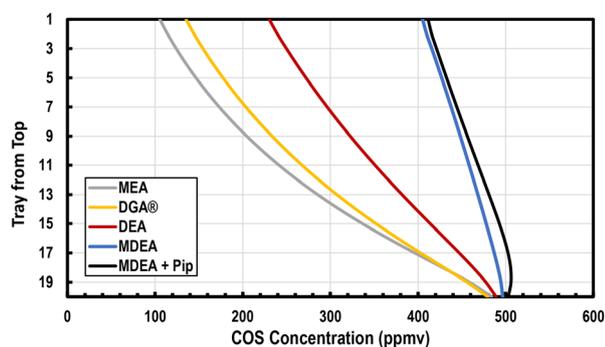


Figure 1. Absorber COS concentration profiles for various amines.

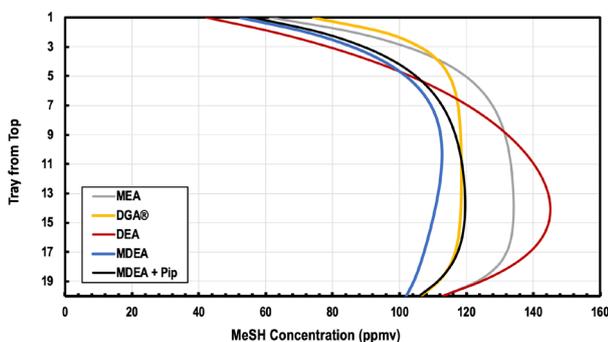


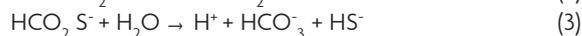
Figure 2. Absorber MeSH concentration profiles for various amines.

results from the chemical reactions of COS with the amine.

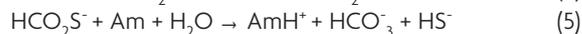
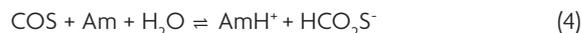
Reactions

The reactions of H₂S and CO₂ in aqueous amines are well-known and require no discussion in this article. RSH merely dissociates in aqueous media, as seen in reaction 1. However, to describe the decomposition of COS in water just by the reaction $\text{COS} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{S}$ is a deceptive oversimplification. The reaction mechanisms and kinetics of COS in amines are more complex than that, and although well-described in literature¹, they still deserve a brief portrayal in this discussion.

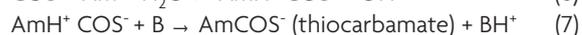
COS reacts in aqueous solutions first to form thiocarbonate (reaction 2), which further hydrolyses to bicarbonate and bisulfide (reaction 3):



The combined form of reactions 2 and 3, along with other speciation reactions of CO₂ and H₂S, is equivalent to the overall simplified hydrolysis of COS to CO₂ and H₂S that has already been mentioned. Reactions 2 and 3 are very slow unless there is a base in the solution to catalyse the reactions. In the presence of amines, it is postulated that COS reacts by a base-catalysed mechanism according to:



In addition to these reactions, COS forms thiocarbamate with primary and secondary amines via a zwitterion mechanism:



Reaction 6 represents the zwitterion formation, and reaction 7 describes its deprotonation reaction. Any base, B, present in solution deprotonates the zwitterion. These reactions are responsible for quite significant COS absorption into primary and secondary amines, but do not occur with tertiary amines. Reaction 4 is known to be equilibrium-limited. The rate of reverse reaction is observed to be practically zero for reaction 5, indicating that for any amine, COS will completely hydrolyse to CO₂ and H₂S in the fullness of time.

Reaction 1 is a simple dissociation reaction involving a single hydrogen ion and, as such, is known to be essentially instantaneous. Thus, it is always at equilibrium. The problem with RSH is that it is an extremely weak acid so that even a low level of acidification of the solvent will drive reaction 1 back towards formation of molecular RSH, which has a very low physical solubility in water. Significant acidification can be witnessed even with a modest amount of dissolved CO₂ or H₂S. In regenerative caustic solutions,

the CO₂ and H₂S spend the caustic from its intended purpose of RSH removal.

Thiocarbamate formation is significantly limited by the rate of deprotonation (reaction 7). In fact, for several amines, the COS absorption rate is almost completely determined by the rate of deprotonation. This is unlike CO₂, where the zwitterion deprotonation rate has much less influence on the overall conversion. As a result of these factors, the COS-amine reaction rate is much slower than amine-CO₂. Nevertheless, COS reaction rates are significant enough for a substantial fraction of the COS in a typical feed gas to be removed by primary and secondary amines. This is not the case for mercaptans beyond MeSH, however, because they are very weak acids and are easily displaced by co-absorbed CO₂ and H₂S.

Recently, Optimized Gas Treating Inc. (OGT) finished developing a COS absorption model which regards COS as a rigorous mass transfer rate-controlled component and incorporates it along with its reaction kinetics into the OGT|ProTreat® simulator. The results of the model were validated against some 20 proprietary sets of field-performance data for various amine systems, and showed that the model accurately simulates COS removal in amine absorbers, for the first time. What follows is a case study showing:

- Mass-transfer and reaction-rate control in the COS removal model.
- A comparison between various amines' performance in a simple absorber.
- The effect of a solvent's acid gas loading on the relative removal of COS vs mercaptans.

Case study

This case study involves the simulated performance of a simple 20-tray absorber using MEA, DGA, DEA, MDEA and piperazine-activated MDEA (referred to as MDEA + Pip), all at the same 3M molar strength and circulation rate. Unfortunately, the numerous sets of commercial performance data used to validate the model are proprietary to various operating companies so that nothing can be revealed. Instead, the case study involves a hypothetical feed gas of methane at 300 psig with 5 mol% CO₂ and 2 mol% H₂S, containing 500 ppmv of COS and 100 ppmv each of MeSH, EtSH, PrSH and BuSH. Making comparisons between amines on the basis of the same low CO₂ and H₂S loadings for all of them seems unreasonable given that MEA, for example, rarely has a lean CO₂ loading below 0.1 mole per mole, whereas MDEA commonly has a lean CO₂ loading in the vicinity of 0.002. Therefore, to make comparisons more equitable, the lean solvent loadings shown in Table 1 were taken as typical for the amines shown.

COS removal

Figure 1 shows how COS concentration in the gas varies across the height of the absorber. The most effective solvent is MEA because it is the most alkaline primary amine and forms thiocarbamate with COS faster than any of the others. DGA is a very close second while DEA

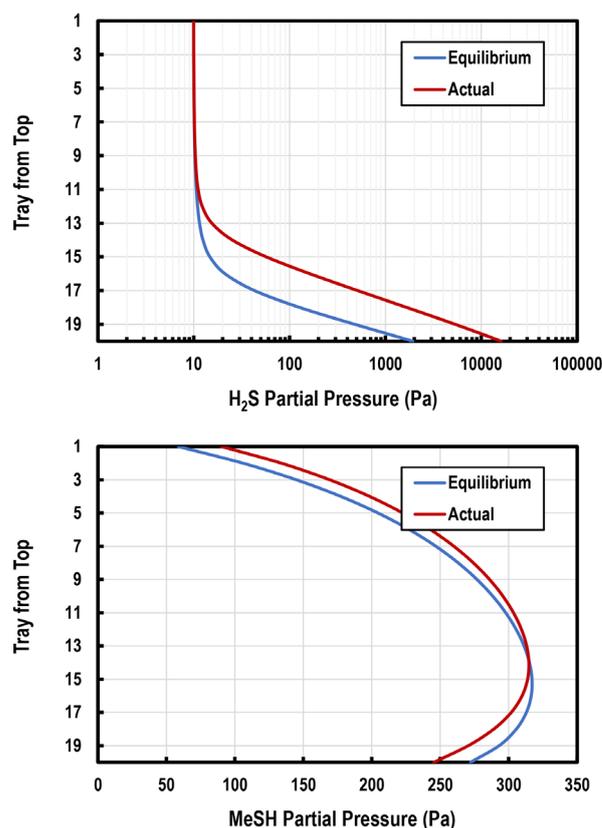


Figure 3. Absorber H₂S and MeSH concentration profiles for DEA.

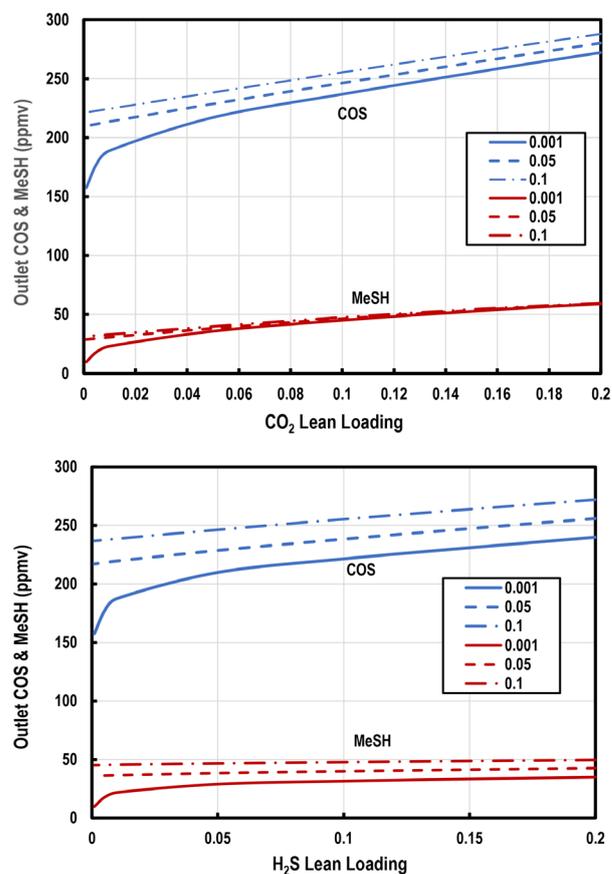


Figure 4. Effect of CO₂ and H₂S lean loading on DEA absorber performance for COS and MeSH removal.

lags behind, and MDEA (and piperazine-promoted MDEA) are the least effective for removing COS. These results are pretty much in line with the pKa values of these amines and, of course, COS forms only the thiocarbonate with MDEA. The particular promoted MDEA formulation used here is 2.6 molar MDEA + 0.4 molar piperazine which is rather a low concentration (30 and 3.3 wt%, respectively) and not truly representative of promoted MDEA used commercially (closer to 38 and 7 wt%). However, as far as COS is concerned, absorber performance is only weakly

Table 2. Comparison between legacy and kinetic models for COS*

Model	DEA			MDEA		
	CO ₂	H ₂ S	COS	CO ₂	H ₂ S	COS
Legacy (equilibrium)	30	0.8	523†	1.7‡	3.9	508†
Kinetic (reaction rate)	30	0.8	189	1.7‡	3.9	405

* Treated gas concentrations in ppmv

† CO₂ and H₂S removal concentrates COS above its 500 ppmv inlet value. CO₂ and H₂S lean loadings are 0.01 and 0.001, respectively

‡ Concentration in mole %

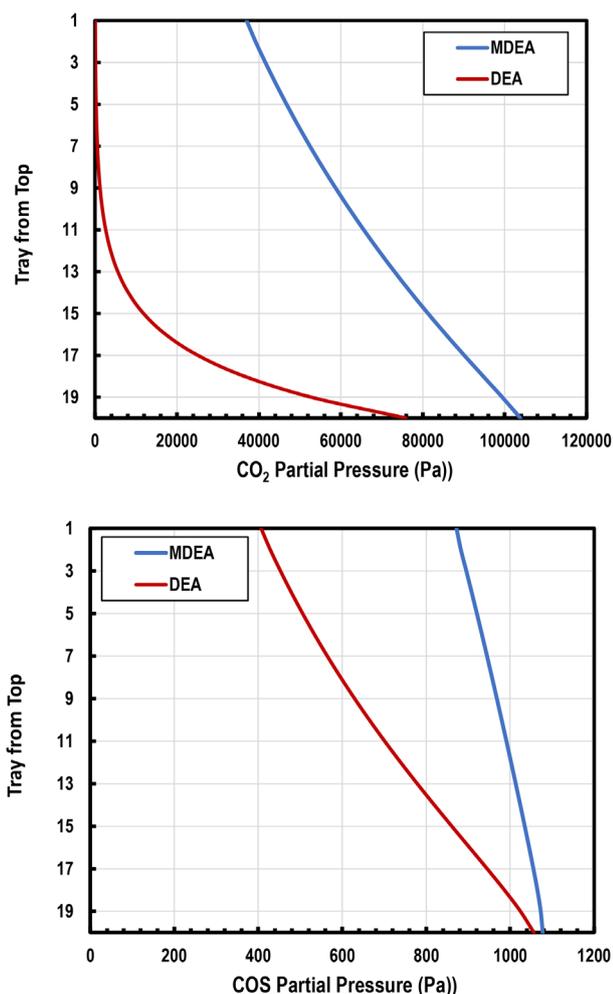


Figure 5. CO₂ and COS partial pressure profiles across DEA and MDEA absorbers.

affected by the details of the formulation. Piperazine mixed with MDEA is ineffective and does not appear to improve COS removal beyond what MDEA alone can do. Even 3.3 wt% piperazine alone will reduce COS to 385 ppmv, but CO₂ and H₂S absorption swamp the piperazine, consuming it all shortly after it enters the column and thereby reducing its effectiveness for COS removal. Obviously, when there are multiple acid gases and multiple reactive solvent components, care must be taken when interpreting results because acid gas loadings can be much higher with respect to one amine than the other in a solvent blend.

MEA shows an almost 80% COS removal efficiency vs only about 20% for MDEA and the promoted MDEA solvents. MDEA is a tertiary amine and cannot form thiocarbamate. Piperazine is a thiocarbamate former; however, in the presence of substantial amounts of CO₂ (as it is when total CO₂ loading is 0.1) it is nearly fully reacted to the carbamate and dicarbamate forms, and so has little or no residual-free amine remaining to form thiocarbamate. In fact, piperazine carbamate gives a solution with sufficiently higher viscosity than MDEA to result in the slightly poorer performance of promoted vs generic MDEA.

Mercaptans removal

Figure 2 shows a plot of methyl mercaptan concentration vs tray number in the absorber. Plots for EtSH, PrSH and BuSH are similar. It should be emphasised that a direct comparison between amines in terms of mercaptans removal should not be inferred from this plot because, for example, amine concentrations and lean solvent acid gas loadings may or may not be representative of the conditions for a particular case. Valid comparisons can be made using only full recycle flowsheets where reboiler duty and other parameters of the process are known.

As is usually the case with maxima and minima, the maxima in MeSH concentrations in Figure 2 are the result of competing effects. H₂S is a much stronger acid than mercaptan. As the solvent flows down the column and H₂S is absorbed, it pushes the mercaptan out of solution and back into the gas phase. Mercaptan is reabsorbed further up the column where almost all of the H₂S has already been absorbed by now, and therefore has little effect on mercaptan removal. This absorption/desorption cycle is illustrated in Figure 3, where H₂S and MeSH concentration profiles are compared for DEA. As the H₂S concentration in the gas approaches equilibrium with the solvent, i.e. the lean loading limits the ability of the solvent to absorb H₂S, the MeSH starts to absorb. Below that level in the column, MeSH is actually being stripped from the solvent, driven out by H₂S absorption. Evidence for this is found in the crossing of the actual and equilibrium MeSH partial pressure curves.

Effect of acid gas loading

Solvent CO₂ and H₂S loadings are reported to have a significantly-negative effect on COS and mercaptans removal. Figure 4 shows how CO₂ loading at various fixed H₂S loadings and H₂S loading at various CO₂ loadings

affect the COS and MeSH removal performance of the DEA absorber. CO₂ loading has a markedly greater effect on performance compared with H₂S. The reason is that CO₂ reacts with two molecules of DEA, forming the carbamate and the protonated form of DEA, whereas H₂S absorption consumes only a single DEA molecule. So, compared with H₂S, CO₂ removes twice the amount of DEA from being able to react with COS to form thiocarbamate.

The entering raw gas contains 500 ppmv COS and 100 ppmv MeSH. When the lean amine acid gas loadings are quite low – at 0.001 each – COS is removed to 150 ppmv, and MeSH to about 8 ppmv. At a small CO₂ loading value of 0.01, the treated gas increases to nearly 200 ppmv COS and 25 ppmv MeSH. Again, H₂S loading has a lesser effect on both COS and MeSH removal than the same loading of CO₂ because of unfavourable CO₂ reaction stoichiometry.

Legacy vs reaction model for COS

Table 2 compares ProTreat's predictions using a new model for COS absorption ('kinetic' in table) with an example of what has been the only type of simulation commercially available until now ('legacy' in table). The legacy and kinetic models produce essentially identical predictions of CO₂ and H₂S removal, as one might expect. However, the legacy model predicts that 2% of the COS is removed by DEA and 3.3% by MDEA. On the other hand, the kinetic model predicts the removal of 65% and 23% by DEA and MDEA, respectively. Users of legacy simulators have complained for years that predicted COS removal has been far from observations. That disparity has now been rectified – ProTreat's Kinetic Model predictions conform well to field measurements.

As illustrated in Figure 5, the kinetic model shows that CO₂ and COS approach final outlet values in the DEA absorber quite differently. The gentler decrease in COS partial pressure reflects the much slower reaction kinetics of COS. In DEA, CO₂ falls rapidly from 5 mol% to a few ppmv, whereas the same 20 trays only take COS from 500 ppmv to 189 ppmv. But relative to MDEA, both CO₂ and COS decrease more rapidly simply because DEA reacts with both the carbamate and thiocarbamate reactions, respectively. MDEA does not.

In a typical amine absorber, COS absorption is mass transfer rate-limited. This is supported by the present cases where the COS equilibrium partial pressures are almost zero. As such, although the driving force for absorption remains high, the absorption rate is slow. COS can not be properly simulated using only its physical (Henry's Law equilibrium) solubility, as evidenced by the legacy predictions. COS reacts with primary and secondary amines at rates that enhance its absorption and therefore significantly affect the ability of any absorber to remove it from the inlet gas. Similarly, mercaptans must be modelled as mass transfer rate-limited components, too, because they dissociate in amines and the amines act as sinks for the released hydrogen ions – the dissociation reaction enhances mass transfer. For meaningful results, it is imperative that the latest version (7.0) of OGT|ProTreat's rigorous mass transfer rate-based simulator is used to simulate COS and mercaptans removal in gas treating. 

Reference

1. VAIDYA, P. D. and KENIG, E. Y., 'Kinetics of carbonyl sulfide reaction with alkanolamines: a review', *Chem. Eng. J.*, 148, 207 – 211, (2009).