OPERATIONAL CONSIDERATIONS OF SIDE REACTIONS IN GAS SWEETENING SYSTEMS

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ABSTRACT

In sour gas treating systems there are a number of potential side reactions that produce unwanted byproducts. These reactions depend on reactant concentrations, reactant absorption rates, temperature, kinetic rates and residence times. Appropriate prediction of the rate of these side reactions can give greater insight into the process, in terms of degradation rate and impact of operating conditions. Three reactions are examined in the context of a typical amine treating process: conversion of hydrogen cyanide to formic acid, hydrolysis of carbonyl sulfide in MDEA, and CO_2 degradation of DEA. In this paper, we will explore the occurrence of these reactions throughout the process and the effect of operating conditions through the use of simulation.

THE IMPACT OF SIDE REACTIONS IN GAS TREATING

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Introduction

In gas treating, there are a great number of chemical reactions that occur ranging from water dissociation to piperazine dicarbamate hydrolysis. For the most part these reactions are reversible and tend towards equilibrium. Some reactions are not reversible and represent a permanent chemical change in the process. These irreversible reactions fall into two major categories: degradation of the solvent and conversion of gas contaminant components. The extent of these reactions is seldom taken into account in simulation and generally not in a rigorous fashion. These reactions are generally slow reactions with time constants of days, weeks or months. This slow behavior also makes research and quantification of the kinetics difficult and relatively rare.

One of the difficulties in assessing these side reactions in gas treating systems is the large number of places the reactions can occur in the gas treating system, including the absorber trays or packing, absorber bottoms holdup, rich flash, lean/rich exchanger, stripper column, reflux drum, reboiler, surge tank, as well as other areas such as sour water stripper or liquid-liquid separators. In addition to the uniqueness of reaction kinetics, each point of possible reaction has its own reaction conditions (concentration, temperature and residence time).

The three reactions that we will examine are hydrolysis of cyanide, hydrolysis of carbonyl sulfide in the presence of methyldiethanolamine (MDEA), and the degradation of diethanolamine (DEA). In each case, we will review the reaction kinetics, demonstrate how well it matches with published laboratory or plant data, and then show by a simulation of a typical amine process where the reaction occurs and to what extent. From these observations, we can assess a reasonable process for remediation.

Typical Amine Process

The amine process examined is purely hypothetical to demonstrate the impact of side reactions. The process is shown in
Figure **1**. It has been modeled using ProMax® 4.0 from Bryan Research & Engineering, Inc. The absorber and regenerator columns have 20 trays with 2" weirs. Both of the columns are sized for 70% of flooding. The flash tank operates at 75 psia and the lean/rich exchanger produces a rich solvent with a temperature of 210°F. In this process, a surge tank is included after lean side of the lean/rich exchanger. Inlet sour gas is 800 psia and 110°F, while the lean amine enters the column at 120°F. The regenerator condenser operates at 120°F.
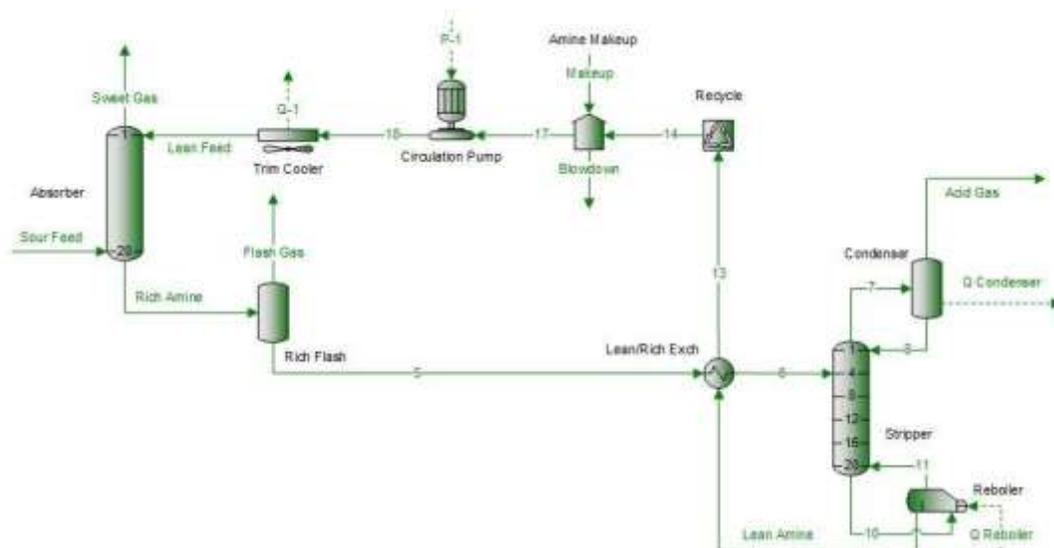
Figure 1: Typical amine treating process.

The reactions described in this work are kinetically limited and are modeled using a perfectly mixed or 'CSTR' style reactor. One of the important factors in determining the extent of reaction is the amount of time that the reaction mixture remains at a particular condition. These liquid residence times vary from plant to plant, but after review of several amine plant designs, the following holdup times were selected as a representation of a typical plant.

Absorber bottoms: 3 minutes	Reflux Accumulator: 10 minutes
Flash Tank: 10 minutes	Reboiler: 3 minutes
Surge tank: 10 minutes	Lean/Rich Exchanger: 1 minute

In this analysis, we will also be looking at the reactions in the mass transfer portion of columns. The tray liquid residence times depend on column hydraulics, but typically vary from 1 to 3 seconds.

Cyanide Hydrolysis

Hydrogen cyanide is a common contaminant in refinery gases, especially in more severe processing units such as fluidized catalytic crackers and coking units. It is a weak acid with lower volatility than H_2S and CO_2 which allows it to become trapped by water and amine systems. It can be driven out of the solution with enough heat, but does accumulate to some extent in a recycled amine loop. As a weak acid it diminishes the ability of the amine to remove acid gases, but the bigger concern is the potential to form heat stable salts (HSS). Once in the aqueous phase it reacts with hydroxide ions to form ammonia and formate ions. The ammonia is an operational problem in the regenerator, while the formate ions can cause increased corrosion. According to Wiegand and Tremeling (Wiegand & Tremelling, 1972), the reaction proceeds as shown in Equation 1.

$$HCN + OH^- + H_2O \rightarrow NH_3 + HCO_2^- \qquad \text{(Equation 1)}$$

With the kinetic rate expression

$$r_{HCN} = k[HCN][OH^-] \qquad \text{(Equation 2)}$$

where the rate constant takes the standard Arrhenius form

$$k = Ae^{-\frac{E_A}{RT}} \qquad \text{(Equation 3)}$$

This reaction is first order in both cyanide and hydroxide. To demonstrate the reasonableness of the kinetic model, a simulation was constructed to represent a case described in the Wiegand and Tremeling paper. They quote that a 0.25 N solution of cyanide lost 0.00024 N per day in cyanide concentration at 'room temperature'. While ProMax cannot simulate a batch reactor in time, the plug flow reactor model with the appropriate flow and reactor dimensions can simulate such a reaction as an analog in space. With a one liter reactor and a one liter per day liquid flow, the 0.00024 N/day loss rate was reproduced at 79°F, within the range of 'room temperature'.

The simulation case has an inlet sour gas with 50 ppm of HCN. Knowing that the process will generate ammonia, the regenerator column has a purge that is 5% of the reflux flow. As a base case, the regenerator operates at 10 psig and has a reboiler duty of 1 MBtu/gallon of circulation. The solvent is 40 wt% MDEA with a circulation rate of 130 gpm giving a treated gas concentration of 1.5 mol% CO_2, 0.1 ppm H_2S and essentially zero HCN. The rich and lean total loadings are 0.3 and 0.002 mole acid gas per mole amine, respectively.

Table **1** shows the reaction conditions at several locations in the process. As one might expect, the highest HCN concentration is at the bottom of the absorber and the regenerator reflux accumulator, while the highest temperature is in the regenerator reboiler. The hydroxide concentration is highest in the lean amine. Because of the confluence of time, temperature, and hydroxide concentration, the lower section of the regenerator, the reboiler, and the surge tank have the highest reaction extent. This proportion can be seen in Figure 2.

Table 1: Conditions for HCN hydrolysis. Bolded text indicates three largest category values.

| Location	Temperature	[HCN]	[OH⁻]	Time	Reaction
	°F	ppmw	pH	s	mol/hr
Absorber Tray 1	124	5.2	10.6	1	0.000
Absorber Tray 10	154	23	10.0	1	0.000
Absorber Bottoms	140	**54**	9.6	180	0.010
Flash	142	**53**	9.7	**600**	0.038
L/R Exch Rich Side	210	41	9.9	60	**0.108**
Reflux Accumulator	120	**332**	7.4	**600**	0.000
Regenerator Tray 3	**225**	28	10.1	1	0.004
Regenerator Tray 20	**252**	2.1	**11.1**	1	0.008
Reboiler	**253**	1.3	**11.3**	180	**1.286**
Surge Tank	185	1.3	**11.3**	**600**	**0.274**
Total				2269	1.869
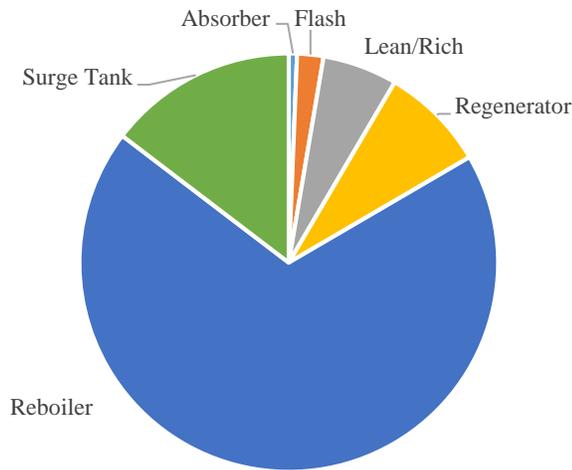
Figure 2: Proportion of reaction by unit operation.

Because formate is a heat stable salt, it does not naturally come out of the amine circulation loop and it will continue to accumulate over time. The information in

Table **1** assumes that the formate level in the lean amine going to the absorber is zero. This is achieved by artificially removing the formate after the surge tank on each cycle. At the operating condition shown, formate would be expected to accumulate at a rate of 1.87 gram-moles per hour, or 4.5 lb per day. As a comparison, there are 108 lb/day of HCN absorbed into the system. The liquid holdup shown corresponds to about 40 minutes of flow, or about 5000 gallons. On a mass basis, the formate accumulation rate is about 100 ppmw formate per day. This clearly indicates a motivation to remove cyanide prior to entering the amine system, commonly with a water / ammonium polysulfide wash.

Unlike the formate, the ammonia byproduct has an exit route in the reflux purge. Only a small fraction of the ammonia produced in the amine loop is not rejected in the regenerator column and will recycle back to the absorber, so buildup is not significant.

As mentioned, the reaction data shown is for a clean, formate-free solvent. As the formate builds up, the reaction behavior would be expected to change. Figure 3 shows the accumulation of formate and the reaction rate over time. At 10,000 ppm formate, the reaction rate is half of the clean solvent rate. The cause for this is shown in Figure 4a. As the formate level increases, it reduces the hydroxide in the reboiler, so that the product of the cyanide and hydroxide decreases, reducing the reaction. An additional effect of the formate accumulation is the treatment performance. Figure 4b shows the treated acid gas concentrations for a range of formate concentrations. As the formate level rises, the lean amine becomes leaner in H_2S with the same reboiler heat input and the treated gas H_2S level decreases. At the same time, the formate shifts the ionic balance of the amine, leaving less free amine which causes the treated CO_2 level to rise slightly.
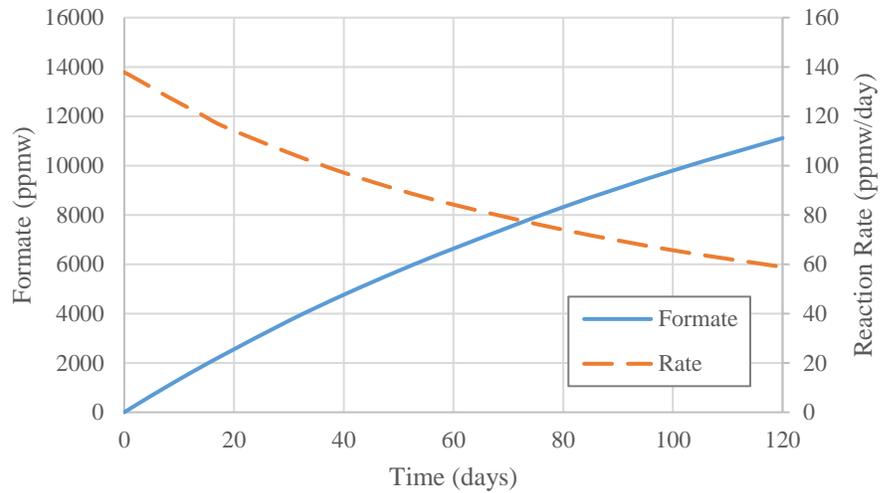
**Figure 3**: Time profile of formate and reaction rate
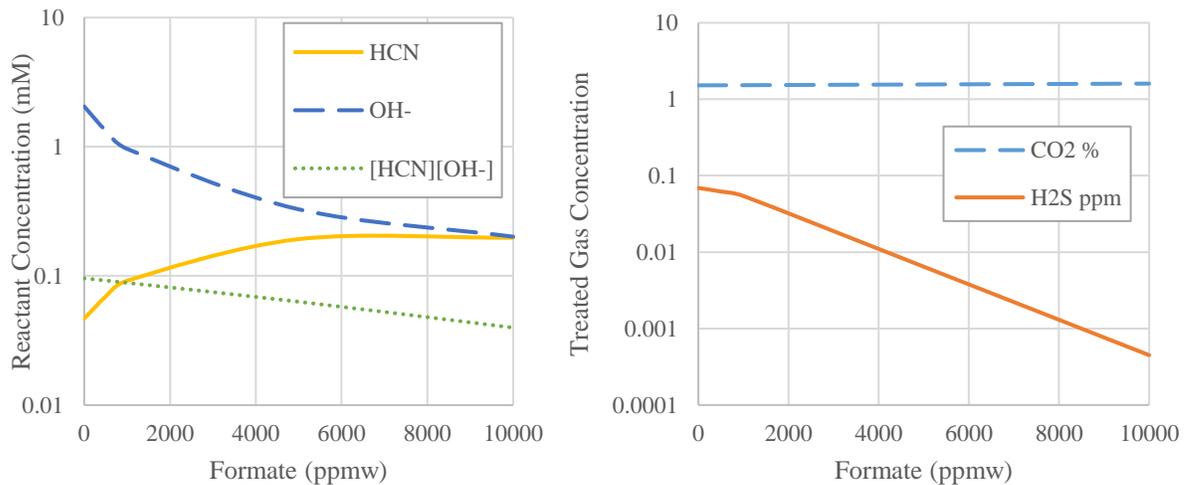
Figure 4: Effect of formate on (a) reboiler reactant concentration and (b) treated gas.

Seeing that increasing acid in the reboiler can reduce the amount of cyanide reaction occurring, one possible operating change would be to lower the reboiler duty, allowing for a less lean amine. Figure 5 shows this effect. As reboiler duty as a ratio to circulation rate is decreased, the hydroxide concentration does indeed decrease. However, with less reboiler duty, more HCN concentrates at the bottom of the column. At a low enough duty (reboiler ratio ~0.65 MBtu/gal), a cyanide 'bubble' forms in the column and the concentration in the reboiler increases dramatically. At this point, the hydroxide concentration also drops off. This combined effect can be seen in the reactant product ([HCN][OH$^-$]), which goes through a peak at reboiler duty ratio of 0.65.
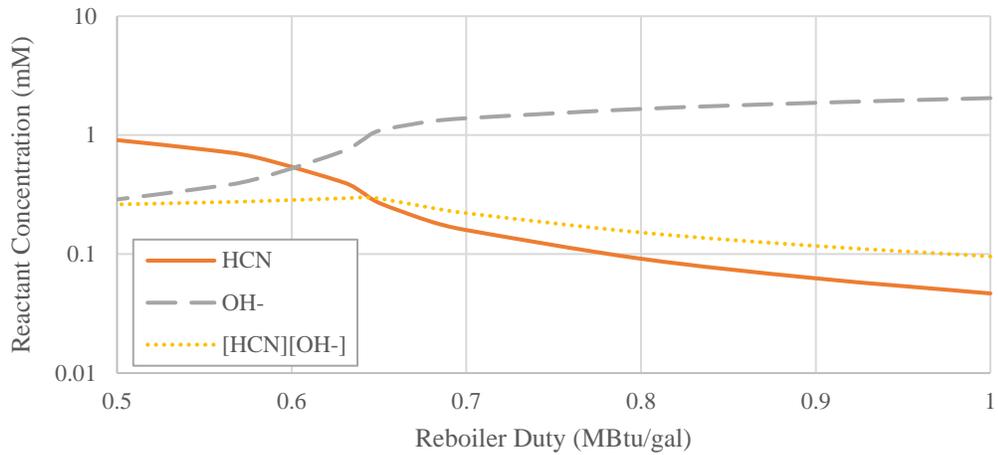
Figure 5: Effect of reboiler duty on reboiler concentration

The reaction rate for the system shows a similar peak in Figure 6, with the reaction rate at reboiler duty of 0.65 MBtu/gal more than twice as fast as the base case reboiler duty of 1.0.
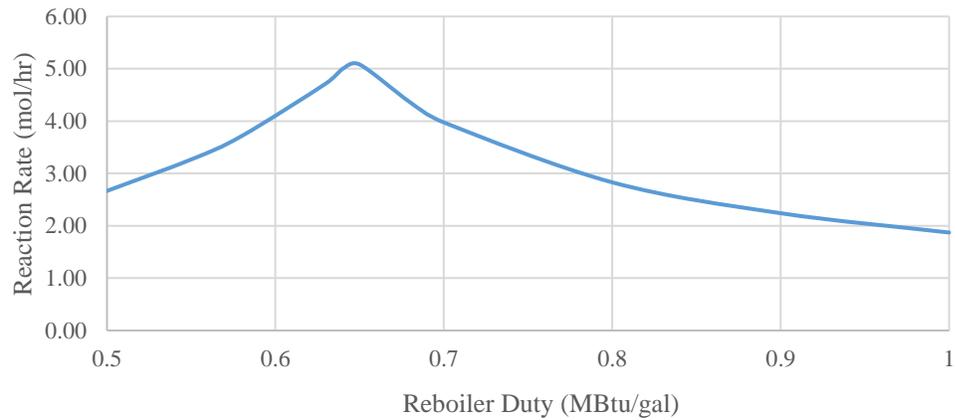

Figure 6: Effect of reboiler duty on reaction rate.

Decreasing reboiler duty did not reduce the cyanide reaction rate, but it is possible that if the temperature of the reboiler was reduced, it would reduce the reaction rate constant, as well as the reaction rate. Because the temperature of the reboiler is primarily governed by the regenerator pressure, the pressure of the regenerator was varied to explore its impact on the reaction rate. Figure 7 shows this effect. As expected, reducing the pressure reduced the reaction rate. In this case, dropping the pressure from 20 psig to 0 psig reduces the reaction rate by a factor of about 16. However, the second plot indicates that the effect of temperature on the rate constant only accounts for a factor of 4.
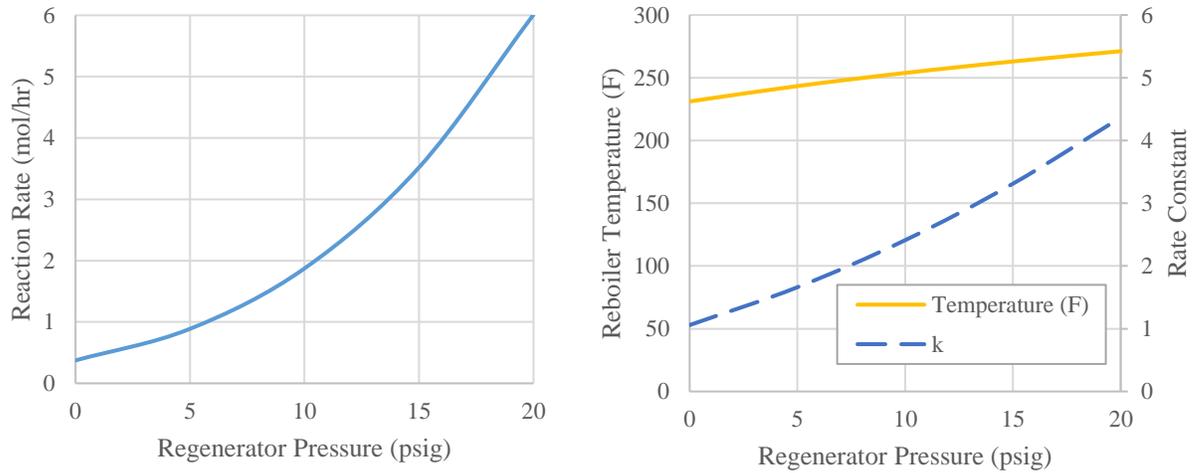
Figure 7: Effect of regenerator pressure on reaction.

It should be noted that the condenser was still specified to be 120°F. As shown in Figure 8, the lower pressure reduces both cyanide and hydroxide concentration in the reboiler, explaining the additional reduction in reaction.
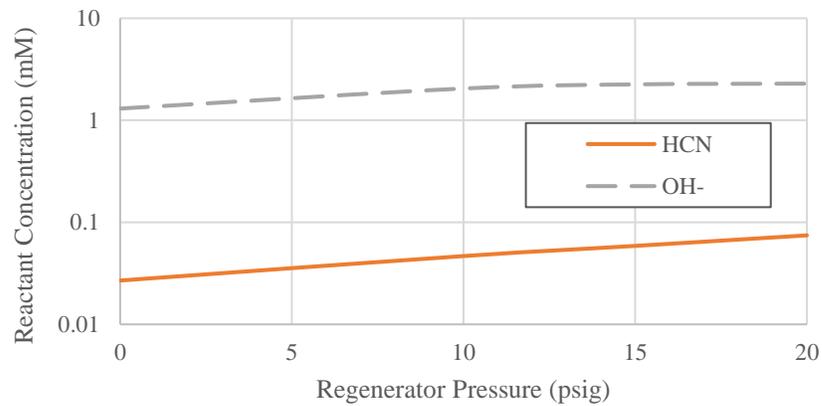

Figure 8: Effect of regenerator pressure on reboiler concentrations

One common technique to reduce corrosion in the presence of acids is to neutralize the solution by adding a caustic. However, because hydroxide is a reactant to the formic acid production reaction, this could cause an acceleration of the reaction. Figure 9 shows the effect of adding KOH to neutralize the acid content. As the caustic increases, the rate of reaction increases relative to the un-neutralized solution. At full neutralization, there is essentially no reaction rate slowdown due to formate accumulation.
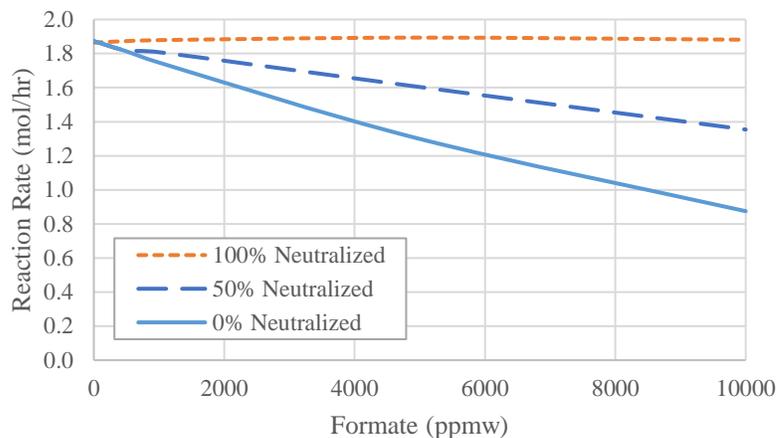
Figure 9: Effect of caustic neutralization

While the rate of HCN hydrolysis in one pass of an amine treating system is small, the fact that the reaction product accumulates requires that the rate of accumulation and consequently the rate of reaction be accounted for in the process simulation. The impact is important both in the short term prediction of treating performance as well as the long term management of the solvent.

COS Hydrolysis

With tightening regulations on total sulfur content of treated products, increasing attention is being paid to organic sulfur contaminants and to what extent they are removed by amine solvents. One of the significant organic sulfur components is carbonyl sulfide. As with carbon dioxide, the rate of absorption of COS can be influenced by chemical reactions occurring in the liquid phase. Accurately accounting for the impact of the reaction kinetics can allow a better prediction of the rate of absorption of carbonyl sulfide in an amine treating system, or at least illuminate the concepts of what benefit can be expected at different operating conditions.

Carbonyl sulfide can undergo a number of reactions that are somewhat analogous to carbon dioxide.

Reaction with water:

$$COS + H_2O \rightarrow CO_2 + H_2S \hspace{3cm} \text{(Equation 4)}$$

Reaction with hydroxide:

$$COS + OH^- \rightarrow CO_2 + HS^- \hspace{3cm} \text{(Equation 5)}$$

Reaction with water, base-catalyzed by MDEA:

$$COS + MDEA + H_2O \leftrightarrow MDEAH^+ + HCO_2S^- \hspace{1.5cm} \text{(Equation 6)}$$

Reaction with primary or secondary amine:

$$COS + 2R_2NH \leftrightarrow R_2NCOS^- + R_2NH_2^+ \hspace{2cm} \text{(Equation 7)}$$
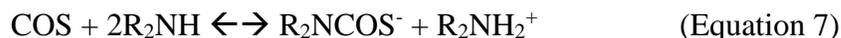
The last reaction is an abbreviation of a zwitterion formation with multiple deprotonation paths. These reactions occur at very different rates. For comparison, we can define an apparent rate constant k_{app} for the forward reaction by the following expression.

$$r_{COS} = -k_{app} [COS] \qquad \text{(Equation 8)}$$

This form assumes the effect of the concentration of any co-reactant such as hydroxide or MDEA is wrapped up into k_{app}. In this form we can compare the relative rates for the various reactions using a nominal value for the co-reactant. This is shown in Table 2. It can be observed that similar to the CO_2 reaction series, the H_2O and OH^- reaction rate is nearly negligible compared to the amines. MDEA is notably faster than those two. The primary and secondary reactions are significantly faster than MDEA.

Table 2: Relative rates of COS reactions.

Reactant	Concentration	k_{app}(120°F)	Reference
	wt%	1/s	
H_2O	50	0.00041	Thompson
OH^-	0.002	0.079	Sharma
MDEA	50	0.57	Littel
MEA	20	720	Littel
DGA	50	1900	Littel
DEA	30	210	Littel
Piperazine	10	1600	Huttenhuis

Danckwerts (Danckwerts, 1970) offers criteria for when a particular gas absorption reaction will be significant to the timescale of a particular location and whether it will impact the absorption of a reacting component. In the case of the reacting absorber, we are interested in whether a reaction will take place in the timespan of a tray. The criterion for negligible reaction is

$$k_{app} \, \tau \ll 1 \qquad \text{(Equation 9)}$$

Where τ is the residence time of the liquid on the tray. With a typical value of one second, the left hand side corresponds to the third column of Table 2. Based on this criterion, the water and hydroxide reactions can be neglected on a tray. The MDEA reaction may be in the on the border, but it should not be inconsequential. If a component being absorbed reacts fast enough, it will not only react in the bulk of the liquid, but will change the concentration profile in the liquid film near the interface, enhancing mass transfer. A criterion for negligible film reaction is shown by Equation 10. D_A is the diffusivity of the absorbing reactant in the liquid and k_L is the liquid film mass transfer coefficient.

$$\frac{D_A k_{app}}{k_L^2} \ll 1 \qquad \text{(Equation 10)}$$

Table 3 shows the values for several amines considered assuming a diffusivity of 2×10^{-9} m^2/s and a mass transfer coefficient of 2×10^{-4} m/s. The primary and secondary amine reactions are clearly fast enough to impact the film profile, while the MDEA reaction is not likely to have a sizeable impact on mass transfer.

Table 3: Criterion for film reaction.

Reactant	Film Indicator
MDEA	0.028
MEA	36
DGA	93
DEA	11
Piperazine	82

Calculating the impact of the enhanced mass transfer due to film reaction is beyond the scope of this work. However, the MDEA reaction has been shown to be non-negligible on the tray and slow enough to be handled as a 'bulk' reaction. The MDEA reaction indicated above is actually the first of two interacting reactions (Littel, van Swaiij, & Versteeg, 1992).

$$COS + MDEA + H_2O \leftrightarrow MDEAH^+ + HCO_2S^- \qquad \text{(Equation 11)}$$

$$HCO_2S^- + MDEA + H_2O \rightarrow MDEAH^+ + HCO_3^- + HS^- \qquad \text{(Equation 12)}$$
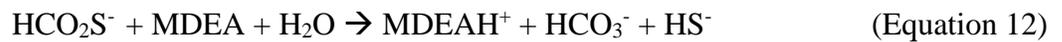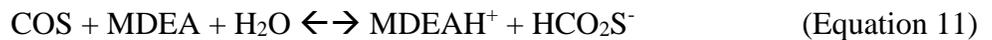
The first reaction to form protonated MDEA and monothiocarbamate (MTC) is reversible. The second reaction is the more conventionally thought of 'hydrolysis' forming H_2S and CO_2. This is essentially irreversible. The first reaction is faster than the second by about a factor of 30, so the MTC will build up and the first reaction will eventually slow down. This effect is shown in Figure 10. The solvent enters the absorber with no COS and the reaction rate is relatively high. As the solvent saturates in COS, the forward rate speeds up. Because the second reaction is slower, the intermediate product accumulates (Figure 11) and the forward reaction slows down significantly until there is almost no net COS reaction at the bottom of the absorber, despite relatively higher temperature. Also, as the solvent loads up with acid gases, the molecular MDEA diminishes as it is protonated.
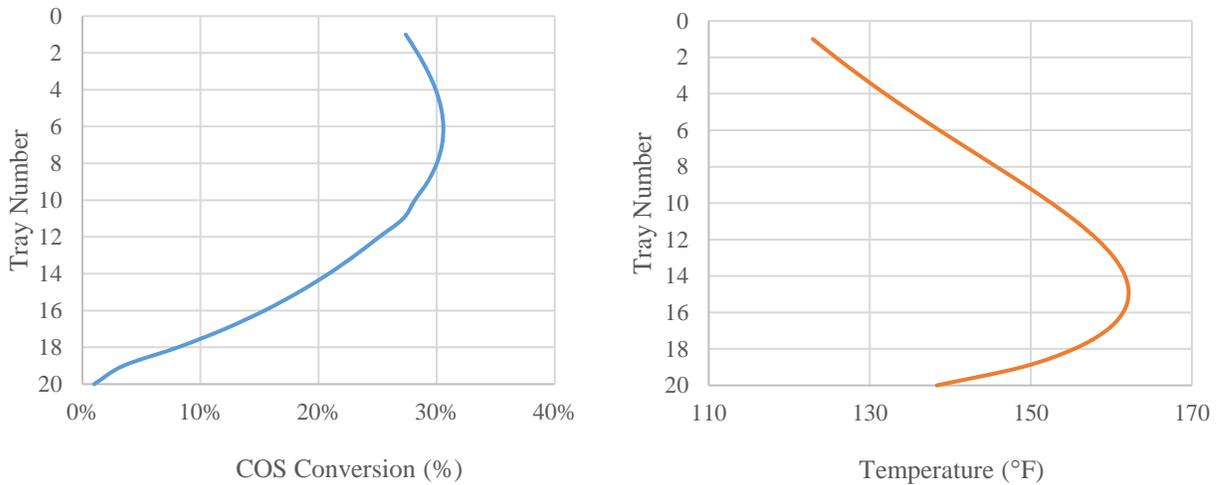
**Figure 10**: COS conversion in absorber.
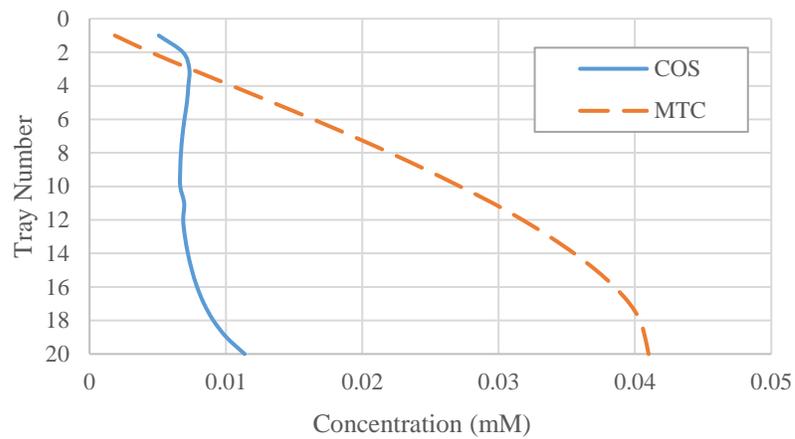
Figure 11: Liquid concentration of COS and monothiocarbamate by tray

Table 4 shows the net effect of the reaction on the absorption of COS into the MDEA. The main observation is that COS absorption by 40 wt% MDEA is low; only about 0.5% is absorbed in the case of no reaction. When the reaction is added in, the absorption is increased by a factor of 4 to over 2%.

Table 4: Effect of reaction on COS absorption

Stream	COS Flow	Removal	Removal
	lb/hr	lb/hr	%
Feed	9.896		
Treated, no reaction	9.850	0.046	0.5%
Treated, with reaction	9.684	0.211	2.1%

While this low solubility may seem surprising considering the behavioral analog between COS and CO_2, it is important to remember that the solubility of molecular CO_2 is not large. It is only

when the CO_2 reaction products HCO_3^- and CO_3^{2-} are included does the CO_2 solubility appear more significant. Because the COS reactions occur about two orders of magnitude slower than CO_2, this may not show up as a solubility increase in the bulk of the solvent, let alone in the mass transfer across the liquid film.

If greater COS reaction is desired, there are a number of steps that could be taken. Table **5** shows the impact of several possibilities. The fact that none of them change the behavior significantly further reinforces the concept that the reaction is becoming equilibrium limited at the bottom of the column.

Table 5: Modifications for COS removal.

Case	Variation	Removal
Base	None	2.1%
More liquid residence time	6" Weir	2.4%
Increase MDEA concentration	50% MDEA	2.2%
Increase circulation rate	150 gpm	2.5%
Increase absorber temperature	130/120°F	2.3%

Once again, the incorporation of the reaction kinetics answers an important question in the amine gas treating system. Namely, with the consideration of hydrolysis, how much more will MDEA absorb COS above physical solubility? The answer is that it improves significantly, but the net 'solubility' is still not large.

DEA Degradation

Primary and secondary amines are susceptible to degradation at higher temperature in the presence of CO_2. Understanding the kinetics of these reactions can allow amine plant operators to troubleshoot the source of the amine degradation and potentially modify their process to reduce its impact. Several resources describe the major steps of the mechanism of degradation for diethanolamine (DEA) as:

Diethanolamine (DEA) + CO_2 $\longleftrightarrow$ Diethanolamine carbamic acid   (Equation 13)

Diethanolamine carbamic acid $\longleftrightarrow$ 3-(2-hydroxyethyl)oxazolidone (HEOD) + H_2O

(14)

HEOD + DEA $\rightarrow$ N,N,N'-tris(2-hydroxyethyl)ethylenediamine (THEED)+ CO_2 (15)

THEED $\rightarrow$ N,N'-bis(2-hydroxyethyl) piperazine (BHEP) + H_2O (16)
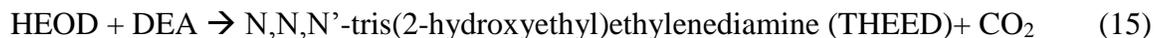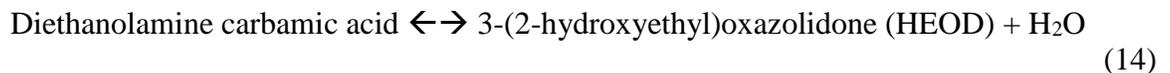
The later degradation products THEED and BHEP are formed by irreversible reactions so they permanently diminish the solvent's performance. They do have the capacity for holding CO_2 in solution through protonation and forming carbamates, however they are less effective per mass of amine as the original DEA. In addition, BHEP and THEED are suspected of enhancing corrosion in process equipment. Finally, THEED also has the potential to form polymeric materials leading

to fouling. Obviously the capacity to predict this behavior in the wide range of reaction locations would be useful for an amine plant operator.

Kim and Sartori (Kim & Sartori, 1984) provide a kinetic model for this process. The kinetic parameters not provided in the original paper were regressed from the experimental data of Kennard (Kennard, 1983).

$$DEA + CO_2 \longleftrightarrow HEOD + H_2O \qquad \text{(Equation 17)}$$

$$HEOD + DEA \rightarrow THEED + CO_2 \qquad \text{(Equation 18)}$$

The first reaction consumes CO_2 while the second reaction produces CO_2. In this manner, CO_2 acts somewhat like a catalyst to the degradation process. Figure 12 shows how the degradation model compares to the data of Kim & Sartori. The DEA and CO_2 concentration follow the experimental data very closely. The model HEOD value does not rise as high as the data, but the initial rise of THEED matches quite well. In the model, the THEED represents all of the permanent degradation products, while in the data, the THEED goes on to react to other components.
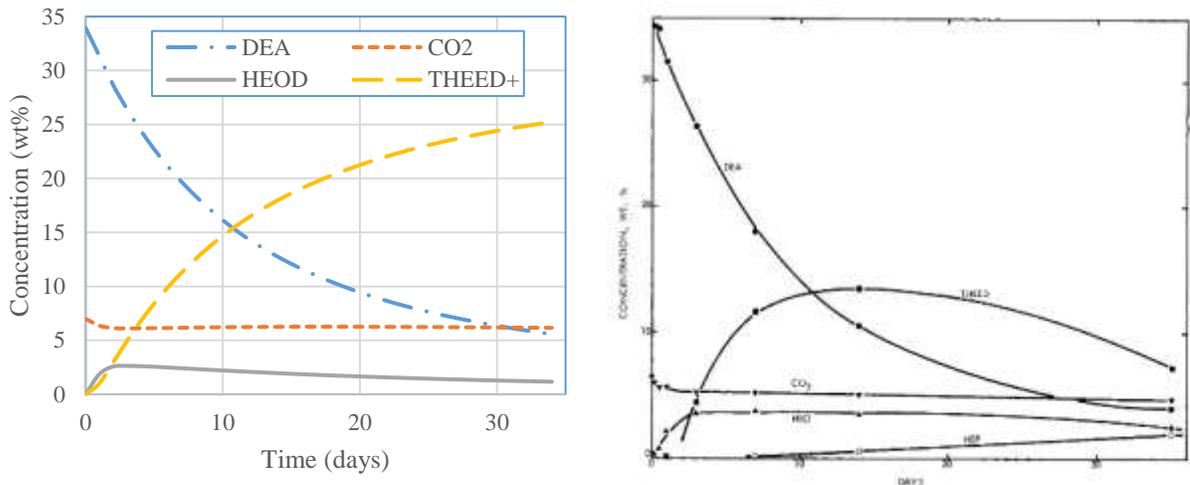

Figure 12: Comparison of model to data of Kim & Sartori (248°F at variable pressure).

To demonstrate the predictive nature of the reaction model, simulations were configured to represent data from other authors. The comparisons to literature laboratory degradation studies (Lepaumier, Picq, & Carrette, 2009) (Eide-Haugmo, Einbu, Vernstad, da Silva, & Svendsen, 2011) are shown in Table 6. While the simulation model slightly overpredicted DEA degradation with the Lepaumier and Eide-Haugmo results, it was reasonably close.

Table 6: Comparison of model with literature data.

Source	Lepaumier	Eide-Haugmo
Conditions	42 wt% DEA, 284°F 275 psig CO_2, 15 days	30 wt% DEA, 275°F 0.5 mol CO_2/mol DEA, 35 days
Degradation	93%	95-96%
Model	94.5%	96.9%

This kinetic model has been applied to the standard simulation, using 30 wt% DEA with no starting degradation products. The results are shown in

Table 7. DEA is consumed in both the HEOD formation and the THEED formation reactions.

Table 7 shows the net forward rate of the HEOD formation reaction (Rate 1) and the rate of the THEED formation reaction (Rate 2). The final column is the combined rate, indicating total DEA loss.

Table 7: Conditions of DEA degradation model

Location	Temperature	[CO_2]	Rate 1	Rate 2	Combined
	°F	mM	mol/hr	mol/hr	mol/hr
Absorber Tray 1	120	48	0.000	0.000	0.000
Absorber Tray 20	143	**771**	0.000	0.000	0.000
Bottoms	143	**771**	0.026	**0.012**	0.038
Flash	145	**771**	**0.111**	0.000	**0.111**
Lean/Rich	210	771	**0.652**	0.000	**0.652**
Reflux Accumulator	120	2	0.000	0.000	0.000
Regenerator Tray 20	**249**	69	0.016	0.000	0.016
Reboiler	**250**	48	**0.989**	0.017	**1.006**
Surge Tank	186	48	0.100	**0.002**	0.103

Figure **13** shows the progress of the reactions over time, including the accumulation of HEOD and THEED. One can observe that HEOD approaches a near steady state value of 0.25 wt% after about 20 days.
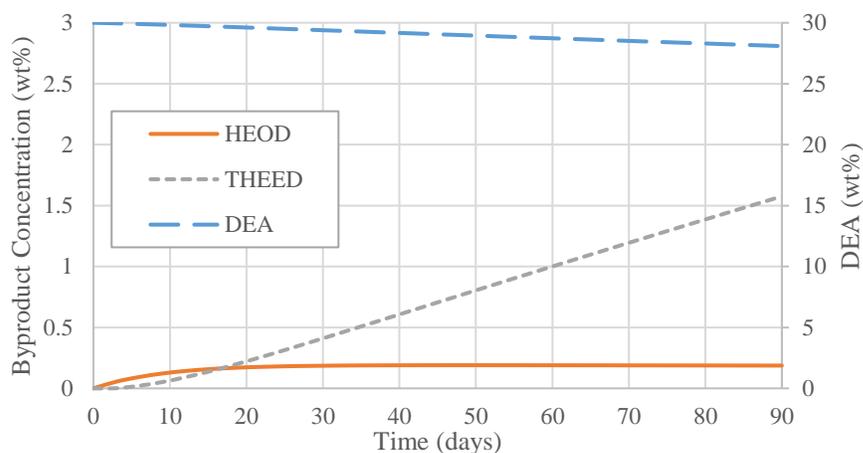

Figure 13: Time profile of DEA system degradation. DEA is represented on the secondary axis.

Once this initial buildup profile is established, the reaction rates change. The net forward reaction of the DEA ←→ HEOD reaction slows down with more product HEOD, while the second reaction accelerates with more reactant HEOD. Figure 14 shows this change, comparing the fresh solvent with the system after 20 days of operation. Most of the locations prior are dominated by the first

reaction, as such there is little change between the fresh and the 20 days of operations. One noticeable difference is the reboiler, where the second reaction (HEOD → THEED) increases significantly at the higher HEOD concentration.
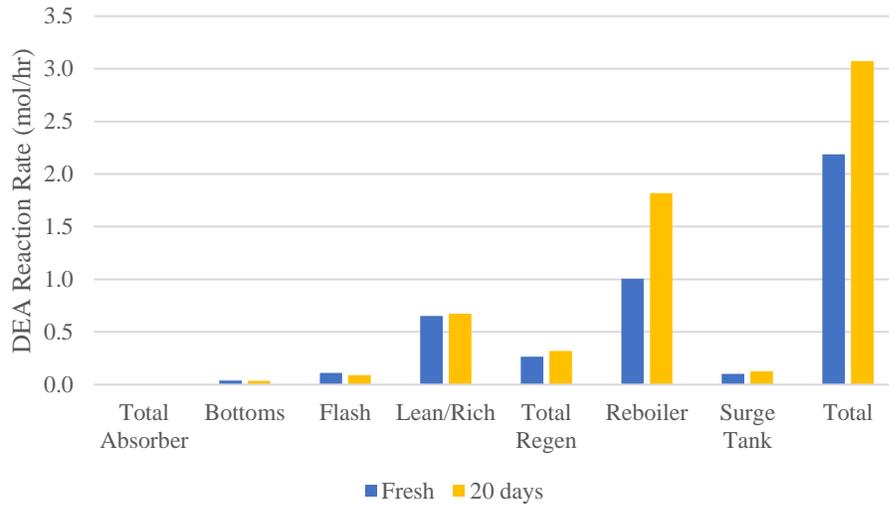

Figure 14: Comparison of DEA degradation reaction by location at two times.

Similar to the HCN reaction that we looked at earlier, most of the reaction is occurring in the reboiler and regenerator. As with that reaction, two possibilities for reducing the degradation would be to increase the reboiler duty to drive off CO_2, or reduce regenerator pressure, thereby reducing temperature and possibly lowering CO_2 concentration.

Figure **15** shows the effect of reboiler duty on the combined loss of DEA. As the reboiler duty increases, the CO_2 content of the solvent decreases and reduces reaction rate of the first reaction. Reaction data is chosen to be at the quasi-steady state HEOD level.
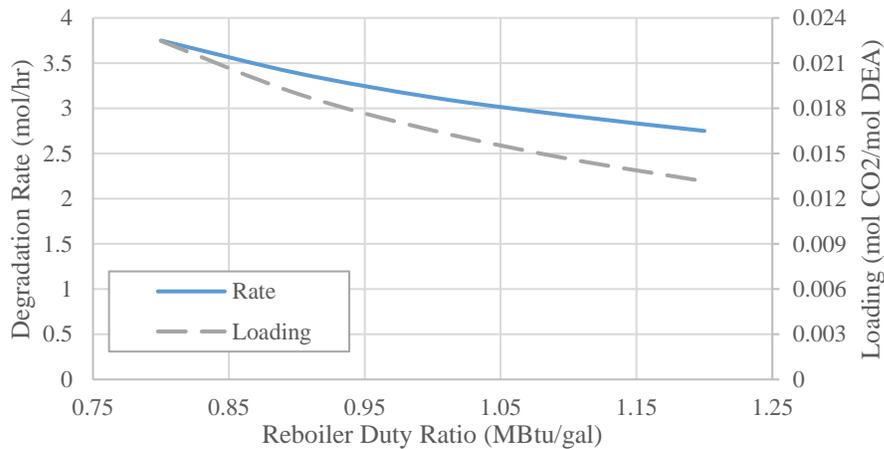

Figure 15: Effect of duty on DEA degradation.

Figure **16** shows the impact of regenerator pressure. As the pressure increases, CO_2 concentration decreases, but the net reaction rate increases due to the increase in reboiler temperature.
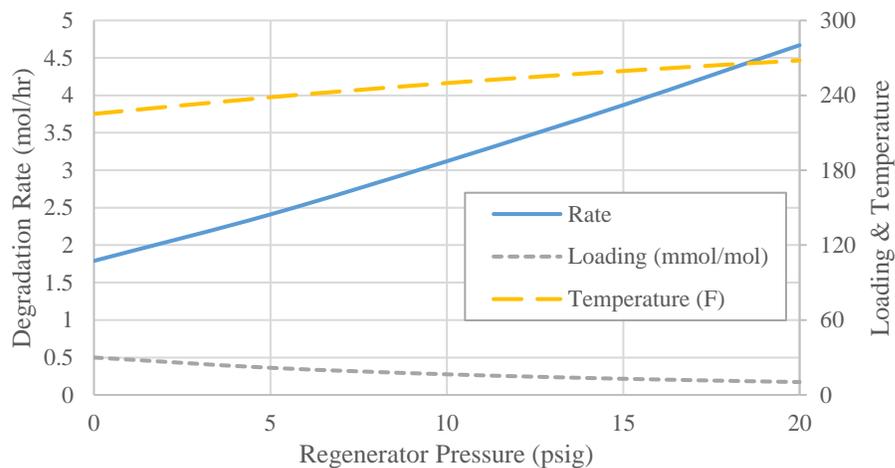
Figure 16:Effect of regenerator pressure on DEA degradation.

One other possibility for managing the degradation rate is decreasing the DEA concentration. Figure **17** shows this effect. The circulation rate is increased to maintain similar rich loading. Because both forward reaction rates are linear in DEA, one would expect the reaction rate to drop by about one third as the DEA concentration dropped from 30% to 20%. However, the reaction rate drops by more than 50%. As the DEA strength decreases, the lean loading at the reboiler remains about the same, so the CO_2 concentration drops as well as the DEA. This slows the first reaction and consequently lowers the quasi-steady state value of the HEOD.
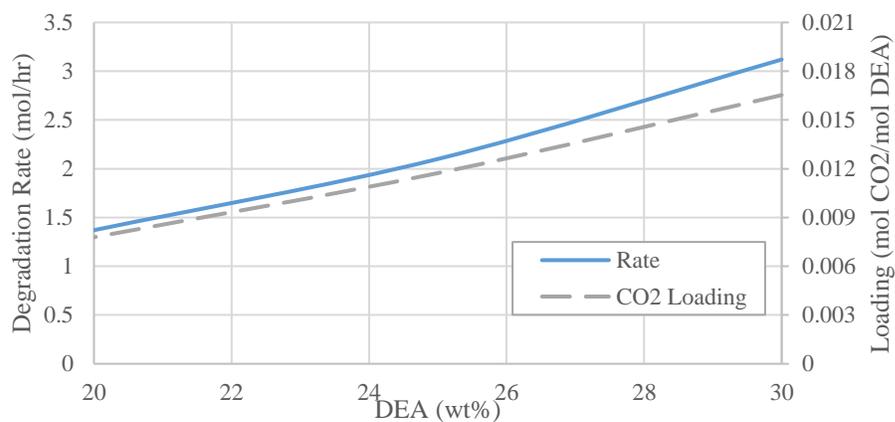

Figure 17: Effect of DEA strength on degradation.

In the case of the DEA degradation reactions, the 'instigator' of the reaction is not a contaminant that can be scrubbed out or avoided, but it is the process itself (CO_2/DEA) that is causing the damage. The reaction enabled simulation offers a view as to how the process conditions impact the long term health of the amine treating system.

Conclusion

The utility of combining experimentally determined reaction kinetics with a commercial simulator has been demonstrated for a variety of reactions relevant to gas treating. Where possible, the implemented kinetics were tested against independent experimental data. The kinetics were then

applied to a standardized amine treating system to study how the amine system was affected by the reaction and how to adjust the process to reduce the negative impact. The reaction enhanced simulation enables the user to predict the short and long-term effects of the reaction to allow for planning and mitigation. Some specific observations about the reactions include:

- Hydrogen cyanide will convert to formic acid primarily in the regenerator column and surge tank. To reduce the reaction, keep the reboiler duty high, while keeping the reboiler temperature low.
- Carbonyl sulfide is reactive in MDEA/water solutions, but the solubility is low enough that absorption is small.
- DEA degradation in the presence of CO_2 happens primarily in the regenerator reboiler. The degradation rate accelerates for the first few weeks of operation beginning with a clean solution before stabilizing. Similar to cyanide, reducing regenerator pressure and increasing reboiler duty reduces the reaction rate. In addition, lowering amine strength lowers the degradation.

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