

The Functionality Remuneration Design Analysis of Phase Reaction in Gas Sweetening

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ABSTRACT

There are a variety of potential side reactions in sour gas treatment systems that produce undesired byproducts. Reactant concentrations, absorption rates, temperature, kinetic rates, and residence periods all play a role in these reactions. In terms of degradation rate and impact of operating circumstances, accurate prediction of the rate of these side reactions can provide more insight into the process. Conversion of hydrogen cyanide to formic acid, hydrolysis of carbonyl sulfide in MDEA, and CO₂ degradation of DEA are all investigated in the context of a typical amine treatment procedure. We will utilize simulation to investigate the occurrence of these reactions throughout the process and the effect of operating parameters in this study.

I. INTRODUCTION

There are numerous chemical reactions that occur in gas treatment, ranging from water dissociation to piperazine dicarbamate hydrolysis. These reactions are, for the most part, reversible and tend to equilibrium. Some reactions are irreversible, resulting in a permanent chemical change in the system. The degradation of the solvent and the conversion of gas pollutant components are the two basic categories of irreversible processes. The magnitude of these responses is rarely considered in simulations, and even when it is, it is rarely done rigorously. These are usually gradual reactions that take days, weeks, or months to complete. This sluggish behavior makes kinetics study and quantification difficult, if not impossible. One of the challenges in assessing these side reactions in gas treating systems is the

large number of locations where they can occur, such as absorber trays or packing, absorber bottoms holdup, rich flash, lean/rich exchanger, stripper column, reflux drum, reboiler, surge tank, and other areas like sour water stripper or liquid-liquid separators. Aside from the uniqueness of reaction kinetics, each feasible reaction point has its own set of reaction circumstances (concentration, temperature and residence time). The three reactions we'll look at are cyanide hydrolysis, carbonyl sulfide hydrolysis in the presence of methyldiethanolamine (MDEA), and diethanolamine degradation (DEA). In each example, we'll go over the reaction kinetics, see how well they match existing laboratory or plant data, and then use a simulation of a typical amine process to show where and how much the reaction happens. We can determine a realistic remedial plan based on these observations.

1.1 Typical Amine Process

The amine process that is being studied is totally fictional in order to show the impact of side reactions. Figure 1 depicts the procedure. Bryan Research & Engineering, Inc.'s ProMax® 4.0 was used to simulate it. There are 20 trays with 2" weirs in the absorber and regenerator columns. Both columns are designed to withstand 70% flooding. The flash tank operates at 75 psia, while the lean/rich exchanger generates a rich solvent at 210°F. A surge tank is used after the lean side of the lean/rich exchanger in this process. The sour gas inlet pressure is 800 psi and the temperature is 110°F, whereas the lean amine enters the column at 120°F. The regenerator condenser runs at 120 degrees Fahrenheit.

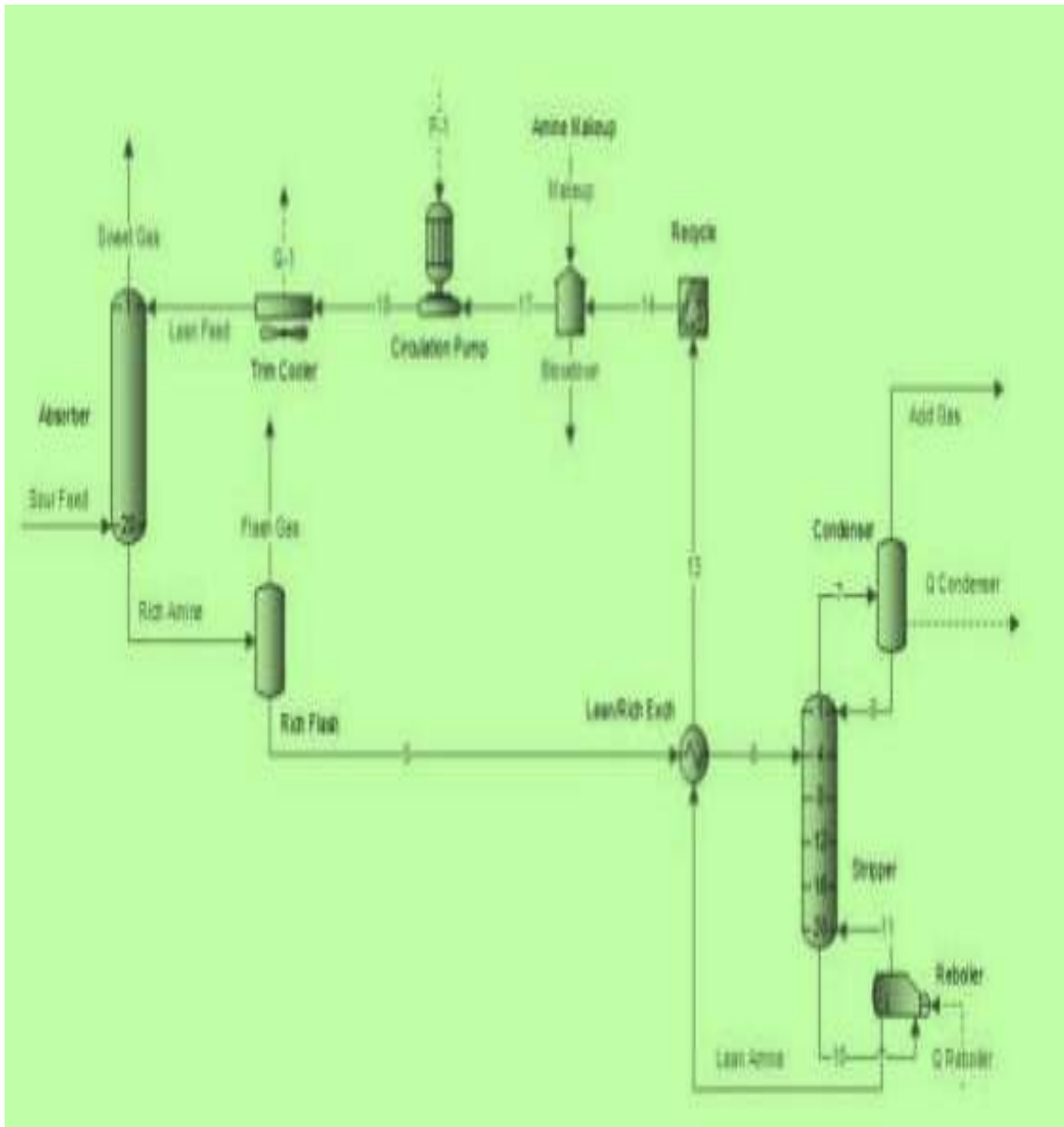


Figure 1: Typical amine treating process.

The reactions described in this paper are kinetically constrained, and they are represented using a perfectly mixed or 'CSTR' reactor. The duration of time that the reaction mixture remains at a certain condition is a crucial factor in determining the magnitude of the reaction. These liquid residence times vary from plant to plant, however the following holdup times were chosen as a representative of a typical plant after reviewing numerous amine plant designs. 3 minutes for absorber bottoms Reflux 10 minute accumulator 10 minutes in the Flash Tank 3 minute reboiler 10 minutes in the surge tank 1 minute Lean/Rich

Exchanger We'll also look at reactions in the mass transfer section of columns in this study. The tray liquid residence times vary depending on column hydraulics, however they commonly range between 1 and 3 seconds.

1.2 Cyanide Hydrolysis

In refinery gases, hydrogen cyanide is a prevalent pollutant, particularly in more severe processing units like fluidized catalytic crackers and coking units. Because it is a weak acid with a lower volatility than H₂S and CO₂, it can be trapped by water and amine systems. With

adequate heat, it can be pushed out of the solution, but it can build to some amount in a recycled amine loop. It reduces the amine's capacity to remove acid gases as a weak acid, but the major worry is the possibility of forming heat stable salts (HSS). It combines with hydroxide ions in the aqueous phase to create ammonia and formate ions. The ammonia in the regenerator is an issue, and the formate ions might lead to increased corrosion. The reaction proceeds as described in Equation 1 according to Wiegand and Tremeling (Wiegand&Tremelling, 1972).



With the kinetic rate expression

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

in which the rate constant adopts the typical Arrhenius form

$$k = A e^{-E/RT} \text{ (Equation 3)}$$

In both cyanide and hydroxide, this reaction is first order. A simulation was built to mimic a circumstance stated in the Wiegand and Tremeling paper to demonstrate the rationality of the kinetic model. They claim that at 'room temperature,' a 0.25 N cyanide solution lost 0.00024 N per day in cyanide concentration. While ProMax is unable to replicate a batch reactor in time, a plug flow reactor model with the right flow and reactor dimensions can simulate such a

reaction in space as an analog. The 0.00024 N/day loss rate was recreated at 79°F, within the range of 'room temperature,' using a one-liter reactor and a one-liter per day liquid flow. In this simulation, the intake sour gas contains 50 ppm of HCN. The regenerator column has a purge that is 5% of the reflux flow because the operation will generate ammonia. The regenerator operates at 10 psig and has a reboiler duty of 1 MBtu/gallon of circulation as a starting point. With a circulation rate of 130 gpm and a solvent concentration of 40 wt% MDEA, the treated gas concentration is 1.5 mol% CO₂, 0.1 ppm H₂S, and nearly negligible HCN. The total loadings for rich and lean acid gas per mole amine are 0.3 and 0.002 mole acid gas per mole amine, respectively.

The reaction conditions at various points in the process are shown in Table 1. As one might imagine, the highest HCN concentration and temperature are found near the bottom of the absorber and the regenerator reflux accumulator, respectively. The lean amine has the largest concentration of hydroxide. The bottom section of the regenerator, the reboiler, and the surge tank have the greatest reaction extent due to the interaction of time, temperature, and hydroxide concentration. Figure 2 illustrates this proportion.

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

Location	Temperature °F	[HCN] ppmw	[OH ⁻] pH	Time s	Reaction 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

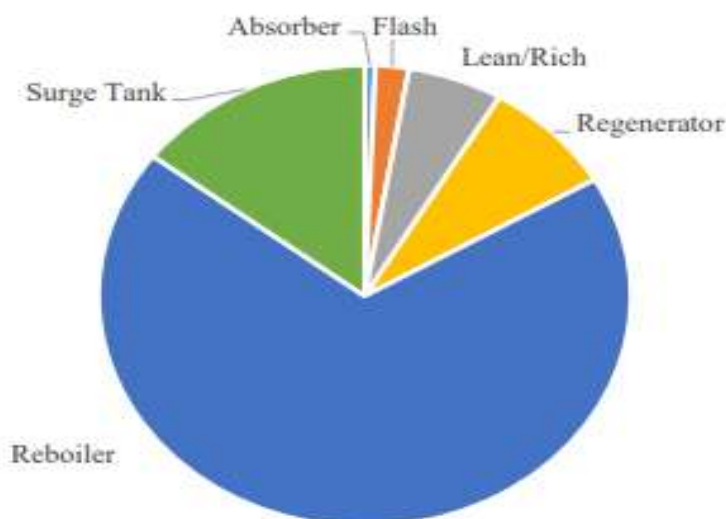


Figure 2:Reaction to unit operation ratio.

Formate does not naturally come out of the amine circulation loop because it is a heat stable salt, hence it will continue to accumulate over time. The formate level in the lean amine passing to the absorber is assumed to be zero in Table 1. This is accomplished by eliminating the formate after each surge tank cycle artificially. Formate would be predicted to accumulate at a rate of 1.87 gram-moles per hour, or 4.5 pound per day, under the operating conditions shown. In comparison, HCN is absorbed into the system at a rate of 108 lb/day. The liquid holdup depicted equates to around 40 minutes of flow, or approximately 5000 gallons. The formate accumulation rate is roughly 100 ppmw formate per day on a mass basis. This definitely suggests a need to eliminate cyanide before it enters the amine system, which is usually accomplished with a water/ammonium polysulfide wash. The ammonia byproduct, unlike the formate, has an exit route in the reflux purge. Because just a small percentage of ammonia created in the amine loop is rejected in the regenerator column and is recycled back to the

absorber, there is no considerable accumulation. As previously stated, the reaction data presented is for a solvent that is free of formate. The reaction behavior should change as the formate builds up. Figure 3 depicts the accumulation of formate as well as the pace of response over time. The reaction occurs at 10,000 parts per million of formate. The reaction rate is half that of the clean solvent at 10,000 ppm formate. Figure 4a depicts the reason for this. As the formate level rises, the hydroxide in the reboiler drops, lowering the product of the cyanide and hydroxide and so slowing down the reaction. The treatment performance is another result of the formate buildup. The treated acid gas concentrations for a variety of formate concentrations are shown in Figure 4b. With the same reboiler heat input, the lean amine becomes leaner in H₂S, and the treated gas H₂S level falls as the formate level rises. At the same time, the formate changes the amine's ionic equilibrium, resulting in less free amine and a tiny increase in the treated CO₂ level.

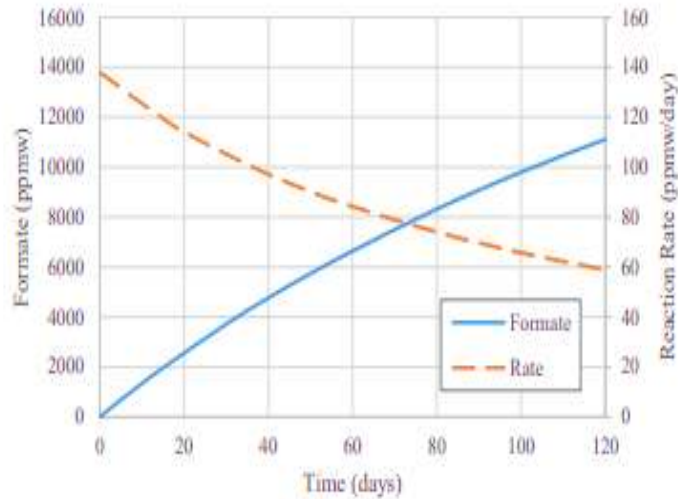


Figure 3: Time profile of formate and reaction rate

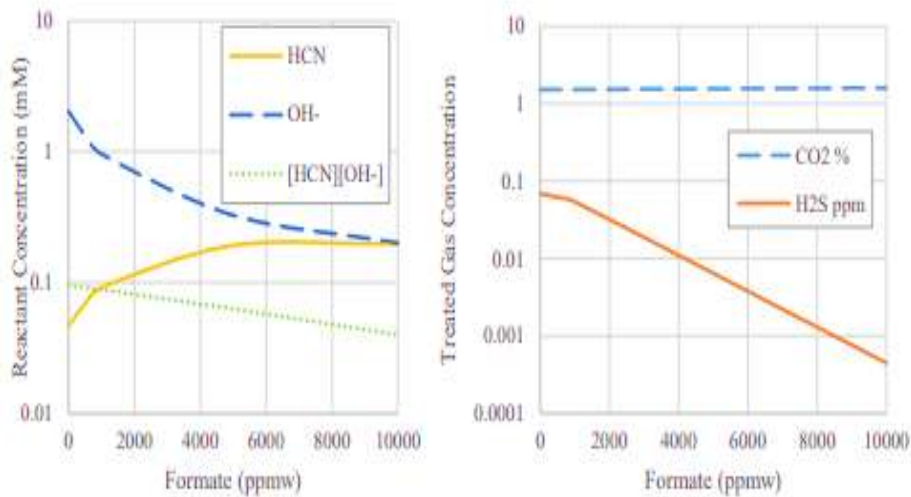


Figure 4: Effect of formate on (a) reboiler reactant concentration and (b) treated gas.

Given that adding acid in the reboiler can minimize the quantity of cyanide reaction, lowering the reboiler duty, allowing for a less lean amine, is one conceivable operating modification. This impact is depicted in Figure 5. The hydroxide concentration decreases as the ratio of reboiler duty to circulation rate decreases. With reduced reboiler duty, however, more HCN settles at the bottom of

the column. A cyanide 'bubble' forms in the column at a low enough duty (reboiler ratio 0.65 MBtu/gal), and the concentration in the reboiler rises dramatically. The concentration of hydroxide also drops at this moment. The reactant product ($[HCN][OH^-]$), which reaches a peak at a reboiler duty ratio of 0.65, demonstrates this coupled impact.

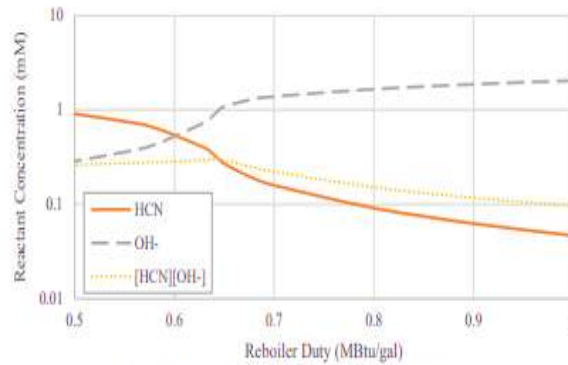


Figure 5: Effect of reboiler duty on reboiler concentration

Figure 6 shows the system reaction rate peaking at 0.65 MBtu/gal, which is more than twice as fast as the base case reboiler duty of 1.0.

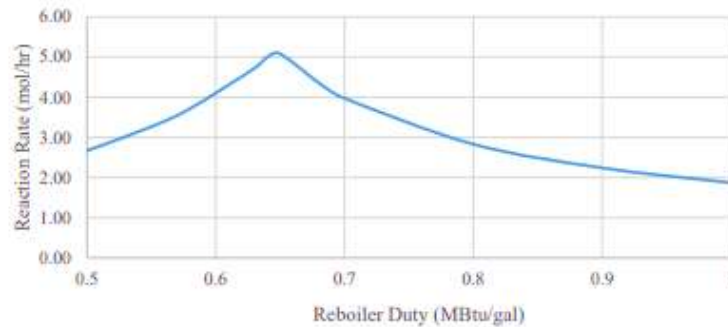


Figure 6: Effect of reboiler duty on reaction rate.

Reducing reboiler duty had no effect on the cyanide reaction rate, but it's feasible that lowering the reboiler's temperature might lower both the reaction rate constant and the reaction rate. Because the regenerator pressure controls the temperature of the reboiler, the pressure of the regenerator was changed to see how it affected the reaction rate. This impact is depicted in Figure 7.

The reaction rate was reduced as expected when the pressure was dropped. The reaction rate is reduced by a factor of around 16 when the pressure is reduced from 20 psig to 0 psig. The effect of temperature on the rate constant, on the other hand, barely accounts for a factor of four in the second plot.

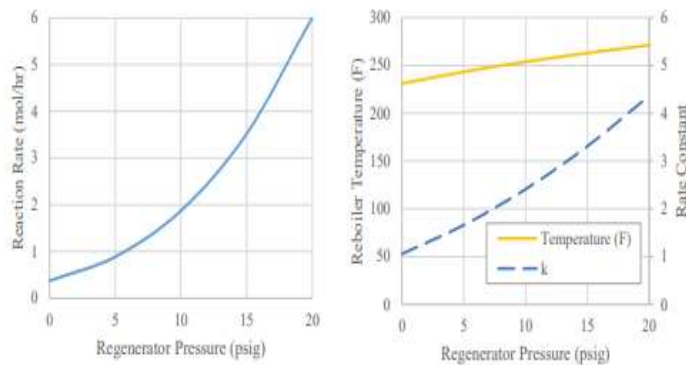


Figure 7: Effect of regenerator pressure on reaction.

The condenser was still stated at 1200F. Less cyanide and hydroxide are present in the reboiler, as seen in Figure 8.

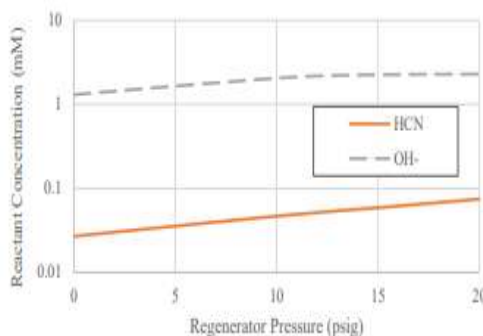
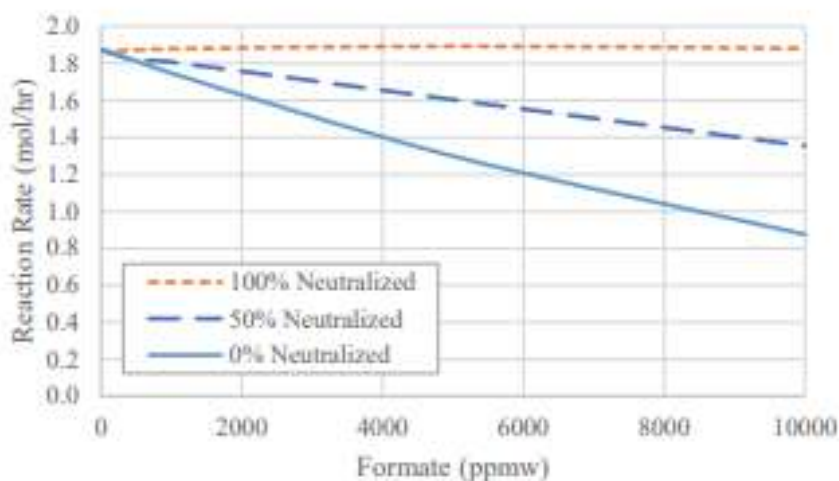


Figure 8: Effect of regenerator pressure on reboiler concentrations

The addition of a caustic to the solution to neutralize it is a popular way to minimize corrosion in the presence of acids. However, because hydroxide is a reactant in the formic acid manufacturing process, this could speed up the process. The impact of applying KOH to neutralize

the acid concentration is seen in Figure 9. In comparison to the un-neutralized solution, the pace of reaction increases as the caustic concentration rises. There is virtually little reaction rate slowdown due to formate accumulation at full neutralization.



While the rate of HCN hydrolysis in one pass of an amine treatment system is low, the fact that the reaction product accumulates necessitates accounting for the rate of accumulation and, as a result, the rate of reaction in the process simulation. The effect is significant both in terms of short-term treatment performance prediction and long-term solvent management.

2. COS Hydrolysis

Organic sulfur pollutants and the extent to which they are eliminated by amine solvents are receiving more attention as rules on total sulfur

content of treated products tighten. Carbonyl sulfide is a substantial organic sulfur component. Chemical processes in the liquid phase can influence the rate of absorption of COS, just as they can with carbon dioxide. Accounting for the effect of reaction kinetics can help forecast the rate of carbonyl sulfide absorption in an amine treatment system, or at the very least highlight the notions of what benefit can be expected under various operating conditions.

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

Reaction with water: $\text{COS} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2\text{S}$
 (Equation 4)

Reaction with hydroxide: $\text{COS} + \text{OH}^- \rightleftharpoons \text{CO}_2 + \text{HS}^-$
 (Equation 5)

Reaction with water, base-catalyzed by MDEA:
 $\text{COS} + \text{MDEA} + \text{H}_2\text{O} \rightleftharpoons \text{MDEAH}^+ + \text{HCO}_2\text{S}^-$
 (Equation 6)

Reaction with primary or secondary amine: $\text{COS} + 2\text{R}_2\text{NH} \rightleftharpoons \text{R}_2\text{NCOS}^- + \text{R}_2\text{NH}_2^+$ (Equation 7)

The final reaction is a zwitterion creation with numerous deprotonation routes abbreviated. These reactions happen at different speeds. For the

forward reaction, we can use the following expression to define an apparent rate constant k_{app} .
 $r_{\text{COS}} = -k_{app} [\text{COS}]$ (Equation 8)

The influence of any co-reactant concentration, such as hydroxide or MDEA, is assumed to be wrapped up in k_{app} in this form. Using a nominal value for the co-reactant, we may compare the relative rates of the various reactions in this form. Table 2 illustrates this. In comparison to the amines, the H_2O and OH^- reaction rate is nearly insignificant, similar to the CO_2 reaction series. MDEA is much faster than the other two. Compared to MDEA, the primary and secondary reactions are more faster.

Table 2: Relative rates of COS reactions.

Reactant	Concentration wt%	$k_{app}(120^\circ\text{F})$ 1/s	Reference
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) proposes criteria for determining when a gas absorption reaction is significant to the timeline of a specific place and whether it affects the absorption of a reactive component. In the case of the responding absorber, we're curious if a reaction will occur inside a tray's timeframe. The criteria for a minimal reaction are as follows:

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

What is the liquid's residence time on the tray? The left hand side corresponds to the third column of Table 2 with a typical value of one second. On a tray, the water and hydroxide reactions can be ignored based on this criterion. Although the MDEA reaction is on the border, it should not be overlooked. If a component being

absorbed reacts quickly enough, it will modify the concentration profile in the liquid film near the contact, boosting mass transfer. Equation 10 shows a condition for negligible film reactivity. The diffusivity of the absorbing reactant in the liquid is D_A , and the mass transfer coefficient of the liquid film is k_L .

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

Table 3 illustrates the results assuming a diffusivity of $2 \times 10^{-9} \text{ m}^2/\text{s}$ and a mass transfer coefficient of $2 \times 10^{-4} \text{ m/s}$ for numerous amines. The main and secondary amine reactions are certainly fast enough to affect the film profile, whereas the MDEA reaction is unlikely to affect mass transfer significantly.

Table 3: Criterion for film reaction.

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

The impact of increased mass transfer due to film reaction is outside the scope of this research. The MDEA reaction, on the other hand, has been proven to be non-negligible on the tray and slow enough to be handled in bulk. The above-mentioned MDEA reaction is actually the first of two intertwined reactions (Littel, van Swaij, & Versteeg, 1992).
 $\text{COS} + \text{MDEA} + \text{H}_2\text{O} \rightleftharpoons \text{MDEAH}^+ + \text{HCO}_2\text{S}^-$ (Equation 11)
 $\text{HCO}_2\text{S}^- + \text{MDEA} + \text{H}_2\text{O} \rightleftharpoons \text{MDEAH}^+ + \text{HCO}_3^- + \text{HS}^-$ (Equation 12)

It's possible to reverse the initial reaction that produces protonated MDEA and monothiocarbamate (MTC). The second step, more often known as 'hydrolysis,' produces H₂S and

CO₂. This is basically unstoppable. Because the first reaction is 30 times faster than the second, the MTC will pile up and the first reaction will finally slow down. Figure 10 depicts this impact. The solvent does not contain COS when it enters the absorber, and the reaction rate is relatively fast. The forward rate in COS increases when the solvent saturates. Because the second reaction is slower, the intermediate product accumulates (Figure 11), and the forward reaction slows dramatically until, despite the higher temperature, there is essentially no net COS reaction at the bottom of the absorber. In addition, as the solvent fills with acid vapors, the molecular MDEA decreases as it protonates.

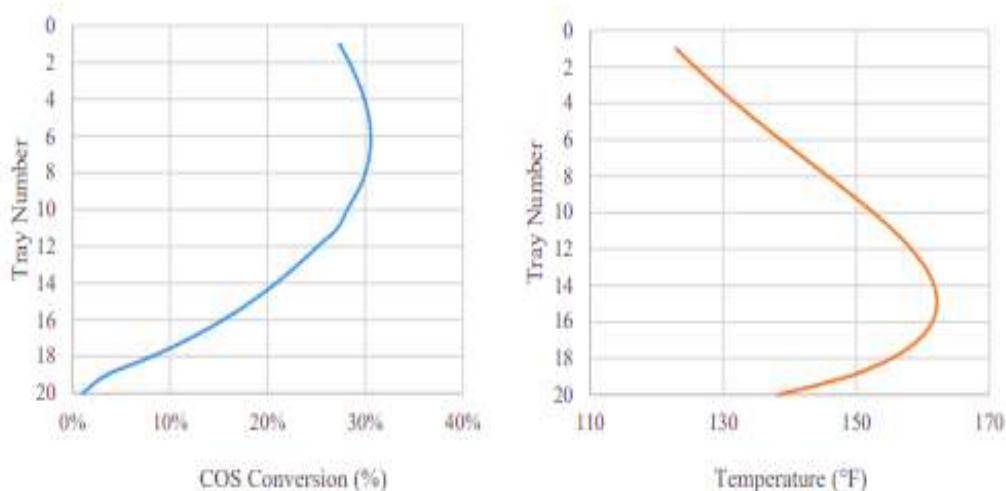


Figure 10: COS conversion in absorber.

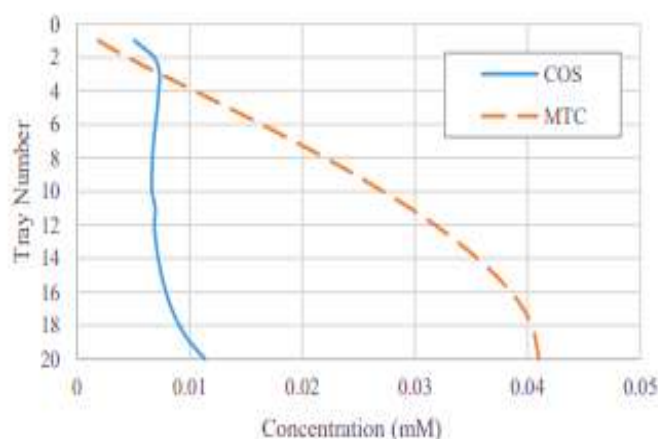


Figure 11: Liquid concentration of COS and monothiocarbamate by tray

The net effect of the reaction on COS absorption into the MDEA is shown in Table 4. The key finding is that COS absorption by 40 wt% MDEA is poor; in the absence of a response, just

about 0.5 percent is absorbed. The absorption increases by a factor of four, to over 2%, when the reaction is applied.

Table 4: Effect of reaction on COS absorption

Stream	COS Flow lb/hr	Removal lb/hr	Removal %
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 CO₂, it is important to remember that the solubility of molecular CO₂ is not large. It is only 0.24681012141618200% 10% 20% 30% 40% Tray Number COS Conversion (%) 0 2 4 6 8 10 12 14 16 18 20 110 130 150 170 Tray Number Temperature (°F) 0 2 4 6 8 10 12 14 16 18 20 0.01 0.02 0.03 0.04 0.05 Tray Number Concentration (mM) COS MTC when the CO₂ reaction products HCO₃⁻ and CO₃²⁻ are included does the CO₂ solubility appear

more significant. Because the COS reactions occur about two orders of magnitude slower than CO₂, 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 reaction kinetics are used to answer a critical question in the amine gas treatment system. Specifically, how much more COS will MDEA absorb above physical solubility if hydrolysis is taken into account? The answer is that it greatly improves, but the net'solubility' remains low.

3. DEA Degradation

In the presence of CO₂, primary and secondary amines are prone to breakdown at higher temperatures. Understanding the kinetics of these events might help amine plant operators pinpoint the cause of amine degradation and, perhaps, change their process to mitigate the problem. Several sources list the major phases in the diethanolamine (DEA) breakdown pathway as follows:

Diethanolamine (DEA) + CO₂
 ⇌ Diethanolaminecarbamic acid (Equation 13)
 Diethanolaminecarbamic acid ⇌ 3-(2-hydroxyethyl)oxazolidone (HEOD) + H₂O (14)
 HEOD + DEA ⇌ N,N,N'-tris(2-hydroxyethyl)ethylenediamine (THEED) + CO₂ (15)
 THEED ⇌ N,N'-bis(2-hydroxyethyl) piperazine (BHEP) + H₂O (16)

The byproducts of subsequent deterioration Because THEED and BHEP are generated through irreversible processes, they degrade the solvent's performance indefinitely. They can store CO₂ in solution through protonation and carbamate formation, although they are less efficient per mass of amine than the original DEA. BHEP and THEED are also suspected of accelerating corrosion in process equipment. Finally, THEED has the ability to form polymeric materials, which can lead to fouling. An amine plant operator would obviously benefit from the

ability to predict this behavior across a wide variety of reaction locations. A kinetic model for this process is provided by Kim and Sartori (Kim & Sartori, 1984). Kennard's experimental data was used to regress the kinetic parameters that were not supplied in the original publication.

DEA + CO₂ ⇌ HEOD + H₂O (Equation 17)

HEOD + DEA ⇌ THEED + CO₂ (Equation 18)

CO₂ is consumed in the first process, whereas CO₂ is produced in the second. In this way, CO₂ functions as a stimulant for the decomposition process. The deterioration model is compared to Kim and Sartori's data in Figure 12. The DEA and CO₂ concentrations closely mirror the experimental results. Although the model HEOD value does not increase as high as the data, the first rise of THEED is very close. The THEED represents all of the permanent degradation products in the model, whereas the THEED reacts to other components in the data.

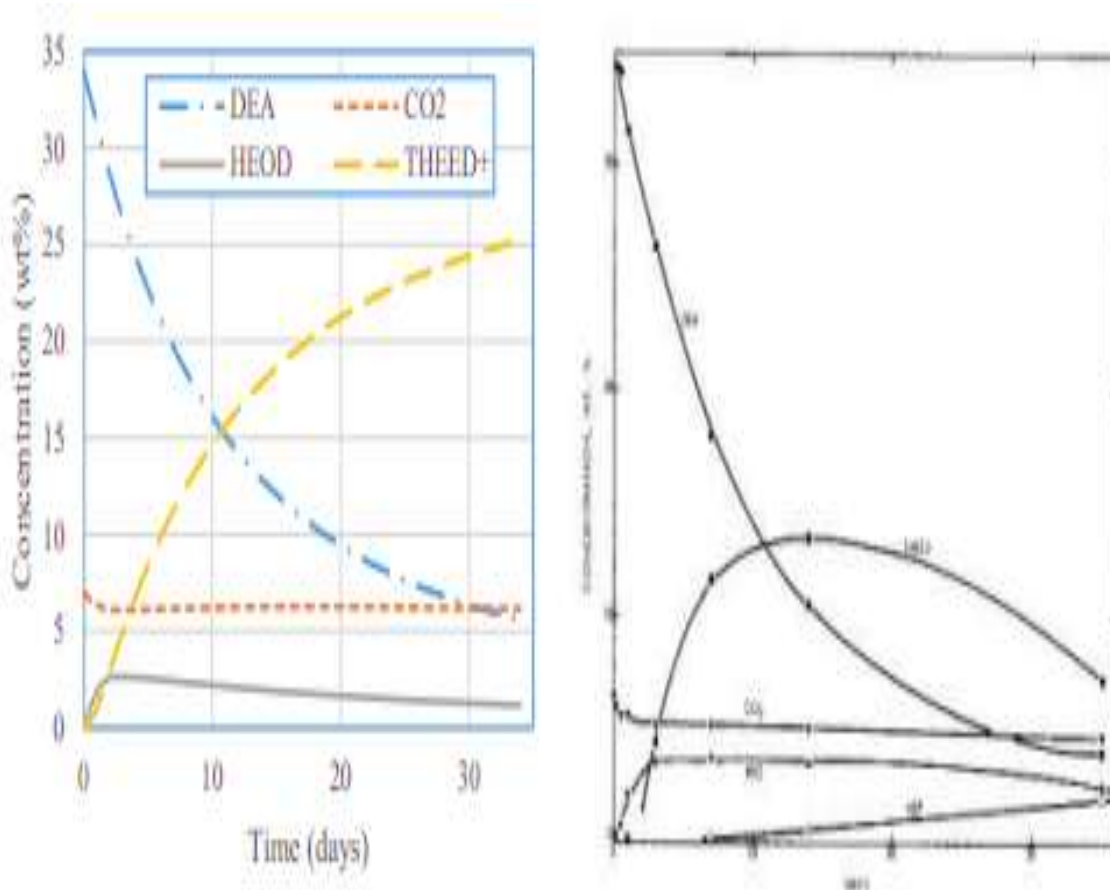


Figure 12: Comparison of model to data of Kim & Sartori (248°F at variable pressure).

Simulations were set up to reflect data from other authors in order to demonstrate the response model's prediction ability. Table 6 shows the comparability to laboratory degradation studies published in the literature (Lepaumier, Picq,

&Carrette, 2009) and (Eide-Haugmo, Einbu, Vernstad, da Silva, & Svendsen, 2011). With the Lepaumier and Eide-Haugmo results, the simulation model slightly overpredicted DEA degradation, but it was quite accurate.

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%

The standard simulation was run with 30 wt% DEA and no initial degradation products using this kinetic model. The outcomes are displayed 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 °F	[CO ₂] mM	Rate 1 mol/hr	Rate 2 mol/hr	Combined 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.

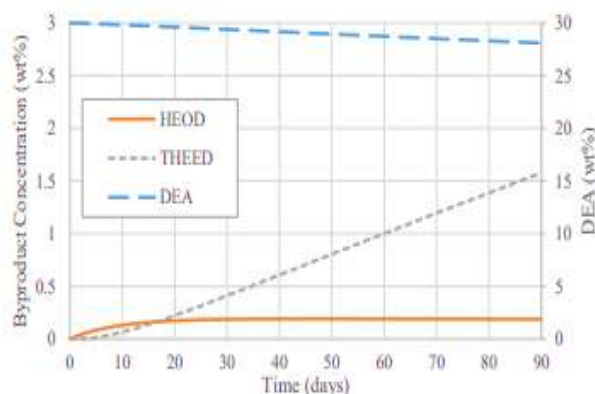


Figure 13: Time profile of DEA system degradation. DEA is represented on the secondary axis.

The reaction rates alter once the first building profile is established. More product HEOD slows the net forward reaction of the DEA HEOD reaction, while more reactant HEOD speeds the second reaction. Figure 14 depicts the change in the system after 20 days of operation, comparing the fresh solvent with the system after 20 days of

operation. Because the initial response dominates most of the places prior, there is little difference between the fresh and the 20-day operations. The reboiler, for example, shows a considerable rise in the second reaction (HEOD THEED) at greater HEOD concentrations.

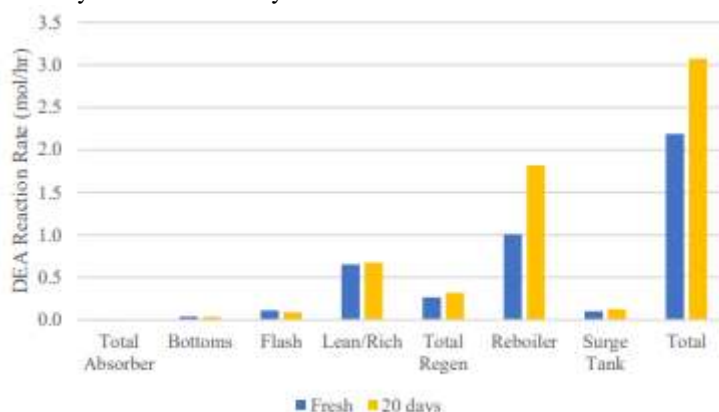


Figure 14: Comparison of DEA degradation reaction by location at two times

The reboiler and regenerator, like the HCN reaction, are where the majority of the reaction takes place. As with that process, increasing the reboiler duty to drive off CO₂ or lowering regenerator pressure to reduce temperature and perhaps lower CO₂ concentration

are two options for reducing degradation. Figure 15 depicts the impact of reboiler duty on total DEA losses. The CO₂ level of the solvent falls as the reboiler duty increases, lowering the reaction rate of the initial reaction. The quasi-steady state HEOD level is chosen for the reaction data.

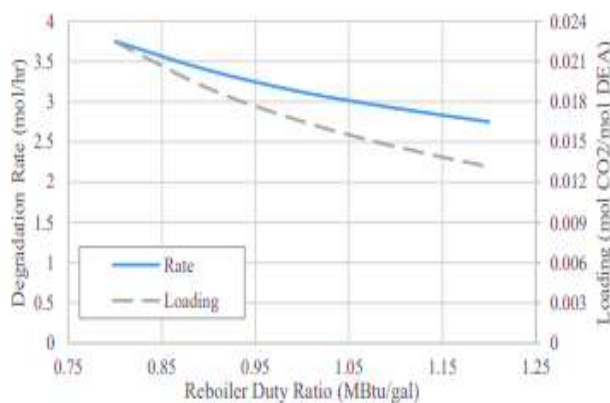


Figure 15: Effect of duty on DEA degradation.

The effect of regenerator pressure is depicted in Figure 16. CO₂ concentration reduces as pressure rises, but the net reaction rate rises due to the higher reboiler temperature.

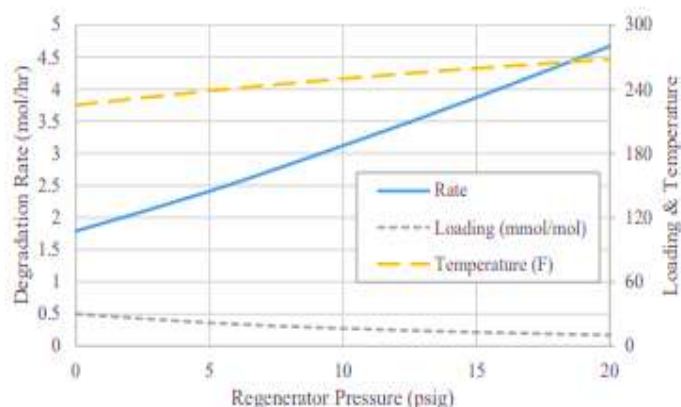


Figure 16: Effect of regenerator pressure on DEA degradation.

Decreased DEA concentration is another option for controlling the breakdown rate. This impact is depicted in Figure 17. To maintain a same rich loading, the circulation rate is raised. Because both forward reaction rates in DEA are linear, the reaction rate should decrease by about one-third when the DEA concentration drops from

30% to 20%. However, the reaction rate plummets by more than half. Because the lean loading at the reboiler remains constant while the DEA strength lowers, the CO₂ concentration drops along with it. As a result, the first response slows down, lowering the HEOD's quasi-steady state value.

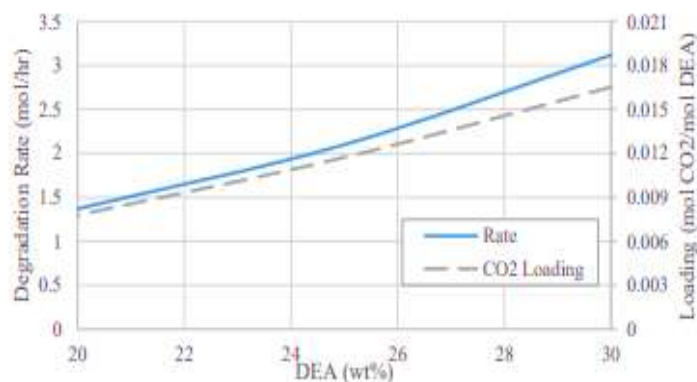


Figure 17: Effect of DEA strength on degradation.

The 'instigator' of the DEA degradation reactions is not a pollutant that can be washed out or avoided, but rather the process itself (CO₂/DEA), which causes the harm. The reaction-enabled simulation shows how the process circumstances affect the amine treatment system's long-term health.

II. CONCLUSION

For a range of reactions important to gas treatment, the value of combining empirically determined reaction kinetics with a commercial simulator has been demonstrated. The implemented kinetics were tested against independent experimental data whenever available. The kinetics were then applied to a standardized amine treatment system to see how the reaction affected

the amine system and how the method could be tweaked to reduce the negative effects. The expanded reaction simulation allows the user to foresee the reaction's short and long-term impacts, allowing for planning and mitigation. The following are some specific observations about the reactions:

- In the regenerator column and surge tank, hydrogen cyanide will largely convert to formic acid. Keep the reboiler duty high while maintaining the reboiler temperature low to limit the reaction.
- Although carbonyl sulfide is reactive in MDEA/water solutions, its solubility is low enough to prevent absorption.
- In the presence of CO₂, DEA degradation occurs largely in the regenerator reboiler. Starting with a clean solution, the degradation rate accelerates

during the first few weeks of operation before stabilizing. Reducing regenerator pressure and increasing reboiler duty decreases the reaction rate in the same way that cyanide does. Furthermore, lowering the amine strength reduces deterioration.

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