Decreasing Contactor Temperature Could Increase Performance

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ABSTRACT

Gas treating process variables such as solvent type and concentration, pressure, and circulation can be manipulated to produce specification quality hydrocarbon products. Interest has increased recently in exploring the effects of inlet gas and solvent temperatures as an aid in meeting these specifications. In general, lower temperatures tend to promote absorption of lower molecular weight components based on vapor-liquid equilibrium.

Physical solvents exploit this principle by absorbing acid gases and water at lower temperatures. If the absorption process is reactive and allowed to reach equilibrium, lower temperatures still favor the absorption of low molecular weight components.

However, if the reactive absorption is kinetically limited as is the case with CO_2 and certain amines, it is impossible to determine how temperature affects the absorption in the absence of additional information. This ambiguity results from the competing phenomena and opposite effect temperature has on reaction rates and solubility. For absorption of H_2S and CO_2 in alkanolamines or mixtures of amines with physical solvents, H2S absorption reaches equilibrium conditions while CO_2 absorption is kinetically limited in some situations. The performance of various amines and physical solvents are compared based on solvent and feed gas temperatures. Understanding the competing phenomena of equilibrium and kinetics may yield situations where this effect can be exploited for more profitable operation.

INTRODUCTION

To process more gas, to meet more stringent specifications, or to operate more profitably, many gas processors are exploring new alternatives for process optimization. One of these alternatives has been to operate the contactor at a colder temperature to promote the absorption of the contaminants in the solvent. For physical solvents and chemical solvents that approach equilibrium, operating the absorber at lower temperatures tends to promote the pickup of light contaminates. However, for chemical solvents whose reactions may have kinetically limiting steps, colder temperatures may actually cause less of a particular contaminant to be absorbed.

Basic gas processing attempts to separate the components of the mixture as efficiently and economically as possible. Many of the components that are separated include H_2O, H_2S and CO_2. The reason for the separation may be dictated by physical mandates, such as hydrate formation, environmental concerns such as H_2S removal

or product quality such as CO_2 concentration.   Many different process solvents and operating conditions have been developed to achieve these specific goals. This paper focuses exclusively on the increased interest in colder absorber temperatures to increase process performance.

For gas treating, process performance is often defined relative to the ability of a solvent to absorb one component to a greater degree than another. This is often referred to as "selectivity." For example, a solvent may have a greater affinity to absorb H_2O relative to methane. For certain operating conditions, the solvent can be used to selectively absorb H_2O in the presence of methane. Selectivity may arise solely from the physical properties of the solvent or the component solubility. This is the case for physical solvents. Lower temperature may or may not increase selectivity. For chemical solvents, selectivity may occur due to reaction kinetics. In these cases, selectivity may be dramatically improved by column operating temperature.

Reported Operating Data

A recent review of the literature has showed that many commercial gas treating units have investigated colder operating absorbers. Kohl and Nielsen [1] present an exhaustive list of commercial operations. Table I shows some of the common gas treating solvents, the specific application and how lower absorber temperatures affect performance. This table is limited to the primary physical, chemical and hybrid gas treating solvents. The physical solvents are glycols, methanol, and Selexol® or Coastal AGR® (a mixture of dimethyl ethers of polyethylene glycol (DEPG)). The chemical solvents include amines, potassium carbonate and caustic. Hybrid solvents include both physical and chemical constituents such as Sulfinol®.

Table I
Application of Physical and Chemical Solvents and Effect of Absorber Temperature

Description	Solvents	D	AGR	MR	HDC	Effect of Lower Absorber Temperature
Physical	Glycol	X				Increased absorption for all components
	Methanol	X	X	X	X	Increased viscosity (problem for glycols)
	DEPG[b]	X	X	X	X	
Chemical	Ethanolamines		X	X		Increased H_2S absorption
	Potassium Carbonate		X	X		Decreased CO_2 absorption from kinetics
	Caustic		X	X		Slightly increased hydrocarbon absorption Less water in treated gas
Hybrid	Sulfinol®		X	X		Increased H_2S absorption

a **D** : Dehydration, **AGR**: Acid Gas Removal, **MR**: Mercaptan Removal, **HDC**: Hydrocarbon Dew Point Control
b Selexol® or Coastal AGR®

Glycol is used primarily to dehydrate gas streams. Glycols include ethylene glycol (EG), diethylene glycol (DEG) and triethylene glycol (TEG). Smith [2] describes how glycol contactor normal operating ranges can be extended from 50-140°F to temperatures as low as 31°F. At low temperature and high pressure, the glycol absorbs more light hydrocarbons, decreasing the solvent viscosity. Low pressure operations at low temperature would probably be subject to excessive viscosity since the absorption of light hydrocarbons would be diminished. Since hydrocarbon pickup is enhanced, foaming problems could increase. For this service, the absorber internals should not contain bubble or sieve trays but a structured packing to minimize foaming. The authors do not report any operating conditions aside from the contactor temperature and pressure.

Methanol was the first physical solvent used in gas processing. Methanol's ability to absorb water, acid gases, mercaptans and hydrocarbons make it extremely attractive for processing a wide range of compositions. Furthermore, methanol can be operated at temperatures from –50 to –100°F without problems due to high viscosity. Methanol is used in such licensed processes as RECTISOL® and IFPEXOL®. These methanol processes use cold conditions to enhance the solubility of the components and minimize the methanol loss. Many

of these licensed processes do not completely report operating data. However, Staton *et al.* [3] report pilot plant operation for a methanol acid gas removal system.

DEPG or Selexol is a physical solvent with characteristics similar to those of glycol and methanol. DEPG is used for dehydration, acid removal, and hydrocarbon dew point control. Hegwer and Harris [4] report that colder DEPG solvent temperatures increase the solubility of the acid gas resulting in decreasing circulation rates. Epps [5] describes how DEPG is used for both water removal and hydrocarbon dew point control. The author concludes that DEPG circulation rate was not as significant as the ambient temperature in the absorber performance. Both hydrocarbon and water pickup increased in the winter months. During the summer months the units had difficulty making the water specification. The author suggested that solvent refrigeration was a possibility but was eliminated because of economic reasons.

Chemical solvents such as the ethanolamines MEA, DEA, DGAâ, and MDEA are thoroughly discussed by Kohl and Nielsen [1]. Chemical solvents show different behavior with respect to absorber temperature when compared to physical solvents. The primary difference is related to the rate of reaction with CO_2 versus other components such as H_2S. This difference may result in the decreased absorption of CO_2 and increased absorber of H_2S at colder absorber temperatures.

Table II provides a historic perspective from 1950 to 1988 on the effect of absorber temperature on the performance of MDEA. Recently, the number of articles on the performance of MDEA has expanded considerably. Anderson *et al.* [12] describe how colder temperatures in the winter resulted in more CO_2 rejection. To produce specification gas in the winter, six more trays were added to the absorber. Denny Law [13] shows some simulation results showing how to increase CO_2 rejection for MDEA by decreasing the number stages, increasing the amine concentration, and decreasing the absorber temperature. Connock [14] recently discussed the trend to more selective amines to reduce energy costs and meet more stringent gas and emission specifications.

Table II
References for Lean Amine Temperature and MDEA Based Solvent Performance

Authors	Year	Description
Frazier and Kohl [6]	1950	MDEA solvent and selective absorption introduced
Miller and Kohl [7]	1953	MDEA commercial test data presented
Vidaurri and Ferguson [8]	1977	Pilot plant data presented
Ammons and Sitton [9]	1981	Selectivity is sensitive to lean amine temperature Commercial absorber data presented Quantified the effect of lean amine temperature on selectivity Limited operating data
Harbison and Handwerk [10]	1987	Commercial absorber Complete operating data presented
Thomas [11]	1988	Proprietary solvents show increased selectivity with decreasing lean amine temperature

Several papers for trouble shooting amine units have been written which include the effect of contactor temperature. Dupart and Abry [15] suggest looking at the feed gas temperature when not meeting specification gas. If the problem is with H_2S, the gas should be less than 120°F. If the problem is because of CO_2, the gas temperature should be increased above 75°F. The authors do not discuss why the CO_2 temperature limit is a minimum. Street [16] suggests increasing the lean amine solution temperature to increase CO_2 removal for MDEA based solvents. The minimum lean amine temperature should also not be lower than 90°F.

The effect of absorber temperature for the hot potassium carbonate process and caustic washes is discussed to a lesser degree in the literature compared with the amines. The potassium carbonate process is operated at elevated temperatures to enhance the rate of absorption of CO_2. Many authors have reported on promoters such as amines to increase the rate of CO_2 absorption in potassium carbonate solutions. Ferrell *et al.* [17] provides pilot plant data and concludes that more selective operation is achieved at lower absorber temperature and lower solvent concentration.

Caustic washes are used to absorb trace amounts of CO_2, H_2S, and mercaptans. The process is regenerable for the removal of mercaptans. The other components consume the caustic. Selective absorption of H_2S in caustic wash is reported by Holhfield [18] and Kent and Abid [19]. The affect of temperature on the contactor was not discussed.

Only one paper describing the effect of temperature on a hybrid solvent was located. Wallace and Flynn [20] describe how a refrigeration unit was used to cool the Sulfinol solvent to 80°F to remain below design emission at the Eustace gas plant during the summer.

Fundamentals of Physical Solvents

Physical solvents, such as glycol, methanol, and DEPG absorb contaminants based solely on solubility. Equations of state and other thermodynamic models have been developed to predict this equilibrium or solubility. A less complicated and more limited expression, Henry's law, is given in equation (1). This method is usually valid in regions of low concentration but can be reasonably accurate in certain cases. For most components, solubility increases with decreasing temperature.

$$p_i = H_i x_i \tag{1}$$

where P_i is the partial pressure

H_i is the Henry's law constant for the solvent at a certain temperature, pressure

x_i is the mole fraction

Table III shows the Henry's law constants for EG, TEG and methanol for H_2S, CO_2 and methane. For both H_2S and CO_2 in these solvents, the Henry's law constant increases with temperature (*i.e.* solubility decreases). For methane, the Henry's law constant is somewhat independent of temperature. Henry's law constants for the heavier hydrocarbons tend to have greater temperature dependency than methane.

Table III
Henrys Constants for Some Solvents and Gas Components as a
Function of Temperature

Solvent	Temp. K	Henrys Constant MPa		
		H_2S	CO_2	Methane
Ethylene Glycol	300	7.13[a]	42.04[a]	656.3[b]
	350	17.81	82.69	682.3
	400	27.95	112.30	636.9
Triethylene Glycol[c]	300	2.11	11.95	179.2
	350	4.82	23.55	182.0
	400	8.51	35.95	172.0

Methanol	213.15	0.30[d]	1.02[d]	55.0[e]
	273.15	1.77	9.63	100.0
	313.15	3.87	15.18	110.0

a F.Y. Jou *et al*. [21]
b F.Y. Jou *et al*. [22]
c F.Y. Jou *et al*. [23]
d R.W. Rouseau *et al*. [24] and Ranke and Mohr [25]
e R. Kobayashi *et al*. [26] and Ranke and Mohr [25]

Fundamentals of Chemical Solvents

Chemical solvent absorption mechanisms are more complicated than physical solvents. Chemical solvents use the same premise as physical solvents to absorb the component into solution. However, the chemical solvent now has the ability to change the absorbed component either by causing it to ionize or to transform into another component. In either case, the absorbed component in solution is depleted by this reaction, resulting in the ability of the solvent to absorb more of the component from the gas phase. This process continues until chemical and physical equilibrium is reached. Contact time in the absorber might prevent the attainment of equilibrium conditions depending on the rate of reaction.

The important difference between physical and chemical absorption is the chemical conversion of the component being absorbed. This difference gives the chemical solvent the ability to absorb components to a much greater extent than physical solvents. Acid gasses, H_2S or CO_2, dissociate to a greater degree in chemical solvents such as caustic wash, potassium carbonate, and alkanolamines, than in water only.

Chemical Reactions

A reversible chemical reaction describing the reactions between components *A* and *B* going to components *C* and *D* is shown in equation (2).

$$aA + bB \leftrightarrow cC + dD$$
(2)
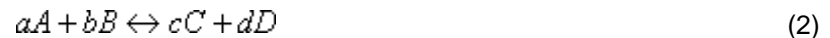
The lowercase *a*, *b*, *c*, and *d* represent the stoichiometric coefficients that balance the elements in the equation.

Equilibrium Constants

Reactions are governed by equilibrium constants, which are related to the Gibbs free energy. The reaction proceeds to a minimum in the Gibbs free energy. The equilibrium constant is used to determine the concentration of species at equilibrium at a given temperature and an initial feed. Large equilibrium constants result in larger concentrations of the products.

Equation (3) shows the equilibrium constant for the reaction given in equation (2).

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$
(3)

where:

K is the equilibrium constant

[*A*] is the concentration of A

a is usually the stoichiometric coefficient

Table IV shows the equilibrium constants for some common reactions in the gas processing industry as a function of temperature. The table shows the negative log of the equilibrium constant for the dissociation of H_2O, CO_2, H_2S, MEA, and DEA. For all of the reactions, the *pK* value decreases with temperature or the *K* value increases with temperature.

Table IV
Equilibrium Constants for Some Chemical Reactions in Gas Processing as a
Function of Temperature

Component	Reaction	0°C	pK[a] 25°C	50°C
H_2O^b	$H_2O \leftrightarrow H^+ + OH^-$	14.944	13.997	13.262
CO_2^b		6.58	6.35	6.29
		10.63	10.33	10.17
H_2S^b	$H_2S \leftrightarrow H^+ + HS^-$	--	6.97	6.69
	$HS^- \leftrightarrow H^+ + S^-$	--	12.9	--
$MEAH^{+c}$	$MEAH^+ \leftrightarrow H^+ + MEA$	10.76	9.98	9.32
$DEAH^{+c}$	$DEAH^+ \leftrightarrow H^+ + DEA$	10.09	9.34	8.70

a Concentrations of species in gmole/L
b *Langes Handbook of Chemisty* [27]
c Kent and Eisenberg [28]

This table suggests that more acid gas could be absorbed at higher temperature based solely on the equilibrium constants. However, the chemical reaction of the acid gas is not the only process occurring. The absorption of acid gas is less at higher temperatures for equilibrium processes due primarily to the decrease in solubility as shown in Table III.

Table V shows the pH of an unloaded MEA and DEA solution at different temperatures [29]. In both cases, the pH decreases (*i.e.* hydrogen ion increases) which favors the regeneration of the MEA or DEA solution.

Table V
pH of Lean Amine Solutions
at Two Temperatures [a]

Solution	70°F	pH[b] 140°F
15 wt % MEA	12.9	11.65
25 wt % DEA	11.5	10.85

a Dow Fact Book [29]
b Hydrogen ion concentration in gmole/L

Kinetics

The rate at which a chemical reaction happens is described by kinetics. If a chemical reaction is kinetically limited, then the reaction may not necessarily approach equilibrium. The extent to which the reaction approaches equilibrium depends on the time allowed to react, the temperature and the driving forces or concentrations.

An irreversible reaction where components A and B form C and D is given in equation (4). The stoichiometric coefficients are necessary to balance the equation.

$$aA + bB \rightarrow cC + dD \qquad (4)$$

In general, a rate expression usually has the form given in equation (5).

$$r_A = k[A][B] \qquad (5)$$

where:

r_A is the rate of disappearance of A in units of mole/volume time

k is the rate constant as a function of temperature

$[A]$ and $[B]$ are the concentrations of species in the reactions

For the absorption of H_2S, the reaction is so fast that equilibrium is approached for any finite time in a commercial absorber. For CO_2, the reaction rate is much slower. The rate expressions may be simple or complex depending on the particular reaction mechanism.

Table VI shows rate constants and the Arrhenius parameters for some common gas processing reactions. The model parameter b or activation energy is negative. This suggests that the CO_2 reaction rate increases with increasing temperature and decreases for decreasing temperature.

Table VI
Literature Sources for Reaction Rate Constants for Some Reactions in Gas Processing [†]

Reaction Description	Source	Order	Model Parameters a	b K
$CO_2 + OH^- \rightarrow HCO_3^-$	Danckwerts [30]	2	13.635	-2895
$CO_2 + 2NH_3 \rightarrow NH_2COO^- + NH_4^+$		2	11.13	-2530
$CO_2 + 2MEA \rightarrow MEACOO^- + MEAH^+$		2	11.07	-2144
$CO_2 + 2DEA \rightarrow DEACOO^- + DEAH^-$		2	9.61	-2038
	Rinker et al. [31]	2	7.35	-1974

[†] The model is log10 (k) = a + b/T where T is in Kelvin and k is in L/gmole s

For CO_2 the following scenarios are possible for a colder absorber. If the rate of reaction decreases to a greater extent than the increase in solubility, the process will tend to reject more CO_2. However, if the rate of reaction decreases to a lesser extent than the increase in solubility, the process will tend to absorb more CO_2.

Operating Limitations

Physical limitations restrict the operation of most processes to a predefined range, which may not be related to the specific objective. Common operating concerns for colder absorbers include solids formation, hydrocarbon absorption, and solvent viscosity.

Solids Formation

For columns under high pressure and gas streams that are saturated with water, hydrate formation temperatures must be considered. Hydrates can form at temperatures as high as 60°F [32]. Neglecting to consider this potential problem in the design and operation may result in catastrophic failure.

Hydrocarbon Absorption

Lower temperatures promote unwanted pickup of saleable product or hydrocarbons.   Hydrocarbon pickup can result in poor column operation due to foaming [33]. However, increased hydrocarbon pickup may also be the objective of the process for hydrocarbon dew point control. Additional hydrocarbon pickup may serve to decrease viscosity [34].

Solvent Viscosity

Some solvents' viscosities increase dramatically with decreasing temperature. Sources report physical properties of common gas treating solvents [29, 35, 36]. The solvent viscosity directly affects pumping cost, pressure drop, and rates of mass transfer. However, the increase in solvent viscosity at colder temperature may not be as pronounced if the cold temperature results in a richer solvent.

CASE STUDIES

Five case studies are investigated. These include a cold temperature glycol process, a methanol process to remove acid gases and mercaptans, a Selexol process decreasing both the hydrocarbon and water dew points, a MEA unit which processes sour gas, and a MDEA unit which processes sour casinghead gas.

For each of the cases, a base was established with the given operating data. The technology that was used to perform the calculations were the process simulation programs PROSIM® and TSWEET® version 98.0, licensed by Bryan Research & Engineering, Inc. [37]. The capability to simulate DEPG and methanol systems for water, acid gas, and hydrocarbon removal has recently be added to PROSIM. Other simulation programs with similar capabilities could have been used to perform the calculations. Literature references [38, 39, 40] have compared PROSIM and TSWEET's predictions for glycol, and amine processes. Once the base case was established, the solvent and gas temperatures were varied and the performance of the absorber is shown.

Case Study 1: Glycol

Extending the operating temperature range of glycol columns has been the subject of a recent paper by Smith [2]. As mentioned previously, the only operating data provided by the authors was temperature and pressure. In the absence of this data, some assumptions about the composition and flow rate were made. Table VII shows the temperature, pressure and assumed composition. The water content was approximately 85 % of saturation or 5.5 lb/MMSCF. Higher water content results in hydrate formation. The assumed water specification was 0.7 lb/MMSCF (*i.e.* -5°F hydrate formation temperature for this case. The TEG circulation rate was determined by 3-5 gallon of glycol per pound of water removal [32].

PROSIM was used to determine the composition of the rich glycol from the bottom of the absorber as shown in Table VII. The calculation show that about 0.5 wt % of the solvent is methane. The simulator was also used to evaluate the viscosity of the rich TEG solution with the absorbed hydrocarbons as compared to the viscosity with no hydrocarbons at different temperatures.

Table VII
Case Study 1 Composition and Conditions

Component	Feed Mole %	Overhead[†] Mole %	Rich glycol[†] Wt %

Methane	95	95	0.46
Ethane	2.5	2.5	0.066
Propane	1	1	0.066
Butane	0.5	0.5	0.042
Nitrogen	0.5	0.5	0.007
Water	0.01	0.001	5.173
TEG	0	0	94.18

Condition			
Temperature (°F)	39	39	39
Pressure (psia)	1400	1400	1400

† Calculated from PROSIM.

Figure 1 shows the viscosity of the rich TEG solution with and without hydrocarbons. The calculations show the hydrocarbons can reduce solvent viscosity by 50%.
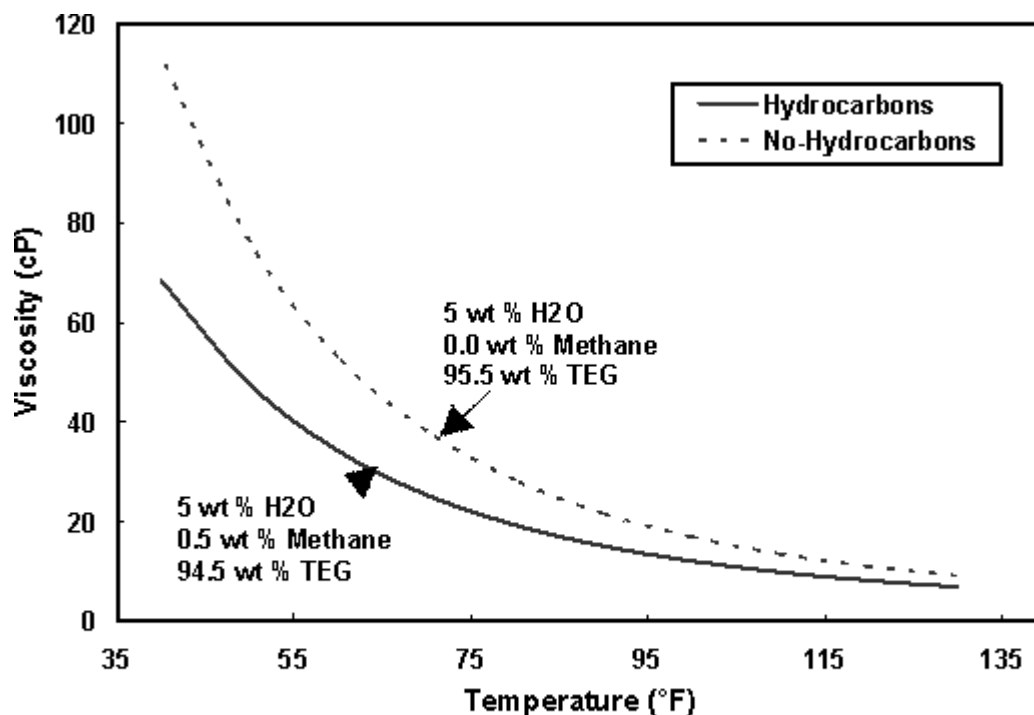
Figure 1. Case 1 Effect of Temperature on Rich TEG Viscosity.

After regeneration, the lean glycol contains little or no hydrocarbons. However, the lean glycol temperature should be maintained at a higher temperature than the incoming gas. In fact the glycol temperature has no significant effect on the overhead temperature of the column since the gas to the liquid glycol mass flow rate is about 350 to 1.

Case Study 2: Methanol

Pilot plant data from a coal gasification plant is presented by Staton et al. [3]. In the process, chilled methanol is used to remove both acid gas and organic sulfur species. Figure 2 shows the schematic of the flow diagram. Table VIII reports the composition and some operating conditions, which use both a flash tank and stripping column to regenerate the methanol in the base case. Comparisons of the treated gas composition with

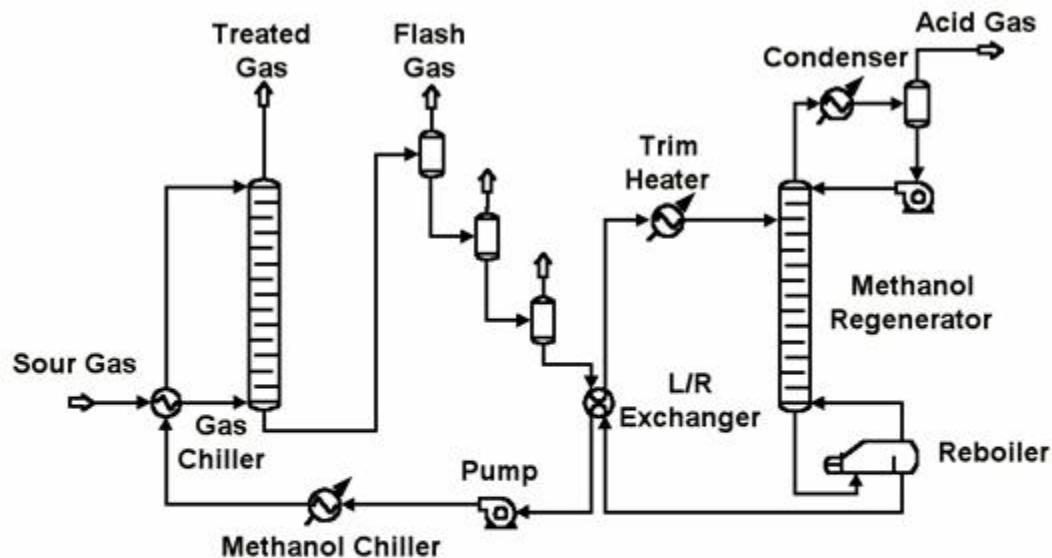predictions from PROSIM are also given in the table. Other process data are given in the reference.

Figure 2. Case 2 Methanol Acid Gas Removal System.

Table VIII
Case Study 2 Composition and Conditions†

Component	Methanol	Sour Gas	Treated Gas	
			Actual	PROSIM
	Mole %	Mole %	Mole %	Mole %
H_2S	--	0.26	0.00	2.2e-6
CO_2	--	27.38	0.00	2.6e-4
RSH	--	0.0034	0.00	1.4e-6
Methanol	--	0	0.00	1.3e-2
Conditions				
Temperature (°C)	-37.0	14.14	-37.0	-36.9
Pressure (atm)	31.1	31.1	31.1	31.11
Flow Rate (kg/hr)	175.3	15.64	--	6.38

† From Staton et al. [4]

Figure 3 shows the H_2S and the CO_2 content of the overhead gas as a function of the overhead temperature. The temperature of both the methanol and the inlet gas were allowed to vary. For the physical solvent, the decrease in temperature increases absorption of both the acid gas components. The colder operation tends to absorb more CO_2 relative to H_2S. Figure 4 shows the mercaptan absorption. As expected this figure shows increased mercaptan absorption at decreased temperature.
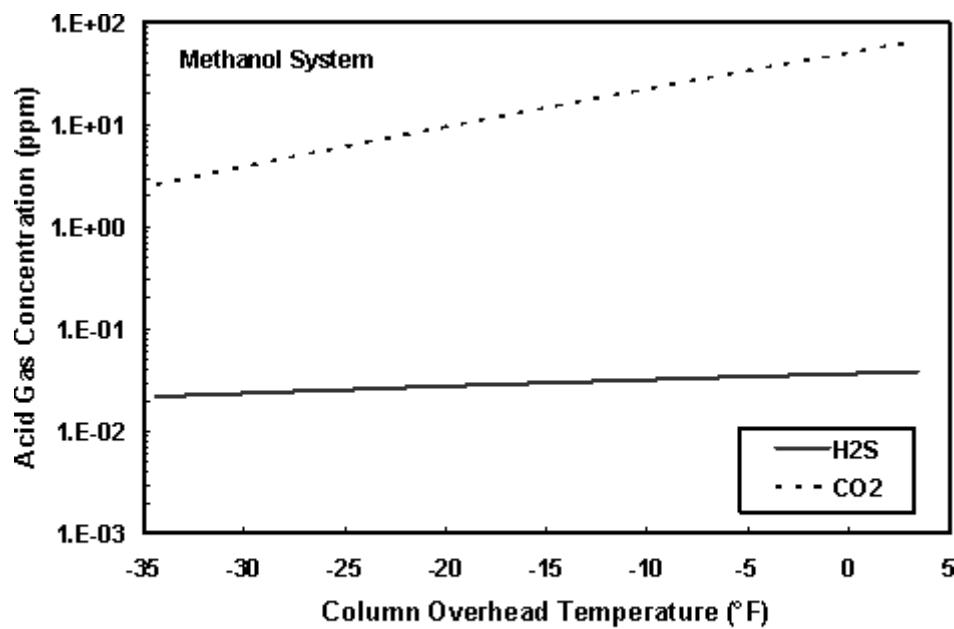
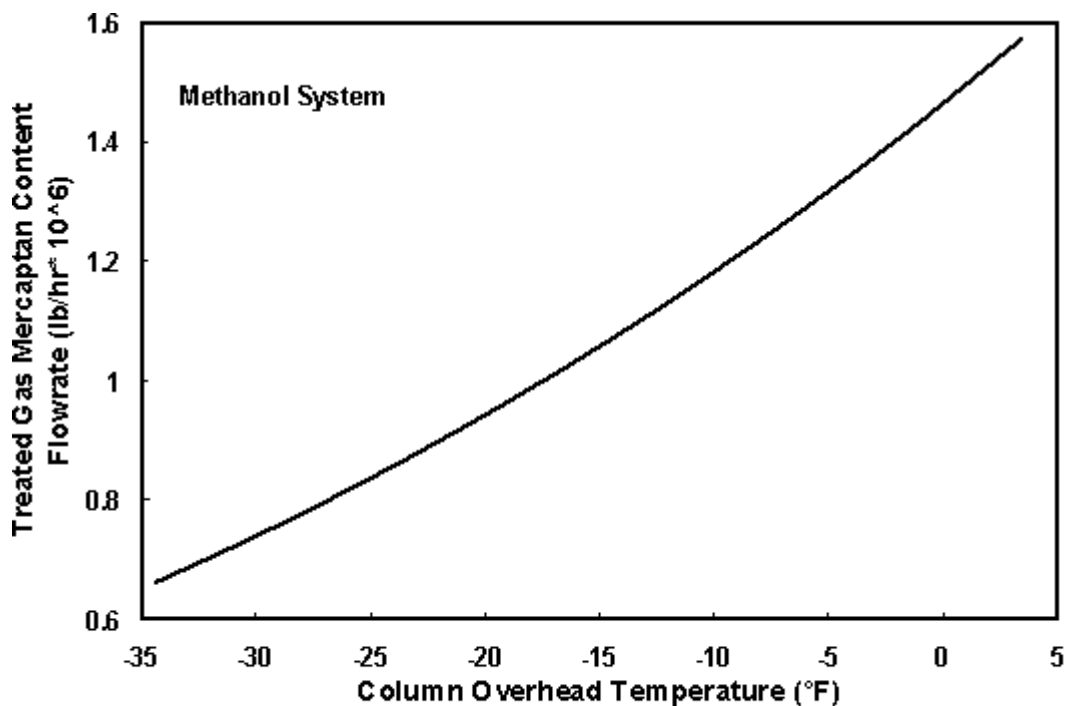Figure 3. Case 2 Effect of Temperature on Processed Gas Content.

Figure 4. Case 2 Effect of Temperature on Mercaptan Flowrate in Processed Gas.

Case Study 3:DEPG (Selexol)

The Galveston Island Gathering System uses DEPG to both dehydrate the inlet gas and decrease the hydrocarbon dew point as described by Epps [5]. The inlet conditions, circulation rate, operating conditions, and product flow rates are provided in the reference. Table IX gives the key operating parameters along with PROSIM's predictions for the lean/dry gas. Figure 5 shows the flow diagram. This diagram is surprisingly similar to an amine sweetening unit with the primary difference being the three phase condenser at the top of the DEPG regenerator. This condenser produces vent gas, hydrocarbon condensate, and water. Part of the water is used as reflux. The stripper conditions were not provided in the reference so the stripper temperature was assumed to operate 325°F or 25°F below the maximum feasibleoperating temperature [1].

Table IX
Case Study 3 Composition and Conditions†

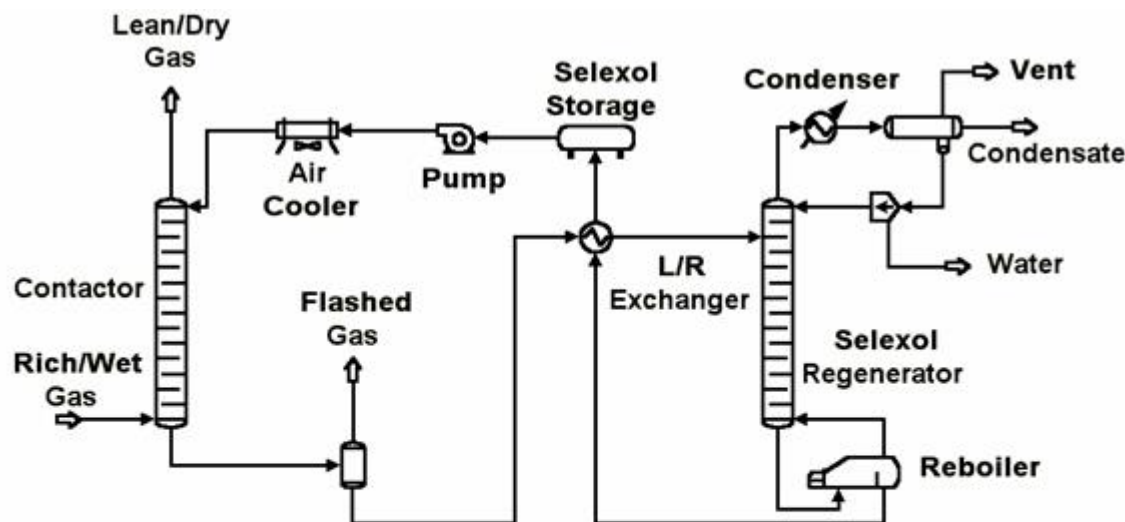| Composition	Lean DEPG	Rich/Wet Gas	Lean/Dry Gas Specification	PROSIM
Water Content (lb/MMSCF)	--	45	7	5.94
H.C. Dew Point (°F)	--	70	32	22.5
Condition				
Temperature (°F)	--	76	--	81.1
Pressure (psia)	--	865	865	865
Flow Rate (lb/hr)	12,680	166,500	--	165,100

† From Epps [5]

Figure 5. Case 3 Galveston Island Gathering System.

The inlet gas was varied from 55 to 80°F and the water content in the overhead and hydrocarbon dew point is shown in Figure 6. The decrease in the water content is partially the result that the colder inlet gas has less water. However, the decrease in the hydrocarbon dew point is a result of the increased pickup by the solvent.

This decrease in the hydrocarbon dew point corresponds to a decrease from 200 to 90 lb/hr of the C6+ fraction in the overhead.
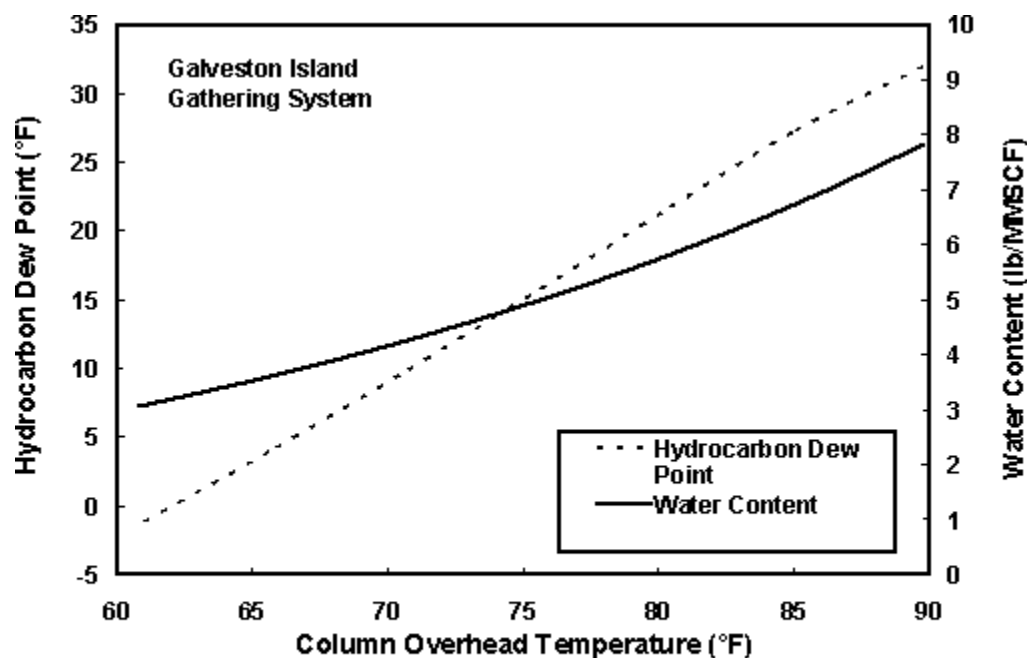

Figure 6. Case 3 Effect of Feed Gas Temperature on Processed Gas Water Content and Dew Point.

In the paper, the authors discussed the difficulty in reaching the 7-lb/MMSCF specification during hot days. The specific temperature was not mentioned. They further suggest that to alleviate this problem, the lean solvent could have been refrigerated but the economics were not justified. For the inlet gas at 90°F, Figure 7 shows the effect of cooling the solvent. This appears to have little to no effect; the overhead temperature remains relatively constant. Since the gas to solvent flow rate is about 13 to 1 on a mass basis, there is no amount of feasible cooling which could result in a colder overhead temperature.
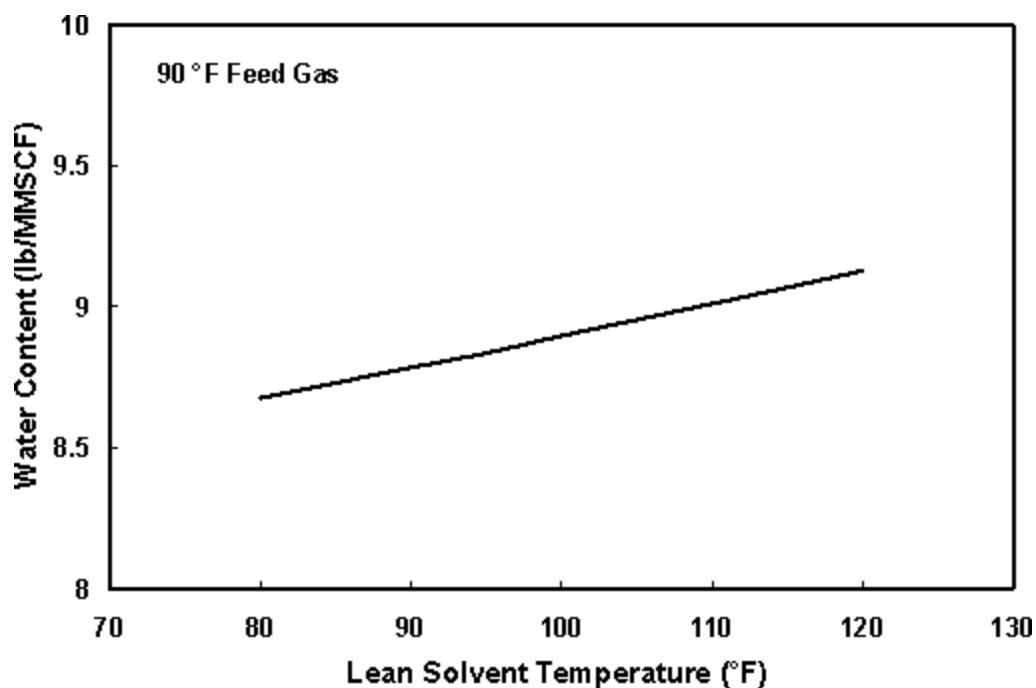
Figure 7. Case 3 Effect of DEPG Solvent Temperature on Overhead Water Content.

Case Study 4: MEA

Estep *et al.* [41] describes the Worland MEA sour natural gas sweetening unit. Table X shows the operating conditions and comparisons with TSWEET predictions. Figure 8 shows a schematic of the facility that processes both high pressure and low pressure gas with 15 wt % MEA solution. The residence time for the packed tower was estimated to be 7.3 secs based on correlations in Perrys [42].

Table X
Case Study 4 Composition and Conditions[†]

Component	Lean Amine	HP Sour Gas	Treated Gas	
			Actual	TSWEET[‡]
	Wt %	Mole %	ppm	ppm
H_2S	0.15	23.7	3.9	2.64
CO_2	0.22	2.3	0.0	4.45
H_2O	84.98	--	--	--
MEA	14.65	--	--	--
Conditions				
Temperature (°F)	--	75	112	112
Pressure (psia)	300	300	298	298
Flow Rate (lb/hr)	496,000	69,054	--	40,123

† From Estep *et al.* [41]
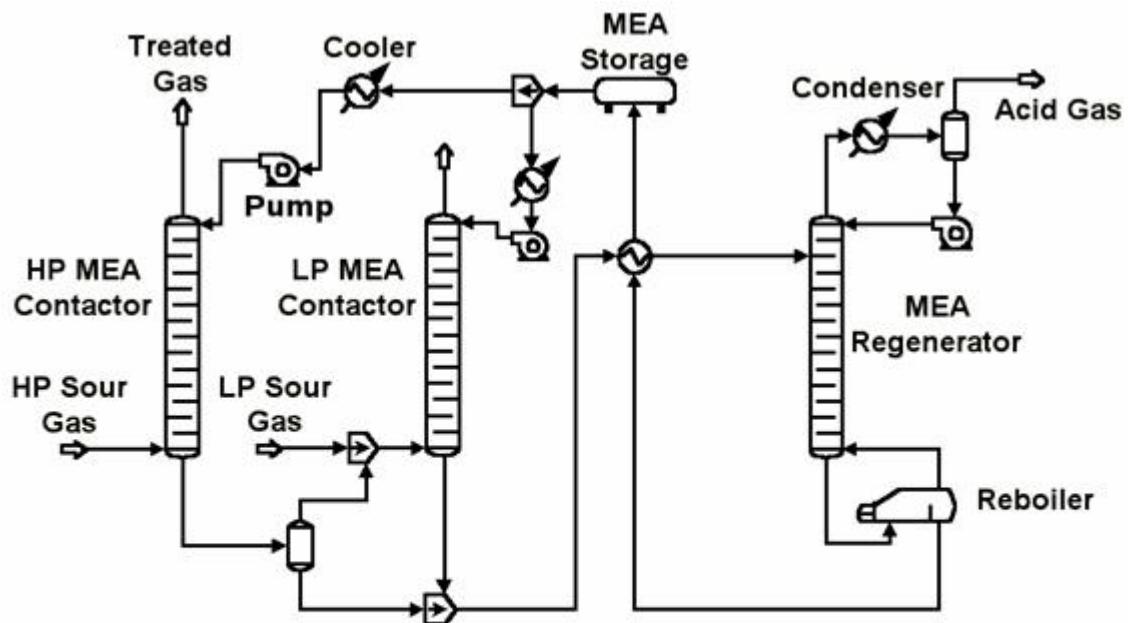‡ With 7.3 sec residence time and 4 ideal stages.

Figure 8. Case 4 Worland MEA Gas Plant.

Figure 9 shows the effect of lean amine temperature on the sweetened gas H_2S and CO_2 concentration based on TSWEET.   The effects of CO_2 kinetics are accounted for in the simulation used to compile this figure by specifying the liquid residence time. The H_2S in the sweet gas decreases from 20 to 4 ppm with decreasing temperature from 135 to 75°F. For CO_2 the concentration increases from 10 to 40 ppm due to the decreased rate of reaction at lower temperatures.
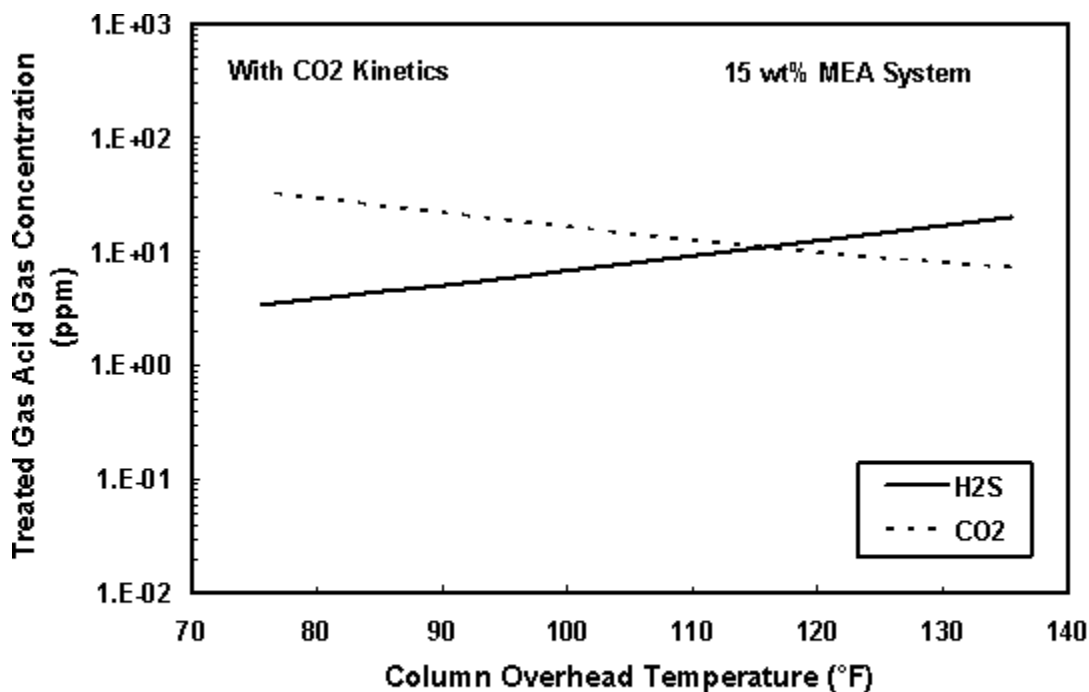
Figure 9. Case 4 Effect of Temperature on Overhead Acid Gas Concentration with CO2 Kinetics.

By contrast, Figure 10 shows both acid gas concentrations as a function of temperature for the same cases but with the CO_2 reaction allowed to proceed to equilibrium. The H_2S concentrations in both Figures 9 and 10 are essentially the same. However, the CO_2 concentration drops to below 1 to 0.05 ppm for temperatures from 135 to 75°F.
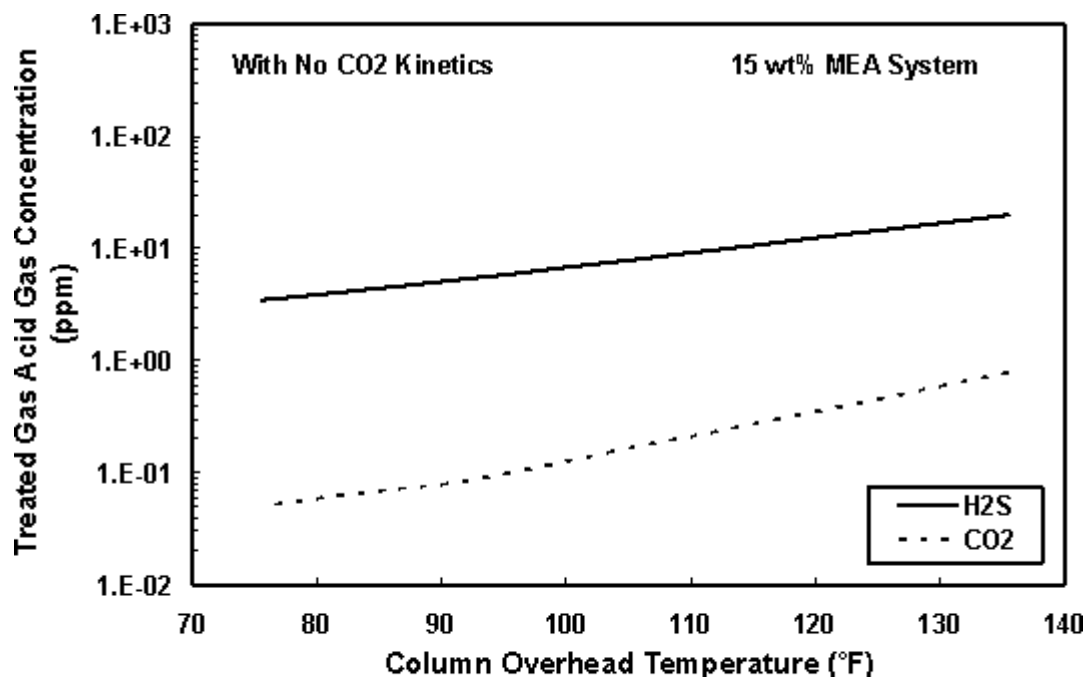
Figure 10. Case 4 Effect of Temperature on Overhead Acid Gas Concentration with CO2 Reaction at Equilibrium.

Based on the rate constants given in Table VI and the difference between the MEA predictions with and without the kinetic model as shown in Figure 9 and 10, primary amines are affected by the CO_2 kinetics. This effect is much more pronounced for tertiary amines such as MDEA. In fact, for gas treating to very low concentrations of CO_2, not accounting for the kinetic effect could result in under predicting CO_2 concentrations in the overhead by about three orders of magnitude.

Case Study 5: MDEA

Table XI gives the operating conditions for this MDEA unit, which processes about 6 MMSCFD of sour casinghead gas in northern Wyoming [10]. This table also compares the TSWEET results for this base case. Figure 11 shows the MDEA unit. The purpose of this processing step was to remove the required amount of H_2S and a small enough amount of the CO_2 to make a suitable Claus plant feed. The CO_2 content was decreased from 19 to 14 mole %. As described by the authors, both the inlet gas and the lean amine are cooled by air coolers. The paper provided data for a mixed amine analysis. To determine the effect of temperature on the tower, both the mixture of amines and a 25 wt% MDEA solution was used.

Table XI
Case Study 5 Composition and Conditions[†]

Component	Lean Amine	Sour Gas	Treated Gas	
			Reported	TSWEET[‡]
	wt %	Mole %	Mole %	Mole %
H_2S	0.03	2.078	0.022	0.0316
CO_2	0.19	19.202	14.383	15.243
H_2O	73.8	--	--	--
MDEA	21.8	--	--	--

DEA	4.2	--	--	--
Condition				
Temperature (°F)	118	94	125	126.9
Pressure (psia)	134	134	134	134
Flow Rate (lb/hr)	41,100	17,622	--	15,945

† From Harbison and Handwerk [10]
‡ With H_2S and CO_2 heats of reactions set to 514 Btu/lb and 4 ideal stages.
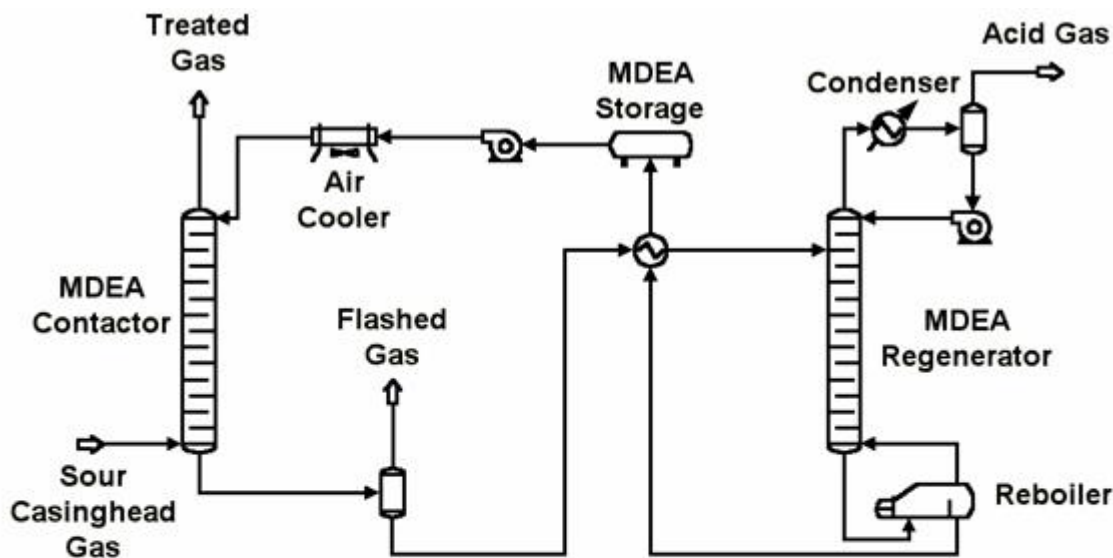

Figure 11. Case 5 Cody MDEA Casinghead Gas Plant.

The effect of absorber overhead temperature on the H_2S and CO_2 in the sweetened gas is shown in Figure 12 abased on TSWEET. This figure includes the mixed amine predictions with 21 wt% MDEA and 4 wt% DEA and the single amine at 28 wt % MDEA. The H_2S concentration decreases with temperature from about 6000 to 10 ppm on a logarithmic scale over a temperature range of 165 to 85°F. This decrease is primarily due to the increased solubility of the H_2S in the amine solution at lower temperature. The DEA increases the absorption of H_2S at the colder temperatures but not at the hotter temperatures. The CO_2 concentration is also superimposed as a dashed line. In this case, the CO_2 concentration increases from 14 to 18 mole % on a linear scale for the same temperature range. This increase occurs because the decreased rate of reaction for CO_2 is reduced to a greater extent than the increase in the solubility of CO_2 at the lower temperature. The DEA increases the absorption of CO_2 for the temperature range. For this facility, operating at the coldest temperature possible should yield the highest quality sulfur recovery feed.
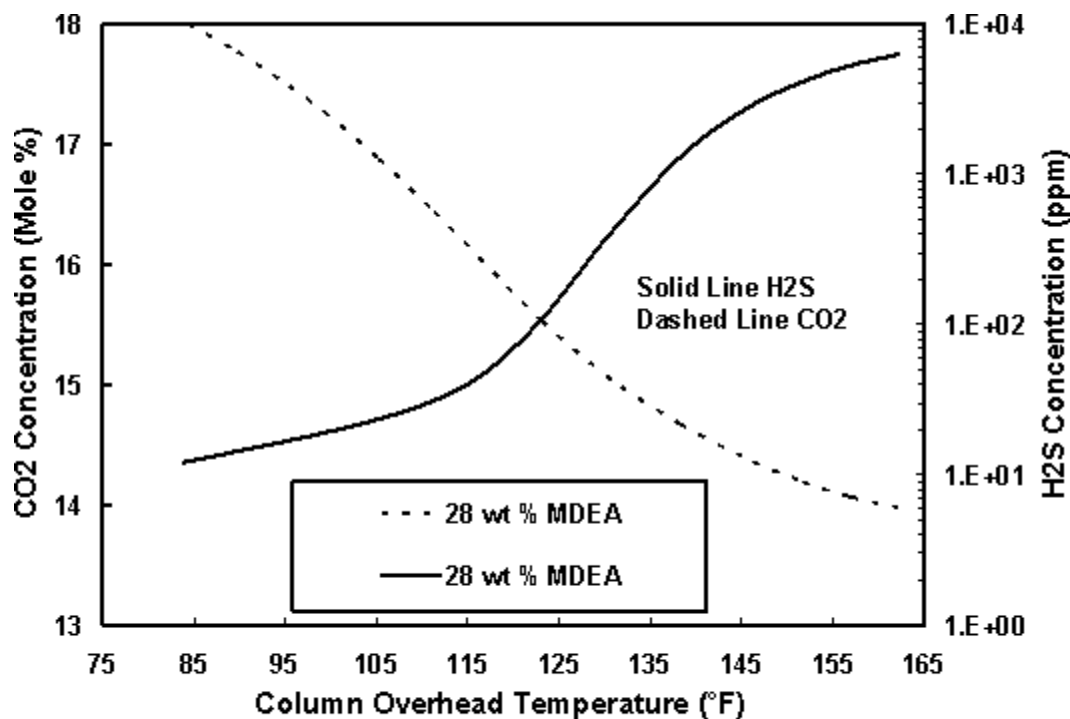
Figure 12. Case 5 Effect of Temperature on Overhead Acid
Gas Composition.

This gas may be further processed by glycol dehydration or mole sieve to remove water. Figure 13 shows the water content of the sweet gas as a function of contactor temperature. The water content increases by a factor of eight over the temperature range. This is because the gas exits the contactor saturated with water. The higher temperature gas has a much larger capacity to hold water than the colder gas. This increase or decrease in water content could have a dramatic effect on the design of dehydration equipment further downstream.
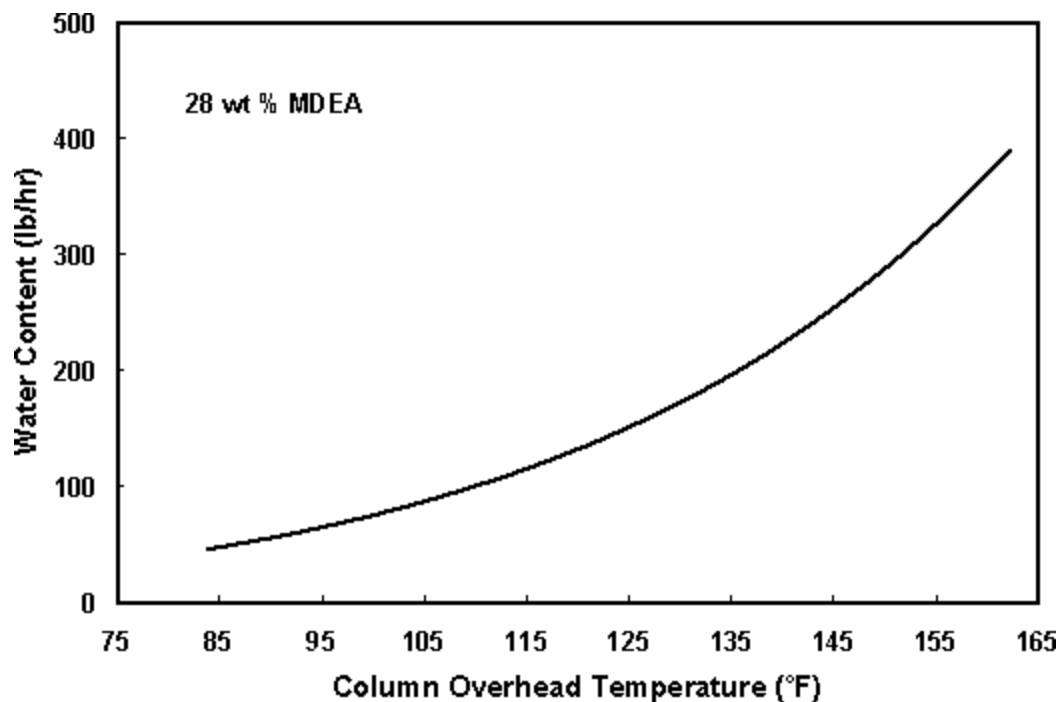
Figure 13. Case 5 Effect of Temperature on Overhead Water Content.

CONCLUSION

Decreasing contactor temperatures can either promote or hinder the absorption of water, acid gases or heavy hydrocarbons. For physical solvents such as methanol, glycol, and DEPG, the decreasing temperature promotes absorption. For chemical solvents such as alkanolamines, decreasing temperature increases the absorption of components that reach equilibrium such as H_2S. However, for CO_2 where the reaction is kinetically limited, decreasing the temperature causes the absorption of CO_2 to decrease. Depending on the process criteria and specifications, this may be a desirable result. Contactor temperatures are often limited by operating problems other than the required specifications. Designing for colder contactor temperatures requires that the engineer account for other potential limiting criteria including solids formation, hydrocarbon solubility, and solvent viscosity. However, even with these limitations, colder contactor temperatures may result in more efficient and economical operations.

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